Chitosan-based adsorbents & nanocomposite membranes for separation applications

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CHITOSAN-BASED ADSORBENTS & NANOCOMPOSITE MEMBRANES FOR SEPARATION APPLICATIONS

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ABSTRACT

Chitosan (CS) is an important biomaterial widely used in purification and separation applications. This project has developed two novel CS-based materials for industrial applications, i.e. (1) CS hydrogel beads for wastewater treatment, and (2) CS nanocomposite membranes for pervaporation separations.

In application (1), native CS beads were modified with ammonium sulphate to remove anionic dyes in aqueous solutions at a high pH of 8.2, which was designated for direct treatment of wastewater discharged from textile plants. The adsorption capacities of the modified CS beads towards acid orange-7 (AO-7) and acid red-18 (AR-18) in a fixed bed were 445.6 mg/g and 427.2 mg/g, respectively, which were about 7.4 and 14.4 times of those of native CS beads at pH 8.2 (60.4 mg/g for AO-7 and 29.7 mg/g for AR-18), respectively. The ion-exchange mechanism of dye adsorption on the modified beads was proposed and verified experimentally. The modified beads were found to be easy to regenerate (with common chemicals) and possessed excellent re-use capability (up to 20 cycles without significant loss in capacity). The fixed bed breakthrough kinetics of AO-7 was measured on the modified beads and was modeled successfully by the Wheeler-Jonas equation with a 'two-segmented' approach.

In application (2), four types of polyhedral oligosilsesquioxanes (POSS) with different R vertex groups were incorporated into CS via solution blending. The dispersion of POSS fillers in the CS-POSS composite membranes depended on the hydrophilic/hydrophobic nature of POSS. The thermal stability of the

composite membranes was improved compared to that of native CS membrane. The mechanical properties (Young's modulus, strength and elongation at break) of the composite membranes changed significantly with POSS type. The permeation of sodium chloride and riboflavin in the CS-POSS composite membranes was also measured. It was demonstrated that the composite membranes containing hydrophilic POSS had higher partition coefficients but lower diffusion coefficients of riboflavin, when compared to the composite membranes containing hydrophobic POSS.

The CS-POSS composite membranes were employed for pervaporation dehydration of ethanol solutions. It was found that, with a small amount of POSS (1 to 5 wt.%) as the nano-fillers, all the composite membranes showed significantly improved water selectivity. The effects of feed concentration and temperature on the pervaporation performance of membranes were investigated. The apparent activation energy for permeation was calculated using the Arrhenius equation. It was found that the apparent activation energies for ethanol permeation in the composite membranes were much higher than that in the CS membrane, which may account for the enhancement on the selectivity of the composite membranes.

In conclusion, the modified CS hydrogel beads are very promising low-cost bio-adsorbents for direct treatment of dye-containing wastewater, which eliminates the need of pre-acidification of basic wastewater discharged from textile industry. As a new type of nano-filler, POSS are able to significantly modify/improve the structural, physical and chemical properties of native CS materials, paving the way for their future applications in biomedical and separation fields.

LIST OF ABBREVIATIONS

AO-7	Acid orange-7
APTEOS	3-Aminopropyl-triethoxysilane
AR-18	Acid red-18
BC	Bacterial cellulose
BDST	Bed depth service time model
CMCNa	Sodium carboxymethyl cellulose
CNT	Carbon nanotube
CS	Chitosan
DD%	Degree of deacetylation
DMC	Dimethyl carbonate
DS%	Degree of swelling
ECH	Epichlorohydrin
EG	Ethylene glycol
EGDE	Ethylene glycol diglycidyl ether
EtOH	Ethanol
FT-IR	Fourier transform infrared
GA	Glutaraldehyde
GC	Gas chromatography
GlcN	Glucosamine
GlcNAc	N-acetyl glucosamine
GPTMS	γ -(Glycidyloxypropyl)trimethoxysilane
HEC	Hydroxyethylcellulose
HPC	Hydroxypropyl cellulose
MeOH	Methanol
MMT	Montmorillonite
MTBE	Methyl-tert-butyl ether
MTZ	Mass transfer zone
OA	Octaanion POSS
OAPS	Octaaminophenyl POSS
OAS	Octaammonium POSS

ONPS	Octanitrophenyl POSS
PAA	Poly(acrylic acid)
PAAm	Poly(acrylamide)
PAN	Polyacrylonitrile
PBD	Polybutadiene
PC	Polycarbonate
PDMS	Polydimethyl siloxane
PEO	Poly(ethylene oxide)
PMAA	Poly(methacrylic acid)
PMMA	Poly(methylmethacrylate)
PNIPAM	Poly(N-isopropylacrylamide)
POSS	Polyhedral oligosilsesquioxanes
i-PrOH	i-Propanol
PSf	Polysulfone
PSI	Pervaporation separation index
PTA	Phosphotungstic acid
PU	Polyurethane
PVA	Poly(vinyl alcohol)
PVP	Poly(vinylpyrrolidone)
SDS	Sodium dodecyl sulphate
SEM	Scanning electron microscope
STA	Silicotungstic acid hydrate
TEOS	Tetraethoxysilane
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TPP	Sodium tripolyphosphate
UF	Ultrafiltration
VOC	Volatile organic compounds
XRD	X-ray diffraction
W-J	Wheeler-Jonas

NOMENCLATURE

A	Area (m^2)
a	Slope
b	Intercept
C	Concentration
D	Diffusion coefficient (m^2/s)
E	Activation energy of permeation (kJ/mol)
H_s	Heat of adsorption
J	Permeation flux ($\text{g}/\text{m}^2 \text{ h}$)
K	Partition coefficient
k_v	Parameter of W-J equation, overall adsorption rate coefficient (min^{-1})
l	Diffusion path (m)
m	Mass fraction in the membrane
P	Permeability coefficient (m^2/s)
Q	Total amount of dye adsorbed (mg)
q	Adsorption capacity (mg/g)
R	Universal gas constant
T	Temperature
t	Time
V	Volume
W	Weight (g)
W_e	Parameter of W-J equation, dynamic adsorption capacity (mg/g)
X_0	Constant in Arrhenius equation
x	Mass fraction in the feed (%)
y	Mass fraction in the permeate (%)

Greek letters

α	Separation factor
δ	Membrane thickness (m)

ρ	Density (g/ml)
v	Flow rate (ml/min)

Subscripts

B	Bulk
b	Breakthrough
bat	Batch
col	Column
d	Decomposition
dry	Dry membrane
diff	Diffusion
E	EtOH
e	Equilibrium
f	Feed
i	Component i
j	Component j
m	Membrane
p	Permeate
s	Surface
sol	Solution
swol	Swollen membrane
W	Water
0	Inlet or initial

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CHAPTER 1 INTRODUCTION

1.1. Background

The ever-increasing human activity and rapid industrialization have exerted much pressure on natural resources and have resulted in issues such as climate change, water and air pollution, shortage of energy supplies, loss of biodiversity, etc. To achieve sustainable development, many efforts have been devoted to developing technologies which can reduce emissions, increase energy efficiency/productivity, and recycle wastes.

Biomaterials are finding more and more applications in various industries, because they are generally versatile, cheap, abundant in nature and environmentally safe. Polysaccharides, for example, which are polymeric carbohydrate, can be found in nature in various forms (e.g. starch, cellulose, glycogen, etc.). They possess some unique physical, chemical and biological properties, which are distinctive from the synthetic polymers. Chitin and its N-deacetylated derivative chitosan (CS) are important examples of polysaccharides. Their excellent biocompatibility, non-toxicity, biodegradability and versatility make them among the most popular biopolymers in research and industrial applications [1]. In addition to their extensive applications in medical and food industries, they also show great potential in the fields of packaging, wastewater treatment, agriculture, and so on [2].

Huge volumes of wastewater are discharged from industry every day. Wastewater contains large quantities of toxic substances including heavy metals,

dyes, arenes, acids and alkalis, etc. Without adequate treatment, wastewater would cause tremendous damages to the environment. Meanwhile, treating industrial wastewater is one of the key technologies that ensure a sustainable supply of fresh water. Dye contaminants are commonly found in industrial effluent. They interfere with the photosynthesis of aquatic organisms and are toxic or carcinogenic to human beings. Recently, dye removal using low cost adsorbents has been intensively studied [3]. Chitin and CS-based materials are found to be among the most efficient adsorbents. However, the adsorption capacity of CS towards dyes is highly pH dependent, particularly the adsorption of anionic dyes. In acidic media (pH 3-4), the fully protonated amine groups ($-\text{NH}_3^+$) of CS have strong electrostatic attractions towards anionic dyes. However, modifications such as crosslinking are necessary to maintain the structural integrity of CS in acidic solutions, which may compromise the adsorption efficiency. Moreover, adding acids to adjust the pH of wastewater incurs high cost and introduces new pollutants.

Membrane technology is regarded as a 'clean' technology, because of its low energy/materials consumption, high efficiency, and ease of operation and maintenance. Membrane pervaporation [4] is particularly attractive for separation of azeotropic mixtures, heat sensitive mixtures, mixtures with close boiling points, and recovery of volatile organic compounds (VOC). Some of these applications have been commercialized and are becoming more and more popular. The key of this technology is to develop low-cost, high-performance membranes. So far, various types of polymeric, inorganic, and composite membranes have been explored. The bio-polymer CS has been found to possess many advantages towards this application.

1.2. Objectives

This project will develop CS-based low-cost and high-performance adsorbents and nanocomposite membranes for purification and separation applications.

Most CS-based adsorbents reported in literature can only effectively adsorb anionic dyes at low pH (3.0 to 4.0). In this study, native CS beads will be modified to efficiently recover dyes from wastewater at effluent conditions (pH > 8.0). Therefore, crosslinking is not necessary for CS beads and pre-acidification is not required to basic wastewater. The breakthrough performance of the modified CS beads will be investigated. The breakthrough kinetics will be studied by mathematic models to provide information for industrialization. The desorption/regeneration processes will be carried out and the mechanisms of modification and adsorption/desorption process will be explored.

Nanocomposite membranes composed of polymer matrix and nano-fillers are found to have excellent performance in pervaporation. However, to our knowledge, the applications of composite membranes filled with polyhedral oligosilsesquioxanes (POSS) – a zero-dimensional nano-structured particle where all the dimensions are on nano-scale – in pervaporation have not been reported yet. We hereby fabricate a novel of CS-POSS composite membrane and use for the dehydration of ethanol (EtOH) by pervaporation. The composite membranes will be thoroughly characterized. The effects of POSS, feed concentration and temperature on the pervaporation performance of the composite membranes will be investigated.

1.3. Overview of the thesis

This thesis consists of seven chapters:

Chapter 1 outlines the background and the objectives of this study.

Chapter 2 introduces the theoretical background of this project, including structure and properties of CS, current research on CS-based adsorbents for dye adsorption, concept of organic-inorganic composite membranes, overview of pervaporation process and current research on pervaporation using CS-based membranes.

Chapter 3 describes the experimental materials and methods, including the sample synthesis, characterization of CS-based beads and composite membranes, dye adsorption procedures, and pervaporation set-up.

Chapter 4 presents the dye adsorption isotherms, the fixed bed breakthrough behaviors of the native and modified CS beads, adsorption mechanism and regeneration process, as well as study of fixed bed kinetics by the Wheeler-Jonas (W-J) equation.

Chapter 5 presents characterizations of the CS membrane and CS-POSS composite membranes including the data from Fourier Transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), scanning electron microscope (SEM), thermogravimetric analysis (TGA), tensile testing, as well as swelling and diffusion measurements.

Chapter 6 presents the sorption behavior and pervaporation performance of the CS membrane and CS-POSS composite membranes. The effects of POSS type, feed concentration and temperature will be discussed.

Chapter 7 draws conclusions of this study and gives some recommendations for future studies.

CHAPTER 2 LITERATURE REVIEW

2.1. Chitin and Chitosan

Chitin, or poly(β -(1 $\rightarrow$ 4)-N-acetyl-D-glucosamine), is the most abundant natural polymer only after cellulose [2]. Chitin is produced by many living organisms. The commercial sources of chitin are the shells of crustaceans (mainly crabs and shrimps) from the byproducts of marine processing plants [5]. Chitosan (CS) is the N-deacetylated derivative of chitin resulting from alkaline treatment. CS consists of linear β -1, 4-linked D-glucosamine (GlcN) and N-acetyl glucosamine (GlcNAc) units. The molecular structures of chitin and CS are shown in Figure 2.1.

Figure 2.1. Molecular structures of chitin (predominantly contains GlcNAc) and chitosan (predominantly contains GlcN).

The degree of deacetylation (DD%) generally dictates the physico-chemical and biological properties of CS. CS, which has a DD% higher than 50%, is soluble in acidic aqueous media owing to the protonation of $-\text{NH}_2$ groups of GlcN. This water-soluble property largely improves its processability. The

preparation and characterization details of chitin and CS can be found in a few recent review articles [5-8].

As a natural biopolymer, CS possesses a number of intrinsic advantages such as low cost, biodegradability, biocompatibility, and non-toxicity. More notably, the amine and hydroxyl functional groups of CS allow it to form complexes with many compounds, such as metals, surfactants, dyes and some polymers [2]. These appealing properties make CS and its derivatives versatile for various applications [6-13]. In the biomedical field, they are used in tissue engineering, drug delivery, wound dressing, bone substitution, sutures material, etc. [1, 14-15] In biotechnology, they are used as the enzyme immobilization matrix, and in cell-stimulating materials and antibacterial agents, etc. [10, 16-19] In water treatment, they are low cost and effective adsorbents for heavy metals, dyes and other contaminants [20-24]. Furthermore, CS also finds vast applications in the food industry[10], packaging [25], cosmetics [6, 18], agriculture [26], chromatographic separations [27], catalysts support [28], and liquid and gas separations [29-30].

Various forms of CS (such as fibers, gels, beads, microcapsules, microspheres and membranes) have been fabricated for various applications. Among them, CS beads with large surface area have great dye and metal adsorption capacity [20]. CS membranes, which allow the selective transport of specific components, have been commonly used to provide solutions for separation in biological, chemical and environmental systems [31].

2.2. CS-based materials for dye adsorption

Dye containing wastewater discharged from the textile, leather, rubber and paper industries poses serious environmental pollution. Even the presence of a very small amount of dyes in water is highly visible and harmful to aquatic biota or humans due to their mutagenic and carcinogenic effects [32]. However, the synthetic origin and complex molecular structure of dyes make them hard to be biodegraded. Therefore, numerous approaches have been studied for dye removal from wastewater including physical, chemical, biological processes [3]. Among these methods, adsorption is recognized to be one of the most efficient techniques in terms of high quality treated water with low generation of residue, ease of operation and possibility of adsorbent recycling [33].

Conventional adsorbents (e.g. activated carbons) show good adsorption capacity towards various dyes due to their large surface area. However, they are expensive and hard to regenerate. Therefore, low-cost adsorbents such as natural products (zeolite [34], silica [35], clay [36], etc.), waste materials from agriculture and industry (sawdust [37], de-oiled soya [38], or sludge [39], etc.) and biosorbents (biomass [40], Chitin and CS [41],) are considered to be attractive alternatives. Among them, CS has received much attention because of its unique characteristics including:

- (1) Large numbers of functional groups (amine and hydroxyl groups) endow CS with high affinity towards various dyes, especially anionic dyes.
- (2) Modifications such as carboxymethylation, crosslinking, grafting, etc. can be easily realized by reaction with the amine groups or hydroxyl groups of CS [41]. The structural stability, hydrophilic/hydrophobic

properties, adsorption capacity and selectivity, etc. can thereby be manipulated.

- (3) CS can be fabricated to various forms such as beads, nanoparticles, fibers, membranes, etc. suitable for different applications.
- (4) The exhausted CS adsorbents can be easily regenerated.

However, the adsorption efficiency of CS is significantly affected by its physical and chemical properties, such as crystallinity, DD%, distribution of amine groups, molecular weight, etc. which depend on the source of the raw material and the processing conditions. Therefore, structural modification is frequently needed for the commercially available CS [2].

2.2.1. Batch studies

2.2.1.1. Dye adsorption using CS-based adsorbents

As a cationic polyelectrolyte, CS presents high affinity towards anionic dyes (including acidic, reactive and direct dyes) via electrostatic interactions. Nevertheless, CS can also adsorb cationic dyes (basic dyes) after some modifications. The adsorption can be conducted in both batch and fixed bed systems. It is relatively simple and easy to measure the adsorption isotherm and kinetics in a batch system. Therefore, most studies reported were carried out in such conditions. Some of the batch adsorption results in recent literature are summarized in Table 2.1.

At low pH (pH 3-4), the amine groups of CS are nearly completely protonated, hence maximizing the adsorption capacity. However, CS will lose

its integrity in acidic media. Crosslinking is one of the popular techniques to enhance the structural stability. Glutaraldehyde (GA), epichlorohydrin (ECH), ethylene glycol diglycidyl ether (EGDE), H_2SO_4 , and sodium tripolyphosphate (TPP) are some of the commonly used crosslinking agents. Studies showed that the CS beads crosslinked by ECH presented higher adsorption capacity towards anionic dyes compared to those crosslinked by GA and EGDE [42]. This was because ECH generally reacted with the hydroxyl groups of CS, while the other two crosslinking agents reacted with the amine groups of CS and thus decrease the sites for anionic dye adsorption.

CS has been grafted with poly(acrylamide) (PAAm) [43-44], poly(acrylic acid) (PAA) [44], poly(methacrylic acid) (PMAA) [45] and poly(methylmethacrylate) (PMMA) [46] to introduce anionic groups. The new functional groups make the adsorption of CS-based adsorbents less pH dependent [43], and improve their adsorption capacity towards basic dyes [44-45]. The composites of CS with inorganic materials such as carbon nanotubes (CNT) [47], silica [48], montmorillonite (MMT) [49], Fe_3O_4 nanoparticles [50] have been reported to exhibit enhanced adsorption capacity towards various dyes. Other techniques such as imprinting [51], surfactant impregnation (TX-100 and sodium dodecyl sulphate (SDS)) [52-53] have also been reported.

Table 2.1. Batch adsorption results of various dyes on CS-based adsorbents.

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Concentration of dye (mg/L)	pH	Source
Acid dyes					
CS flakes	Acid Blue 161	472	50-500	3.0	[54]
CS beads	Acid orange 12	1954	2089-5286	3.0	[55]
	Acid red 14	1940		3.0	
	Acid orange 7	1940		4.0	
CS-Fe ₃ O ₄ nanoparticles	Acid orange 12	1883	200-5000	3.0	[50]
	Acid green 25	1471			
Reactive dyes					
CS flakes	Reactive red 222	380	50-500		[56]
CS beads	Reactive red 189	1840	2900-5096	3.0	[57]
CS/MMT/octadecylamine beads	Reactive red 120	6	60-140	5.0	[58]
Templated CS beads	Remazol black 5	2500	100-5000	3.0	[51]
CS/oil palm beads	Reactive blue 19	909	50-500	6.0	[59]
CS grafted PMMA	Orange G	94	300 ^a	7.0	[60]
Quaternary CS flakes	Reactive orange 16	1060	100-1000	4.0	[61]
CS beads	Congo Red	116	10-1000	5.0	[53]
CS/CNT beads	Congo Red	450	10-1000	5.0	[47]

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Concentration of dye (mg/L)	pH	Source
CS/TX-100 beads	Congo Red	379	10-1000	5.0	[52]
CS/SDS beads	Congo Red	319	10-1000	5.0	[52]
Other dyes					
CS flakes	Direct Scarlet B	37	40	8.5	[62]
CS beads crosslinked by ECH	Direct 81	2383	2089-5286	4.0	[55]
CS flakes grafted PAA	Remacryl red TGL	511	0.047- 1.175 ^b	10.0	[63]
CS/MMT composites	Basic blue 9	49	500		[64]
	Basic blue 66	49			
	Basic yellow 1	46			
CS-g-PAA-vermiculite	Methylene blue	1690	700-1200	7.0	[65]

^a ppm, ^b mmol/L.

2.2.2. Fixed bed process

2.2.2.1. Overview

The batch process is simple to operate, but it is only suitable for small- and medium-scale applications. From an industrial point of view, fixed beds are more attractive because of continuous operation and re-generation. Moreover, a continuous concentration gradient can be formed at the interface zone when the

feed solution is eluted through the column. Therefore, a higher adsorption capacity is often obtained in the fixed bed process when compared to that of the batch process [38].

The removal of some contaminants such as phenols [66], arsenic species [67], perchlorate [68] and heavy metals [69] using fixed bed rigs filled with CS-based adsorbents has been reported. However, the studies on dye adsorption in fixed bed using CS-based materials are very rare. Yoshida et al. [70] reported the adsorption of a direct dye, brilliant yellow, using a fixed bed of cross-linked CS fiber. The effects of flow rate, bed height, influent concentration, pH and temperature on the breakthrough curves were investigated. Elwakeel [71] conducted the column studies on the uptake of reactive black 5 using magnetic CS resin. The breakthrough curves were well modeled by bed depth service time model (BDST). The exhausted fixed bed was regenerated by $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ buffer. A study on the sorption of reactive black 8 in an *air-lift* reactor using CS flakes showed that the flow rate played an important role in adsorption efficiency [72].

2.2.2.2. Modeling breakthrough curves

Fixed bed breakthrough curves present different characteristics with different adsorbent/adsorbate systems and varying operating conditions. Modeling the breakthrough curve is important to understand the mechanism of adsorption and analysis the influence factors. Furthermore, some models can give predictions on the dynamic process of adsorption which are meaningful guides for the practical application. So far, many models for breakthrough curves have been

developed. Each of them has its own requirements and applicable conditions. For example, in Bohar-Adams model, which is based on the surface reaction theory, the sorption rate is proportional to the remaining sorption capacity of the adsorbent [73]. The parameters of adsorption capacity and rate constant calculated from the model can be used for the scale-up design of the fixed bed. The BDST model proposed by Bohart and Adams deals with the relationship between the bed depth and the breakthrough time [74]. The service time and minimum service time of fixed bed can be calculated and compared under different operating conditions.

The modified Wheeler-Jonas (W-J) equation [75-76] is a semi-empirical model derived from the mass balance between the substances entering the fixed bed and the sum of the substances adsorbed in the bed and coming out. The W-J equation has been widely used to analyze the breakthrough behaviors of gas and vapor adsorption in activated carbons [77]. From limited sets of experiments, macroscopic variables such as the dynamic adsorption capacity and the overall adsorption rate coefficient can be estimated and related to the flow rate, influent concentration and the characteristics of the adsorbents (diameter, etc.). Therefore, it is a simple and useful tool in characterizing the fixed bed and to aid in exploring the adsorption mechanism [78-79].

2.3. Composite membranes

2.3.1. Organic-inorganic composite membranes

Most of the polymeric materials have some intrinsic drawbacks, such as insufficient thermal and mechanical stability, poor solvent resistance and low selectivity efficiency, which constrain their applications in industry [80]. Inorganic membranes present good stability and encouraging selectivity for gas and liquid separation [81]. However, their fabrication processes are complex and thus expensive. In recent years, organic-inorganic composite membranes (also known as the mixed matrix membranes), in which inorganic fillers are spatially dispersed in a polymer matrix (as shown in Figure 2.2), have received much attention. If the inorganic components are of nano-scale, they form the so-called nanocomposites [82]. Such organic-inorganic nanocomposites may not only combine the advantages of the polymers (e.g., flexibility and processing-ability) and the inorganic fillers (e.g., selectivity, thermal and mechanical stabilities), but may also exhibit some unique properties that surpass those of the individual components [83]. The addition of inorganic fillers (especially nano-fillers) offers a method to adjust the molecular packing and refine the radius of free volume [84-85]. Therefore, enhancements in the mechanical properties [86], optical properties [83], flame retardancy [87], etc., are possible. When the organic-inorganic composite membranes are used for pervaporation or gas separation, simultaneous improvements on permeability and selectivity can be achieved, i.e., pushing up the ‘trade-off’ curve between the flux and selectivity [88].

Depending on the structure, the organic-inorganic composite materials can be classified into two types, i.e., ‘Class I’ materials, in which the inorganic and organic components interact through weak hydrogen bonding, van der Waals or electrostatic forces; and ‘Class II’ materials, in which the inorganic and organic components are linked through strong ionic/covalent bonding [89].

Figure 2.2. Schematic diagram of organic-inorganic composite membranes.

2.3.2. POSS and its nanocomposites

Organosilicate molecules with the basic formula $R_nSi_nO_{1.5n}$ (where R can be hydrogen, alkyl, alkylene, aryl, arylene, etc.) are referred to silsesquioxanes. The molecular architecture of silsesquioxanes can be random, ladder, partial-cage or cage structure. The cage-like silsesquioxanes, called as POSS, are widely studied due to their well-defined and highly symmetric structures. The basic structure of POSS is illustrated in Figure 2.3. POSS are hybrid molecules with both inorganic (silica core) and organic (vetex groups) parts. The R groups, which are attached to the vertex of the Si-O cage, can be hydrogen, alkyl, alkylene, aryl, and arylene, or other functional groups [90]. The inorganic silica core of POSS is thermally and chemically robust, while the diversity of the R groups endows POSS with versatile chemistry. A POSS molecule has an

approximate linear dimension of 1.5 nm, taking into account the R vertex groups. Therefore, POSS are regarded as the smallest possible particles of silica [90]. They are widely used as nano-fillers in polymers and can be incorporated into polymers through copolymerization [91], grafting [92] or physical blending [93]. The resulting nanocomposites can present very different properties compared to the native polymer.

Figure 2.3. Basic molecular structure of POSS.

POSS can interact with polymers via covalent bonds acting as crosslinkers or pendant units in polymers. With strong interactions between these two phases, the reinforcements on thermal and mechanical properties are significant. Other physical and chemical properties can also be modified. Zheng et al. prepared a copolymer composed of polybutadiene (PBD) and cubic POSS [91]. The bottom-up approach made it possible to build a layered nanostructure of organic-inorganic composites via self-assembly. POSS can be introduced into polyurethane (PU) as chain extenders [94] or network crosslinkers [95]. The presence of POSS can improve the thermal stability and tensile strength of the

resulting hybrids. The flame retardancy was enhanced via intumescent mechanism [96]. Moreover, the surface hydrophobicity of PU can be enhanced [97], hence making the hybrid material a good barrier to water [94]. POSS can also enhance the water-sensitive shape memory ability of PU [98] and the temperature-sensitivity of poly(N-isopropylacrylamide) (PNIPAM) networks [99]. Copolymers of POSS with many other monomers such as epoxy [100-101], styrene [102-103], acrylate [104], ϵ -caprolactam [105], etc. have also been reported.

Compared to copolymerization or grafting, physical blending is a simple way to fabricate polymer based composites. However, phase separation sometimes occurs due to the poor miscibility of POSS with the polymer matrix [106]. Blending POSS with amorphous polymers such as PMMA improves the toughness of these polymers [107]. The gas transport in bisphenol-A-polycarbonate (PC) film [108] and the amino acid diffusion in CS membrane [109] were also modified by blending these polymers with POSS.

The modifications of POSS fillers on the composite material properties depend substantially on the interactions between POSS and the polymer matrix. Hence, by varying the R groups of POSS, it is possible to tailor the structures and bulk properties of polymer-POSS nanocomposites [110].

2.4. Pervaporation

2.4.1. Overview

The separation of azeotropic mixtures, close-boiling mixtures, or heat-sensitive liquid mixtures using conventional processes such as distillation, extraction and adsorption are either energy intensive or inefficient [111]. Pervaporation, which employs a membrane as the selective barrier, provides an efficient and economical alternative for the separation of these mixtures due to mild operating conditions, low energy cost and high selectivity [112].

The pervaporation process is illustrated schematically in Figure 2.4. The liquid mixture is placed in the feed compartment and is in contact with one side of the membrane. The fraction penetrating across the membrane is in vapour phase, known as the permeate. A condenser is applied to condense and collect the permeate vapor. At the permeate side, either a vacuum pump is used to maintain the vacuum environment, or a carrier gas is applied to purge the permeate vapor. As a result, a concentration gradient between the feed side and the permeate side is maintained, which is the driving force for the mass transport across the membrane.

Compared with the traditional distillation process, which relies on the relative volatilities between the components, the pervaporation process is not restricted by the vapor-liquid equilibrium, but rather depends on the separation properties of the membranes. As shown in Figure 2.5, molecules penetrate through the membranes with different rates, depending on their molecular properties, as well as the sorption and diffusion behaviors of the membrane

[113]. This constitutes the key advantages for the separation of azeotrope mixtures and close-boiling mixtures with this technology.

Figure 2.4. Basic pervaporation process.

Figure 2.5. Schematic diagram of mass transport in pervaporation process.

Two important parameters are generally used to evaluate the performance of pervaporation process: permeation flux, J , and selectivity, α . Robeson [114] summarized the literature for gas separation and found that a trade-off phenomenon existed between the selectivity and permeability for polymeric membranes. That is, to obtain a high selectivity the permeation flux has to be sacrificed, and vice versa. Only some inorganic molecular sieves exhibited both high selectivity and permeability. This trade-off phenomenon is also widely

found between the selectivity and permeation flux for polymeric membranes in pervaporation process [115].

2.4.2. Applications of pervaporation

Generally, pervaporation can be used for the dehydration of the aqueous solutions of organic solvents, VOC removal and separation of organic-organic mixtures [80] as illustrated in Figure 2.6.

Figure 2.6. Applications of pervaporation

Dehydration of organic solvents has been intensively studied. Many organic solvents (such as EtOH, i-propanol (i-PrOH), n-butanol, and tetrahydrofuran (THF), etc.) form azeotropes with water, which are hard to be separated by conventional distillation. Pervaporation provides a clean and cheap alternative. Hydrophilic membranes with good water affinity can selectively adsorb water. Therefore, high separation factors can be obtained [116].

Removal of trace VOC from their aqueous water is an attractive issue in the treatment of industrial wastewater and polluted ground water [117]. Compared to the adsorption technique, pervaporation can easily and continuously concentrate or recover VOC at the permeate side. Furthermore, pervaporation is also used for the recovery of substances from fermentation broth [118], recovery of aroma compounds in food and cosmetics production [119], as well as removal of sulfur impurities from gasoline [120].

Separation of organic-organic solvents is important in petrochemical industry. However, the selectivity is usually low for current membranes because of the similar molecular properties of the components, such as boiling point, molecular size, solubility parameters, and so on. Recently, progress have been made with the developments of new membrane materials, advances on membrane fabrication techniques and membrane modules, particularly for the separation of benzene/cyclohexane [113], methyl-tert-butyl ether (MTBE)/methanol (MeOH) mixtures [121].

2.4.3. Pervaporation membranes

The materials and structures of membranes, the selective barriers in the pervaporation process, have to be carefully designed to achieve a high performance. There are two types of membranes used in pervaporation: polymeric membranes and inorganic membranes.

Polymeric membranes are the most popular membranes used in pervaporation. Three types of polymeric membranes are commonly reported, i.e. hydrophilic, organophilic and organoselective membranes [4]. Hydrophilic membranes with high water affinity are widely used for the dehydration of organic solvents. Poly(vinyl alcohol) (PVA) [122-124] and alginate [125-127] are representative materials. Organophilic membranes are often used to removal trace organic solvents from aqueous solutions. Polydimethyl siloxane (PDMS) based materials [128-129] are predominantly commercial organophilic membranes. Other rubbery polymers such as PU [130] have also been utilized. Organoselective membranes are used for the separation of the most challenging organic solvent mixtures. Because of the varying characteristics of different solvent mixtures, many materials have been used. For example, in the separation of benzene/cyclohexane mixtures, the use of both hydrophilic (PVA [131]) and organophilic (PDMS [132], PU [133]) membranes are reported.

Polymeric materials often suffer from excessive swelling and poor resistance to organic solvents. In comparison, inorganic membranes have tough and regular pore structures and show no swelling in solvents, which generally result in high selectivity and flux. Ceramic and zeolite membranes are the most popular inorganic membranes for pervaporation application [116].

2.5. Solution-diffusion model

The solution-diffusion model is generally used to describe the mass transport mechanism in pervaporation processes [28]. It was first proposed by Graham for the mechanism of gas permeation through rubber membranes. In 1961, Binning et al. adopted it for pervaporation [73]. In this model, the permeate first dissolves in the membrane, followed by diffusion through the membrane with the chemical potential gradient as the driving force. Thus, mass transport through a dense membrane can be divided into three steps [6]:

- (1) Sorption of the permeate molecules in the upstream surface of the membrane;
- (2) Diffusion across the membrane;
- (3) Desorption in the downstream surface of the membrane.

The upstream surface of the membrane is in contact with the feed solution. Therefore, a thermodynamic equilibrium is believed to be reached instantly at the interface:

$$\frac{C_{ms,i}}{C_{f,i}} = K_i \quad (2.1)$$

where $C_{ms,i}$ is the concentration of component i in the membrane surface in contact with the feed, $C_{f,i}$ is the concentration of component i in the feed, and K_i is the partition coefficient of component i . The diffusion of component i across the membrane is governed by the Fick's first law:

$$J_i = -D_i \frac{dC_{ms,i}}{dl} \quad (2.2)$$

where J_i is the permeation flux of component i , D_i is the diffusion coefficient, and l is the diffusion path. If it is assumed that the concentration profile along the membrane is linear, Eq (2.2) becomes:

$$J_i = D_i K_i \frac{\Delta C_i}{\delta} \quad (2.3)$$

where δ is the membrane thickness, ΔC_i is the concentration gradient between the feed side and the permeate side of the membrane of component i . The permeability, P , of component i can be defined as:

$$P_i = D_i K_i \quad (2.4)$$

Therefore, the ideal separation factor, α , is defined as:

$$\alpha = \frac{P_i}{P_j} = \frac{D_i}{D_j} \frac{K_i}{K_j} = \alpha_{diff} \alpha_{sorp} \quad (2.5)$$

which shows that the overall separation factor is a product of the sorption selectivity and diffusion selectivity.

2.6. CS membranes for pervaporation

Because of its hydrophilic nature and good solvent resistance, CS membranes have been intensively studied for the dehydration of alcohols. However, native CS membranes often suffer from low selectivity [134-135] caused by excessive swelling in aqueous solution. Chemical or physical modifications are therefore necessary to overcome this hurdle. Crosslinked, blended, multilayered CS membranes, as well as CS membranes containing inorganic fillers have been developed.

2.6.1. Crosslinked, blended and multilayered CS membranes

Crosslinking is the most popular method to improve mechanical strength and to control the swelling of CS membranes. The interactions between the crosslinking agents and CS can be generally classified into two types: (1) ionic interaction (e.g. use of metal salts [136-138] and inorganic acids [139-142]), and (2) covalent bonding (e.g. use of several organic chemicals [30, 143-152]). Crosslinking often leads to a decrease in polymer crystallinity and shrinkage of crystal size [141, 143, 148-150], which would contribute to enhanced selectivity but compromise the permeation flux (the trade-off phenomena [114]). The use of bulk and hydrophilic crosslinking agents, binary crosslinking agents [153], or combining with the bulk structure modification [154] may overcome this limitation.

Polymer blending is a common modification for polymers [80]. Since CS is an anionic polymer, it is able to form polyelectrolyte complexes with negative-charged polymers such as PAA [155-158], alginate [159-162], sodium carboxymethyl cellulose (CMCNa) [163], and phosphotungstic acid (PTA) [164], etc. CS has also been blended with non-charged polymers such as poly(vinyl alcohol) (PVA) [165-167], hydroxyethylcellulose (HEC) [168-169], poly(vinylpyrrolidone) (PVP) [170-172], poly(ethylene oxide) (PEO) [173], or hydroxypropyl cellulose (HPC) [174], and some natural polymers (e. g. silk fibroin [175], bacterial cellulose (BC) [176] and gelatin [177]). Blending with partially hydrophilic or hydrophobic nylons allows one to control the hydrophilicity/hydrophobicity of the resulting membrane [178-179].

CS has been coated on several porous supports, such as polysulfone (PSf) [180] [181], polyacrylonitrile (PAN) [182-183] ultrafiltration (UF) membranes

or zeolite [184] membranes to form multilayer membranes. With a very thin active layer and effectively reduced transport resistance, high permeation flux can be obtained [185-188]. The reduction in separation factor can be compensated by crosslinking [180, 186-188] or modification with surfactants [189]. To enhance the adhesion between different layers, various strategies have been reported, including: coating the support with hydrophilic polymer [180], reinforcing interactions between the two layers [182-183], addition of interlayer [190-191] between the support and active layers, etc.

2.6.2. CS-inorganic fillers composite membranes

Both ‘class I’ and ‘class II’ CS-based inorganic composite membranes have been developed, and intensively studied in pervaporation applications. Table 2.2 generalizes their performances in pervaporation for the separation of various solvent mixtures reported in literatures in recent years.

2.6.2.1. ‘Class I’ CS composite membranes

Zeolites, carbon nanotubes, metal oxides and graphite are the most commonly used inorganic fillers to form composites with CS to fabricate ‘class I’ organic-inorganic membranes. The fabrication process can be simply realized by physical mixing.

Continuous zeolites membranes have very high selectivity and excellent thermal stability, but are expensive to produce. Therefore, embedding zeolite particles into a polymer matrix has become an attractive alternative which can

be realized by simple solution mixing. Hydrophilic zeolites with low Si/Al ratio are often used as the filler of hydrophilic CS because of compatibility [192]. Ahmad et al. studied the dehydration of i-PrOH solution using CS membranes containing HY [193] and NH₄Y [194] zeolites, respectively. The performances of these composite membranes were remarkably improved compared to the native CS membranes. The authors attributed the decreased diffusion resistance to the addition of zeolite. Compared to their results, Kittur et al. [195] reported a novel CS-NaY composite membrane showing higher selectivity and flux with 30 wt.% zeolite loading. Furthermore, they found that both the flux and separation factor increased with increasing NaY content. This ‘anti-trade-off’ phenomenon in CS-zeolite composite membranes was also reported by Chen et al. [196] and Varghese et al. [197]. Sun et al. [198] composited CS with unmodified H-ZSM-5 [192] and surface modified H-ZSM-5 membranes, respectively. They found that only the modified H-ZSM-5 was able to enhance the selectivity and flux simultaneously owing to the ionic interactions between the modified H-ZSM-5 zeolite and CS. In addition, the CS-mordenite membranes for the dehydration of ethylene glycol (EG) [199], CS-ZSM-5 membranes for the separation of dimethyl carbonate (DMC)/MeOH mixture [200], and CS-silicalite membranes for the separation of toluene/MeOH and toluene/EtOH mixtures [201] were also reported.

Besides zeolite, several other inorganic fillers are also used to form composites with CS. CS can be intercalated into the MMT interlayer to form nanocomposites due to their electrostatic attractions [202]. In addition to the high separation factor [203], the thermal stability and mechanical properties of the nanocomposites can be improved [204]. The incorporation of graphite [205]

and CNT [206] into CS was also reported to improve the selectivity for the pervaporation of benzene/cyclohexane mixtures.

In general, the incorporation of inorganic fillers into CS improves the thermal and mechanical stability of the resulting membranes, as well as the pervaporation performance. The degree of enhancements largely depends on the type, loading ratio of inorganic fillers, the interactions between CS and inorganic fillers, and the properties of the solvent mixtures.

2.6.2.2. 'Class II' CS composite membranes

In 'Class II' composite membranes, the strong covalent bonds between the organic and inorganic phases reinforce the dispersion of inorganic fillers at the molecular level in the polymer matrix. To fabricate 'Class II' composite membranes, two techniques have been commonly used: (1) in situ polymerization, and (2) sol-gel method [207]. CS is often incorporated with silanes via sol-gel reaction. The introduced inorganic silanes may act as crosslinkers of CS inter-chains with the formation of C-O-Si bonds through esterification reactions between the silanol groups of silanes and hydroxyl groups of CS [208].

The widely used silanes including 3-aminopropyl-triethoxysilane (APTEOS) [208], tetraethoxysilane (TEOS) [209], and γ -(glycidyloxypropyl)trimethoxysilane (GPTMS) [210-211]. Generally, the covalent bonds between CS and silanes reinforce the dispersion of silanes and make the packing of polymer chains in the amorphous region more compact, which may benefit the selectivity [208]. Moreover, these silane-crosslinked CS

membranes were found to have excellent stability for long-term applications. A GPTMS containing CS hollow fiber membrane was found to maintain its pervaporation efficiency after operating for 330 days, while the membrane without GPTMS failed after 8 days [212]. Silica nano particles were functionalized with sulfonic acid groups and introduced into CS as a crosslinker by Liu et al. [213] The presence of nano-sized silica particle provided extra free volume for the permeation of water molecules. Therefore, the separation factor was improved without compromising the flux.

Table 2.2. Performances of CS-based organic-inorganic composite membranes in pervaporation.

Membranes	Solvents to be separated	Separation factor	Flux (g/m ² h)	Thickness (μm)	T (°C)	Source
CS/HY (20 wt.%) zeolite	EtOH (90 wt. %)/water	102	353			[196]
CS/H-ZSM-5 zeolite (8 wt%)	EtOH (90 wt. %)/water	153	231	25	80	[192]
CS/modified H-ZSM-5 zeolite (8 wt%)	EtOH (90 wt. %)/water	275	278.5	25	80	[198]
CS/NaY (30 wt.%) zeolite	i-PrOH (90 wt. %)/water	450	115	40 ± 2	30	[195]
CS/NaY (0.4 wt.%) zeolite	i-PrOH (90 wt. %)/water	48	60	20-30		[193]
CS/NH ₄ Y (0.2 wt.%) zeolite	i-PrOH (90 wt. %)/water	38	39		30	[194]
CS/NaY (40 wt.%) zeolite	THF (95 wt. %)/water	2140	168.8	40 ± 2	30	[197]
CS/PAA/mordenite (4 wt.%)	EG (80 wt. %)/water	258	165	25 ± 2	70	[199]
CS/ZSM-5 zeolite (5 wt.%)	DMC (30 wt. %)/MeOH	6	103	35 ± 2	25	[200]
CS/STA (8 wt.%)	DMC (90 wt. %)/MeOH	67	1163	13 ± 0.5	50	[214]
CS/silicalite (10 wt.%)	Toluene (10 wt. %)/MeOH	264	19.2	55-60	30	[201]
	Toluene (10 wt. %)	217	18.1			

Membranes	Solvents to be separated	Separation factor	Flux (g/m ² h)	Thickness (μm)	T (°C)	Source
	wt. %)/EtOH					
CS/MMT (10 wt. %)	i-PrOH (90 wt. %)/water	14992	142.3	40 ± 2	30	[203]
CS/TEOS	EtOH (96.5 wt. %)/water	∞	8		40	[209]
CS/ST-GPE-S	EtOH (90 wt. %)/water	919	410	32	70	[213]
CS/GPTMS	i-PrOH (70 wt. %)/water	694	1730	1.2 ± 1.2	70	[210]
CS/GPTMS/PAN	i-PrOH (90 wt. %)/water	2991	145	1.86	25	[212]
CS/GPTMS/PTFE-g-PSSA	i-PrOH (70 wt. %)/water	775	1730		70	[211]
CS/GPTMS/PTFE-g-PSSA hollow fiber	i-PrOH (70 wt. %)/water	78	128	1.86	25	[215]
CS/APTEOS	EtOH (85 wt. %)/water	597	887	18 ± 0.5	50	[208]
CS/APTEOS	MeOH (70 wt. %)/DMC	30.1	1265	20 ± 0.5	50	[216]
PVA/CS/graphite (6 wt. %)	Benzene (50 wt. %)/cyclohexane	59.8	124.2	80 ± 5	50	[205]
CS/PVA/CNT (1 wt. %)	Benzene (50 wt. %)/cyclohexane	53.4	65.9	~80	50	[217]

CHAPTER 3 EXPERIMENTS

3.1. Introduction

This chapter describes the experimental procedures and related methods used in this project, including the materials, experimental rigs and their set-up, standard analytical and characterization instruments, operation procedures, and experimental design. As the project employed many analytical instruments (FT-IR, UV/Vis, TGA, SEM, gas chromatography (GC), etc.), only a few key instruments and their testing conditions/procedures will be introduced here. Some home-made rigs will be presented with their diagrams/photos.

3.2. Materials and Reagents

CS flakes with DD% of 90% and Mw ~180,000 were obtained from Bio21 Co. Ltd., Thailand. Acid orange-7 (AO-7) ($C_{16}H_{11}O_4N_2SNa$, MW 350.3, dye content > 85%) and acid red-18 (AR-18) ($C_{20}H_{11}O_{10}N_2S_3Na_3$, MW 604.5, dye content > 75%) were purchased from Sigma. Their molecular structures are shown in Figure 3.1(a) and 3.1(b), respectively. Octaanion (OA), octaaminophenyl (OAPS), octanitrophenyl (ONPS) POSS were purchased from Mayaterials Inc., USA and octaammonium (OAS) POSS was provided by Hybrid PlasticsTM, USA. The chemical structures and properties of these POSS are shown in Table 3.1. Sodium chloride (Fluka), riboflavin (Sigma), ammonia sulphate (Merck), acetic acid (Merck), n-butanol (Merck) and EtOH (99.99%, Merck) were of analytical grade and used as received.

Figure 3.1. Molecular structures of (a) AO-7 and (b) AR-18.

Table 3.1. Chemical structures and properties of POSS.

POSS	R groups	Molecular formula	Mw	Solvent solubility
OA	$\text{O}^-\text{N}(\text{CH}_3)_4^+$	$\text{C}_{32}\text{H}_{96}\text{O}_{20}\text{Si}_8 \sim 60 \text{ H}_2\text{O}$	2219	Water
OAS		$\text{C}_{24}\text{H}_{72}\text{Cl}_8\text{N}_8\text{O}_{12}\text{Si}_8$	1173	Water
ONPS		$\text{C}_{48}\text{H}_{32}\text{N}_8\text{O}_{28}\text{Si}_8$	1393	THF
OAPS		$\text{C}_{48}\text{H}_{48}\text{N}_8\text{O}_{12}\text{Si}_8$	1154	THF, chloroform, hexane

3.3. CS hydrogel beads for dye adsorption

3.3.1. Preparation of CS beads

The native CS hydrogel beads were prepared using phase inversion. CS flakes were dissolved in 1 wt.% acetic acid aqueous solution and stirred for 24

h to prepare 1.5% (w/v) CS solution. The resulting solution was fed drop by drop into a stirred 4% (w/v) NaOH solution through a 27G needle using a peristaltic pump (as shown in Figure 3.2). The beads were allowed to react with the NaOH coagulant solution for 2 h before collecting and washing with de-ionized water until neutral. After blot-drying, the beads were stored in 80% EtOH. Before use, the beads were washed and soaked in de-ionized water for at least 1 h.

Figure 3.2. Photo of the set-up for CS beads preparation.

3.3.2. Modification of CS beads

After blot-drying, the native CS beads were modified by an 0.1 M $(\text{NH}_4)_2\text{SO}_4$ aqueous solution at room temperature using two methods. In Method I, the CS beads were stirred (300 rpm) in 0.1 M $(\text{NH}_4)_2\text{SO}_4$ solution at a ratio of 1: 20 for 6 h. The resulting beads were designated as CS-S. In Method II, the CS beads were loaded in a column and washed with 15 ml 0.1 M $(\text{NH}_4)_2\text{SO}_4$ solution. After that, 30 ml 0.1M $(\text{NH}_4)_2\text{SO}_4$ solution was fed to the column at a rate of 0.5 ml/min and re-circulated for 4 h. The resulting beads

were designated as CS-C. After the modifications, CS-S and CS-C beads were washed with de-ionized water, blot-dried, and stored in 80% EtOH. Before adsorption experiments, the beads were washed and soaked in de-ionized water for at least 1 h.

3.3.3. Characterization of CS beads

The macrographs of CS beads were taken by a JEOL JSM-6390LA SEM at 5kV. To examine the cross-sectional morphology, the beads were freeze-fractured in liquid nitrogen. The surface area of CS beads was measured by a Quantachrome Autosorb-6B using nitrogen isotherm at 77K. Prior to nitrogen adsorption isotherm measurements, the samples were degassed overnight under vacuum using an Autosorb degasser (PSA, Quantachrome Inc.) to remove contaminants, such as water, CO₂, hydrocarbons, etc. The degassing temperature was < 375 K and the vacuum was below 1.0×10^{-4} torr. The diameter of beads was determined under microscope and was taken the average of over 20 freeze-dried beads. The porosity of beads was measured by solvent replacement method [218].

FT-IR spectra were recorded by a Nicolet-5700 spectrophotometer with a DTGS detector. Each spectrum was collected as the average of 32 scans in the range 4000-400 cm⁻¹ with a resolution of 4 cm⁻¹. CS films were prepared for the FT-IR measurement by the following method: 1 % (w/v) CS acetic acid (1%) solution was cast onto a petri-dish and dried at 40 °C, followed by the neutralization with 1 M NaOH solution. After washing and drying at room temperature, the CS film was soaked in 0.1 M (NH₄)₂SO₄ solution for 6 h for

modification. After washing with de-ionized water, the modified CS film was soaked in 0.01 mg/ml AO-7 solution pH 8.2 for 30 min to adsorb the dye. After that, the AO-7 adsorbed film was regenerated by immersing in 1M NaOH solution, followed by washing with de-ionized water. The FTIR spectra of the native CS film, (NH₄)₂SO₄ modified film, AO-7 adsorbed film and regenerated film were recorded, respectively.

3.3.4. Batch studies

Batch adsorptions were conducted in 100 ml Erlenmeyer flasks containing 0.4 g of blot-dried beads and 40 ml dye solutions with different initial concentrations. The pH of the dye solutions was adjusted to 8.2 by adding 0.1 M NaOH solution. The flasks were shaken at 200 rpm at 22°C, as shown in Figure 3.3. The concentration of the dye solutions were monitored continuously and it was found that 24 h was more than enough for the system to reach equilibrium. The dye solutions at equilibrium were analyzed by a Nicolet evolution 500 UV/Vis spectrophotometer at the λ_{max} of 485 and 506 nm for AO-7 and AR-18, respectively. Calibration curves obtained by measuring the absorbance of standard dye solutions with known concentrations are shown in Figure 3.4. Since the UV absorbance was linear with the concentration in the applied concentration range. Thereby, concentration of the sample solution was calculated by comparing the absorbance values with the calibration curves accordingly. The amount of dyes adsorbed per unit mass of beads at equilibrium was calculated as:

$$q_e = \frac{(C_0 - C_e)V}{W_{bat}} \quad (3.1)$$

where q_e is the adsorption capacity at equilibrium (mg/g); C_0 and C_e are the initial and equilibrated dye concentration (mg/ml), respectively; W_{bat} is the mass of blot-dried CS beads used in the batch adsorber (g); V is the volume of dye solution (ml).

Figure 3.3. Photo of the batch adsorption set-up.

Figure 3.4. Calibration curves of UV absorbance vs concentration of AO-7 and AR-18.

3.3.5. Fixed bed studies

About 6.3 g of blot-dried beads (net weight around 0.165 g upon freeze-drying) were packed in a column (with diameter of 14 mm, length of 65 mm and voidage of 0.45). Dye solution was fed into the fixed bed using a peristaltic pump at 22 °C. The pH of the AO-7 and AR-18 influents was adjusted to 8.2, respectively. The effluents at the outlet of the fixed bed were collected by an auto-sampler and analyzed with a UV/Vis spectrophotometer. The fixed bed rig is shown in Figure 3.5.

Figure 3.5. Photo of the fixed bed rig for dye adsorption.

The breakthrough point (t_b , min) and the amount of AO-7 adsorbed per unit mass of CS beads in the column (q , mg/g, the maximum capacity or the optimum uptake capacity of the column) were used to evaluate the adsorption performance of the native and modified beads. t_b is defined as the time when the effluent concentration (C , mg/ml) from the column is about 5% of the inlet concentration (C_0 , mg/ml), while q is calculated by the equation below [219]:

$$q = \frac{Q}{W_{col}} = \frac{\sum_{i=1}^n v(t_i - t_{i-1})[1 - (C/C_0)_i]C_0}{W_{col}} \quad (3.2)$$

where Q is the total amount of dye adsorbed in the column (mg); i is the number of sampling point; W_{col} is the mass of CS beads packed in the column (g, based on the freeze-dried beads); v is the flow rate of the influent (ml/min); and t_i is the i^{th} time point.

3.3.6. Regeneration

The dye exhausted beads in column were desorbed using a 1M NaOH aqueous solution at a flow rate of 0.22 ml/min. The desorbed beads were designated as CS-D. The beads were then re-modified with 0.1 M $(\text{NH}_4)_2\text{SO}_4$ solution using Method II as described in section 3.3.2 and re-used for dye adsorption. Up to 20 cycles of adsorption-regeneration-modification were carried out. The CS beads re-modified for the first, tenth and twentieth cycles were designated as CS-R1, CS-R10 and CS-R20, respectively.

3.3.7. Wheeler-Jonas model

The breakthrough curves were modeled by the W-J equation, which implicitly assumes a linear isotherm and a first order nature for the rate of adsorption:

$$t = \frac{W_e}{C_0 v} \left[W - \frac{\rho_B v}{k_v} \ln \left(\frac{C_0}{C} \right) \right] \quad (3.3)$$

where t is the time to reach the effluent concentration (min); W_e is the dynamic adsorption capacity of the CS beads (mg/g); k_v is the overall adsorption rate

coefficient (min^{-1}); ρ_B is the bulk density of the fixed bed (g/ml), which can be calculated from the volume of the fixed bed and the weight of the adsorbent loaded. Eq (3.3) can be rearranged as:

$$\ln\left(\frac{C_0}{C}\right) = -\frac{k_v C_0}{W_e \rho_B} t + \frac{W k_v}{\rho_B V} \quad (3.4)$$

Eq (3.4) is used to evaluate k_v and W_e from the slope, a , and the intercept, b , of the linear plot of $\ln(C_0/C)$ versus t , that is:

$$k_v = \frac{b \rho_B V}{W} \quad W_e = -\frac{b C_0 V}{a W} \quad (3.5)$$

3.4. Preparation and characterization of CS membrane and CS-POSS composite membranes

3.4.1. Preparation of CS membrane and CS-POSS composite membranes

CS flakes were dissolved in 1 wt.% acetic acid aqueous solution and stirred for 4 h at room temperature to obtain a 1 wt.% CS solution. Various amounts of POSS powders were added to make the eventual CS-POSS composite membranes contain 1, 5 and 9 wt.% of POSS. The CS-POSS suspension was stirred for another 20 h and filtered. The resulting solution was then cast into petri dishes and allowed to evaporate the solvent in an oven at 40 °C for around 12 h. The completely dried membranes were immersed in 1 M NaOH aqueous solution for 15 min for neutralization. After washing thoroughly with de-ionized water, the neutralized membranes were dried at room temperature and peeled off for use. The native CS membrane was prepared following the same procedure except that no POSS were added. The appearance of the resulting CS membrane is shown in Figure 3.6. The CS-POSS membranes were designated

as CS-X, where X was either OA, OAS, ONPS or OAPS. The thickness of the membranes was 30-40 μm .

Figure 3.6. Appearance of the dried CS membrane.

3.4.2. Characterization of CS membrane and CS-POSS composite membranes

FTIR spectra of the membranes were recorded by a Nicolet-5700 spectrophotometer with the parameters described in section 3.3.3. XRD spectra of the POSS powder, CS and CS-POSS composite membranes were obtained by a Siemens D5005 X-ray diffractometer. The measurement was operated at 40 kV, 40 mA (Cu K α radiation) with a 2θ range of 3–36°. The macrographs of the surface and cross-section of the membranes were taken by a JEOL JSM-6390LA SEM at 5kV. TGA was conducted with a TA SDT Q600 thermogravimetric analyzer at a heating rate of 10 °C/min under a nitrogen atmosphere. The mechanical properties of the membranes were measured by an Instron model 5543. Films with a gauge length of 50 mm and width of 10 mm were stretched at a crosshead speed of 2 mm/min at 20 °C. The resulting data were taken from the average of at least 5 samples.

3.4.3. Diffusion of riboflavin and NaCl

A homemade horizontal glass diffusion cell consisting of two cylindrical half-cells with a volume of 60 cm³ each was employed for liquid permeation studies, as shown in Figure 3.7. The membrane to be tested was placed between the two compartments of the diffusion cell. The contact area was 1.78 cm². Permeation studies were conducted for both NaCl and riboflavin aqueous solutions. The feed compartment was filled with 1 M NaCl or 50 mg/L riboflavin aqueous solution while the receiving compartment was filled with de-ionized water and stirred at 500 rpm with a magnetic bar. For NaCl permeation, the concentration of NaCl solution in the receiving compartment was measured continuously by a Thermo Orion 3 Star conductivity meter. For riboflavin permeation, 1 ml of the receiving solution was taken out at certain time intervals and analyzed by a Nicolet evolution 500 UV-visible spectrophotometer at 267 cm⁻¹. After measurement, the sample solution was immediately returned to the receiving compartment. The permeability coefficient, P , was calculated from the flux, J , during the steady state of diffusion where Fick's law was applicable (e.g., a high constant concentration on the feed side and negligible concentration on the other side). Hence, P was determined from the following equations [220]:

$$J = \frac{\Delta C}{\Delta t} \times \frac{V}{A} \quad (3.6)$$

$$P = J \times \frac{\delta}{C_0} \quad (3.7)$$

where V is the volume of de-ionized water in the receiving compartment (m³); A is the membrane contact area (m²); $\Delta C/\Delta t$ is the slope of the concentration in

the receiving compartment versus time during steady state; δ is the thickness of the membrane (m); and C_0 is the initial concentration of the feed solution (mg/L).

Figure 3.7. Photo of the diffusion set-up.

3.4.4. Adsorption of riboflavin

50 mg of dried membrane was added into 50 mg/L riboflavin solution and shaken at 150 rpm for 48 h. The concentration of the equilibrated solution was analyzed by the UV spectrophotometer at 267 cm^{-1} . The partition coefficient, K , was calculated as:

$$K = \frac{C_m}{C_{sol}} = \frac{V_{sol}(C_0 - C_{sol})}{V_m C_{sol}} \quad (3.8)$$

where C_m and C_{sol} are the riboflavin concentration in the membrane and in the solution at equilibrium (mg/L), respectively; C_0 is the initial concentration; V_{sol} and V_m are the volume of the solution and the membrane at equilibrium (L), respectively. The diffusion coefficient, D , was calculated according to the equation:

$$D = \frac{P}{K} \quad (3.9)$$

3.5. Pervaporation

The pervaporation set-up is a home-made stirred batch cell reactor consisting of a liquid feed compartment, an overhead stirrer, a membrane cell, a cold trap and a vacuum pump, as shown in Figure 3.8. 100 g feed solution was placed in the top compartment and in contact with one side of the membrane. The feed was stirred at 100 rpm using an over head stirrer. The temperature of the feed solution was maintained by a thermostatic water jacket. The membrane was fixed in the membrane module and supported by a porous steel disk. The effective membrane area was 13.8 cm². The pressure in the permeate side was maintained around 1 kPa using a vacuum pump. The membrane was equilibrated in the module for 2 h before starting the pervaporation experiment. After the experiment, the permeate condensed in the cold trap by liquid nitrogen was weighed and analyzed by an Agilent 6890N GC.

n-Butanol was used as the internal standard for GC sample. 0.4 g 5 wt.% n-butanol aqueous solution was added to 0.2 g sample solution and injected to GC by an auto-sampler. The GC parameters for the analysis are listed in Table 3.2. Standard EtOH aqueous solutions were prepared and measured to obtain the calibration curves. As shown in Figure 3.9, the percentage of EtOH peak area was found to be linear with the water fraction (wt.%) in the solution in certain concentration ranges. Therefore, by comparing the percentage of EtOH

peak area of the sample solution with the calibration curves, the concentration of the sample solution was obtained.

Figure 3.8. Photo of the pervaporation apparatus.

Table 3.2. GC parameters for the analysis of EtOH samples

Injection volume	1 μ L
Injector mode	Split (50 : 1)
GC inlet temperature	170 $^{\circ}$ C
Total flow	634 ml/min
Column	HP-INNOWax (Agilent), 30 m $\times$ 0.535 mm,
Column flow rate	10.9 ml/min
Oven	130 $^{\circ}$ C hold 2.5 min
Detector	FID, 170 $^{\circ}$ C; H ₂ flow: 40 ml/min, air flow: 450 ml/min, make up (He) flow: 45 ml/min

The permeate flux, J , and separation factor, α , were calculated as follows [113]:

$$J = \frac{W}{At} \quad (3.10)$$

$$\alpha = \frac{y_W / y_E}{x_W / x_E} \quad (3.11)$$

where W is the weight of permeate (g); A is the effective area of membrane in contact with the feed (m^2); t is the pervaporation time (h); y_W and y_E are the weight fractions of water and EtOH in the permeate, respectively; x_W and x_E are the weight fractions of water and EtOH in the feed, respectively. The higher the α value, the better selectivity of the membrane, while a unit value of α indicates no separation occurring [221]. The pervaporation separation index (PSI) was used to evaluate the overall pervaporation performance and was calculated as:

$$PSI = J(\alpha - 1) \quad (3.12)$$

Figure 3.9. GC calibration curves of the area% of EtOH peak vs the solution composition.

3.6. Swelling and sorption measurement

Vacuum-dried membranes were weighed and immersed into de-ionized water or EtOH aqueous solutions and kept at 30 °C for 48 h to reach equilibrium. The swollen membranes were carefully wiped using tissue paper to remove the surface liquid and weighed quickly. The degree of swelling (DS%) of the membranes was calculated by:

$$DS\% = \frac{W_{swol} - W_{dry}}{W_{dry}} \times 100 \quad (3.13)$$

where W_{swol} and W_{dry} are the weights of the swollen and dry membranes, respectively.

The sorption experiments of the CS membrane and CS-POSS composite membranes were conducted in EtOH solutions with water fraction ranging from 5 to 30 wt.%. Around 1 g of vacuum dried membrane was weighed and immersed into 50 g EtOH feed solution at 30 °C. After 48 h, the feed solution was taken out for GC analysis. The composition of the solution adsorbed into the membrane was thereby obtained. Therefore, the sorption selectivity, α_{sorp} , can be calculated as:

$$\alpha_{sorp} = \frac{m_W / m_E}{x_W / x_E} \quad (3.14)$$

where m_W and m_E are the weight fractions of water and EtOH adsorbed in the membrane, respectively; x_W and x_E are the weight fractions of water and EtOH in the feed, respectively. According to the solution-diffusion theory, the diffusion selectivity, α_{diff} , can be calculated as:

$$\alpha_{diff} = \alpha / \alpha_{sorp} \quad (3.15)$$

CHAPTER 4 DYE ADSORPTION ON MODIFIED CHITOSAN BEADS

4.1. Introduction

This chapter is reproduced in part with permission from [D. Xu, S. Hein, S. L. Loo, K. Wang, The fixed-bed study of dye removal on chitosan beads at high pH. *Industrial & Engineering Chemistry Research* (2008), 47, 8796-8800] Copyright [2010] American Chemical Society. Native CS presents poor adsorption capacity towards anionic dyes in a basic environment, because few amine groups of CS are protonated to adsorb dye anions. Therefore, the native CS beads were modified by $(\text{NH}_4)_2\text{SO}_4$ solution in a stirring batch rig and a column resulting in CS-S and CS-C beads, respectively, as described in Chapter 3. This chapter will present the characterizations and the adsorption performance of the beads at pH 8.2 in both batch and fixed bed adsorbers. The fixed bed breakthrough behaviors of the native and modified CS beads will be studied and compared. The adsorption mechanism and the regeneration of the dye exhausted beads will be investigated and discussed. Furthermore, the fixed bed kinetics will be modeled using the W-J equation (Eq (3.3)). The influences of operating conditions/parameters on the kinetics such as influent concentration and flow rate will be studied.

4.2. Experimental

The CS hydrogel beads were fabricated and modified following the procedures described in sections 3.3.1 and 3.3.2. The native CS and modified

beads were characterized using BET, SEM and FT-IR. The dye adsorption was carried out in both batch and fixed bed adsorbers. The set-up and procedure for these experiments were given in sections 3.3.4 and 3.3.5, while the regeneration of the beads was performed using the method described in section 3.3.6.

4.3. Characterization of CS beads

The physical properties of the CS beads are listed in Table 4.1. The surface and cross-section morphologies of CS beads were observed by SEM. The macrographs shown in Figure 4.1 reveal that the pores on the surface (Figure 4.1(a)) are larger in size and packed more densely compared to the pores inside the beads (Figure 4.1(b)).

Table 4.1. Physical properties of the CS beads [222].

Average beads diameter (mm)	1.8 ± 0.2
BET surface area (m²/g)	52.9
Average pore diameter (Å)	127
Porosity	63.2% in i-PrOH, 75.5% in H ₂ O

Figure 4.1. SEM images of the CS beads: (a) surface, (b) cross section [222].

4.4. Adsorption isotherm

Figure 4.2 shows the adsorption isotherm of AO-7 measured on the modified beads (CS-S) in the batch adsorber at 22 °C, pH 8.2. The isotherm is largely linear with the goodness of fit $R^2 = 0.9931$. The adsorption capacity at the initial concentration of 0.015 mg/ml is approximately 80 mg dye per gram of neat CS (based on the weight of freeze-dried beads). This value is among the highest capacities reported under such conditions. In comparison, low-cost adsorbents such as spent brewery grain, coffee ground charcoal and granular activated carbons showed a maximum capacity of 30.5 mg/g, 14.5 mg/g and 15 mg/g, respectively [223-225], while the adsorption of AO-7 is almost zero on titanium dioxide at pH 7.0 [226]. Yoshida et al. [227] cross-linked CS fibers and measured their adsorption capacity towards AO-2 at pH 6.9. The adsorption capacity obtained at our experimental dye concentration (0.015 mg/ml) is around 12 mg/g, which was calculated from the isotherm parameters derived by the authors.

Figure 4.2. Adsorption isotherm of AO-7 on the CS-S beads (pH: 8.2, temperature: 22 °C) [222].

As shown in Table 2.1 that some modified CS showed very high adsorption capacities towards dyes. For example, the TPP crosslinked CS beads presented a capacity towards AO-7 as high as 1946 mg/g at pH 4.0 and an initial concentration of 5455 mg/g [55]; a novel of carboxymethylated CS-conjugated magnetic nano-adsorbent had adsorption capacities towards AO-12 and AG-25 as high as 1883 mg/g and 1471 mg/g, respectively, at pH 3.0 and an initial dye concentration of 5000 mg/g [50]; the templated CS beads showed a capacity of 2500 mg/g towards remazole black 5 at pH 3.0 and an initial dye concentration of 5000 mg/g [51]. However, except the high initial dye concentration, all the high adsorption capacities towards anionic dyes were obtained at low pH (pH 3.0 to 4.0) as shown in Table 2.1. At higher pH (pH > 6.0), the capacity became very low even zero [50]. Furthermore, some modifications were relatively complex involving multiple chemical reactions [50] and the templated CS was

possibly only had high adsorption capacity towards the template dye molecule [51].

Comparatively, the $(\text{NH}_4)_2\text{SO}_4$ modification in this study is feasible and the resulting CS beads showed high adsorption capacities toward acid dyes at a high pH (pH 8.2) and a low initial dye concentration. Therefore, it is specifically advantageous for the direct treatment of wastewater with a low dye concentration and a high pH.

4.5. Comparison of AO-7 adsorption on native and modified CS beads

The fixed-bed breakthrough behaviors of AO-7 on the native (CS) and modified beads (CS-S and CS-C) are shown Figure 4.3. The volumes of the dye solution treated by the CS-S and CS-C beads were 1.00 L and 0.52 L before the exhaust time (corresponding to $C/C_0 = 0.95$), respectively, while that of the CS beads was only 0.16 L. As listed in Table 4.2, the breakthrough times (t_b , corresponding to $C/C_0 = 0.05$) of the CS-C and CS-S beads are 4.7 and 2.1 times of that of the CS beads, respectively, while the maximum adsorption capacities of them are 7.4 and 3.6 times of that of the CS beads, respectively. Therefore, the modified beads, especially CS-C, presents a significantly improved adsorption capacity at pH 8.2 compared to the native CS beads.

Figure 4.3. Fixed-bed breakthrough curves of AO-7 on the CS, CS-S and CS-C beads (inlet concentration: 0.01 mg/min, flow rate: 0.22 ml/min, pH: 8.2, temperature: 22°C).

Table 4.2. Comparisons of the breakthrough time and adsorption capacity of the fixed bed packed with different CS beads.

	CS	CS-S	CS-C	CS-D	CS-R1	CS-R10	CS-R20
Breakthrou							
gh time (t_b, min)	180	375	850	90	860	861	833
Adsorption							
capacity (q, mg/g)	60.4	219.8	445.6	47.2	430.1	421.0	417.9

4.6. Adsorption mechanism

It is known that the protonation of the amine groups is responsible for the capture of anionic dyes through electrostatic attraction in adsorption process [41]. However, the amount of the protonated amine groups is very little at pH 8.2, and the adsorption is mainly governed by physisorption. This is the reason for the low adsorption capacity of native CS beads under such condition. When the native CS beads are exposed to $(\text{NH}_4)_2\text{SO}_4$ solution, it is hypothesized that SO_4^{2-} groups from $(\text{NH}_4)_2\text{SO}_4$ are electrostatically attached to $-\text{NH}_3^+$ groups of CS. Thereby, a large amount of $-\text{NH}_3^+$ groups is shielded and protected by SO_4^{2-} groups. In the following dye adsorption process, the attached SO_4^{2-} groups are displaced by the SO_3^{2-} groups of AO-7 in an ion-exchange manner. Hence, the large adsorption capacity of modified beads is obtained at high pH, which constitutes an advantage for practical applications. When the CS beads are packed in column and re-circulated with $(\text{NH}_4)_2\text{SO}_4$ solution (Method II), the amine groups of the CS beads can be more effectively shielded (or re-shielded) by SO_4^{2-} groups, which explains that CS-C beads have better adsorption efficiency than CS-S beads.

To verify this proposed ion-exchange mechanism of the dye adsorption on modified CS beads, the FTIR spectra of the native, $(\text{NH}_4)_2\text{SO}_4$ modified, AO-7 loaded, and regenerated CS films, AO-7, as well as $(\text{NH}_4)_2\text{SO}_4$ were recorded. As presented in Figure 4.4, the native CS shows characteristic adsorption band at 1583 cm^{-1} , which corresponds to the amide II band. After modification with $(\text{NH}_4)_2\text{SO}_4$, this band shifted to a lower wavenumber of 1537 cm^{-1} accompanied by the appearance of the stretching vibration of SO_4^{2-} at 617 cm^{-1} [228]. This shows that the SO_4^{2-} groups have been attached to the amine groups of CS. For

the AO-7 loaded CS, the band at 617 cm^{-1} disappeared and some of the characteristic bands of AO-7 [229] appeared, such as the N-H stretching at 1508 cm^{-1} , the N=N stretching at 1452 cm^{-1} , the peak at 1037 cm^{-1} owing to the coupling between the phenyl and SO_3 groups and some other characteristic peaks in the range of 850-660 cm^{-1} . At the same time, the amide II band is still at the low wavenumber range and the amide I and II bands broadened because of the interferences of aromatic C=C and C=N stretching in this region. All these changes show that the SO_3^{2-} groups of AO-7 have replaced the SO_4^{2-} groups at the amine sites of CS. After desorption, all the characteristic features of SO_4^{2-} modification and AO-7 adsorption disappeared and the amide II band shifted back to 1583 cm^{-1} . The spectrum of the desorbed CS is almost the same as that of the native CS. It indicates that the dye-adsorbed CS can be effectively regenerated by NaOH.

Based on the above experimental results and analysis, the mechanisms for the CS modification, dye adsorption and regeneration are proposed as follows:

- (1) Modification with $(\text{NH}_4)_2\text{SO}_4$:

- (2) Replacement of SO_4^{2-} by SO_3^{2-} of AO7 during adsorption:

- (3) Desorption of dye by NaOH:

Figure 4.4. FT-IR spectra of (i) native CS, (ii) CS regenerated by 1 M NaOH after dye adsorption, (iii) CS modified with 0.1M $(\text{NH}_4)_2\text{SO}_4$, (iv) modified CS with adsorbed AO-7, (v) AO-7, (vi) $(\text{NH}_4)_2\text{SO}_4$ [222].

4.7. Desorption and regeneration

As shown in Figure 4.5, the OA-7 adsorbed on the CS-S beads was almost completely desorbed by the 1 M NaOH solution. Compared with the adsorption process, the desorption time is less than 20% of the breakthrough time at the same feed rate (0.22 ml/min). The effectiveness and the fast desorption kinetics are the advantages of this method. After desorption, the column (CS-D) was recharged with dye solution under the same conditions. The performance of this desorbed column was found to be similar to that of the original native CS beads but with a slightly lower capacity. However, when the desorbed column was re-treated with $(\text{NH}_4)_2\text{SO}_4$ solution as described in Method II, the high adsorption capacity was recovered to the level of the original CS-C beads. Even after 20 desorption-regeneration-modification processes, the adsorption capacity of the

column was still retained, as shown in Figure 4.5. There were only slight decreases in adsorption capacity of the column regenerated after the first, tenth and twentieth time compared to the original CS-C beads, as listed in Table 4.2. This indicates that the beads can be completely regenerated and exhibit excellent stability for repeated use which is meaningful for practical applications.

Figure 4.5. Desorption (flow rate: 0.22 ml/min, temperature: 22 °C) and fixed bed breakthrough curves of AO-7 on the desorbed and regenerated CS beads (inlet concentration: 0.010 mg/ml, flow rate: 0.22 ml/min, pH: 8.2, temperature: 22 °C).

4.8. Adsorption of AR-18

To further verify the advantages of this modification technique, the adsorption of another anionic dye, AR-18, on the modified CS beads was investigated. Figure 4.6 shows the adsorption isotherms of AR-18 measured on the CS and CS-C beads at pH 8.2 in a batch adsorber. It is seen that the

adsorption capacity of the CS-C beads is significantly higher than that of the CS beads at the same conditions.

Figure 4.6. Adsorption isotherms of AR-18 on the CS and CS-C beads (pH: 8.2, temperature: 22 °C).

Figure 4.7. Fixed-bed breakthrough curves of AR-18 on the CS and CS-C beads (inlet concentration: 0.017 mg/ml, flow rate: 0.22 ml/min, pH: 8.2, temperature: 22°C) and the desorption of CS-C beads (flow rate: 0.22 ml/min, temperature: 22°C).

Figure 4.7 shows the breakthrough curves of AR-18 on the CS and CS-C beads. It is seen that the breakthrough time of the CS-C beads was around 2142 min, while that of the CS beads was only 5 min. A simple calculation using Eq (3.2) revealed that the adsorption capacity of the CS-C beads (427.22 mg/g) is about 14.4 times of that of the CS beads (29.74 mg/g). The dye exhausted CS-C beads can be almost completely desorbed using 1M NaOH solution within 400 min, as shown in Figure 4.7. These experimental results confirm the advantages of the modified beads for treating dye containing wastewater at high pH and the proposed mechanisms/theories.

4.9. Adsorption kinetics

4.9.1. Wheeler-Jonas model

The breakthrough curve of OA-7 on CS-S beads was modeled by W-J equation (Eq (3.3)) to study the adsorption kinetics. Svirbely [75] and Jonas [79] divided the entire breakthrough curve into three ‘segments’ and investigated the adsorption kinetics in each segment with the model. The W-J equation predicts a *J*-shaped breakthrough curve and is applicable when the plot of $\ln(C_0/C)$ vs t is linear. Such characteristics make it a good candidate for studying the breakthrough curves shown in Figure 4.3. Figure 4.8 shows an example plot of $\ln(C_0/C)$ vs t for breakthrough data. It is seen that the experimental data generally fall into two linear segments, with segment I covering C/C_0 from 0 to 0.1 ($\ln(C_0/C) > 2.3$) and segment II covering C/C_0 from 0.1 to 0.9 ($0.1 < \ln(C_0/C) < 2.3$). The goodness of fit, R^2 , equals 0.931 for segment I and 0.997 for segment II. Some deviations from linearity are observed at the first segment as

the partition point was chosen empirically. This two-segmented feature may point to different mass transfer mechanisms in each segment and inspired us to use the W-J model in a two-segmented approach.

Figure 4.8. An example of the two-segmented linear plot of $\ln(C_0/C)$ vs t
(inlet concentration: 0.01 mg/ml, flow rate: 0.34 ml/min, pH: 8.2,
temperature: 22 °C; Δ , experimental data; —, linear plot of W-J equation)
[222].

The modeling of fixed bed kinetics of dye adsorption on CS beads (or hydrogels) was rarely reported. The study of Yoshida et al [70], using the axial dispersion model with linear driving force for the rate of adsorption, was on CS fibers and a different type of dye (direct dye) with a rectangular adsorption isotherm at pH 3. A recent study by Guelli et al. [230] revealed that the fixed bed removal of acid dyes tended to deviate from the common sigmoid breakthrough curve. Their results showed that, for an acid dye (Green-4) to penetrate a fixed bed filled with activated carbon, the axial dispersion model gave reasonable fitting only up to $C/C_0 = 0.2$.

4.9.2. Effects of flow rate

Figure 4.9 shows the experimental breakthrough data (symbols) and optimal fittings (lines) of W-J equation. The calculated W-J parameters are listed in Table 4.3. The feed concentration was constant at 0.01 mg/ml while the feed rate was increased from 0.11 to 0.43 ml/min. The model correctly simulates the majority of the experimental data. It is seen that, as the flow rate increases, the overall adsorption rate, k_v , increases, while the dynamic capacity of the bed, W_e , shows only slightly changes in the second segment.

Figure 4.9. Fixed bed breakthrough curves of AO-7 on the CS-S beads at different flow rates: Δ 0.11 ml/min, $\circ$ 0.22 ml/min, $\square$ 0.34 ml/min, $\diamond$ 0.43 ml/min; — model fittings (inlet concentration: 0.01 mg/ml, pH: 8.2, temperature: 22°C) [222].

Some deviations are observed near the saturation point as observed in Figure 4.9. These are attributed to the intrinsic *J*-shaped characteristic of the W-J equation. It is also noted that the dye concentration in the effluents slightly overshoots the feed concentration (with the maximum ratio of C/C_0 around

1.05) for a short time before it pulls back. According to our adsorption mechanism analysis in section 4.6, AO-7 ions will replace SO_4^{2-} groups that attached to the $-\text{NH}_3^+$ groups of CS. The displaced free SO_4^{2-} groups will then stay in the mass transfer zone (MTZ) and combine with Na^+ to form Na_2SO_4 . It is known that inorganic electrolytes (such as NaCl) are stimulators for dyeing process, which promote equilibrium capacity and possibly the kinetics as well [227]. Therefore, Na_2SO_4 accumulated in the MTZ may enhance the local adsorption capacity. Some of the adsorbed dyes will desorb when the bulk feed sets in to wash away the salts. Therefore, overshoots appeared in the effluent.

Table 4.3. Parameters of W-J equation for breakthrough data at different flow rates with the inlet concentration of 0.01 mg/ml [222].

Flow rate (ml/min)	Segment I		Segment II	
	W_e (mg/g)	k_v (min ⁻¹)	W_e (mg/g)	k_v (min ⁻¹)
	0 to 0.1	0 to 0.1	0.1 to 0.9	0.1 to 0.9
0.11	26.5	2.0	29.7	1.9
0.22	19.2	3.8	31.0	2.7
0.34	14.8	5.7	32.4	3.9
0.43	16.0	6.6	30.7	4.6

It is also seen in Figure 4.9 that, as the flow rate increases from 0.11 to 0.43 ml/min, the time span between the breakthrough point ($C/C_0 = 5\%$) to the

saturation point is shortened from 4,000 to 900 min. This observation suggests that the length of the MTZ is a strong function of flow rate and indicates that the axial dispersion plays an important role at the feed rate of 0.11 ml/min (corresponding to the Reynolds number of 0.04). This is in agreement with the results of Yoshida et al. [70]

4.9.3. Effects of feed concentration

Figure 4.10 shows the breakthrough data (symbols) and model fittings (lines) at constant feed rate of 0.22 ml/min when the feed concentration was increased from 0.007 to 0.015 mg/ml. Reasonable fittings are obtained by the two-segmented W-J model. The derived model parameters are shown in Table 4.4. It is seen that as the feed concentration increases, the dynamic capacity of the bed, W_e , increases almost linearly in each segment while the overall adsorption rate, k_v , remains largely unchanged.

Figure 4.10 Fixed bed breakthrough curves of AO-7 on the CS-S beads at different concentrations: ○ 0.007 mg/ml, △ 0.010 mg/ml, □ 0.015 mg/ml; — model fittings (flow rate: 0.22 ml/min, pH: 8.2, temperature: 22 °C) [222].

Table 4.4. Parameters of W-J equation for breakthrough data at different concentrations with the flow rate of 0.22 ml/min [222].

Concentration (mg/ml)	Segment I		Segment II	
	W_e (mg/g)	k_v (min ⁻¹)	W_e (mg/g)	k_v (min ⁻¹)
	0 to 0.1	0 to 0.1	0.1 to 0.9	0.1 to 0.9
0.007	14.7	3.7	25.0	2.7
0.010	19.2	3.7	31.0	2.7
0.015	25.1	3.8	37.3	2.8

4.9.4. Mass transfer mechanism

The overall adsorption rate coefficient, k_v , is found to present the following trends in Table 4.3 and 4.4: (1) its value is larger in segment I than in segment II indicating a faster adsorption kinetics in the first segment, and (2) it is a weak function of feed concentration but a strong (linear) function of the flow rate. The vapor sorption processes generally present the correlation of $k_v \propto v^r$, where v is the flow rate and r has the value between 0.5-0.8 [231]. In comparison, k_v in this study, where the sorption occurs in liquid phase, shows a much stronger dependence (linear or $r = 1$) on the flow rate.

We further postulate that the fast kinetics observed in segment I occurs on the surface (external) layers of the beads where the rate limiting step is the mass transfer resistance of the thin liquid film around the beads. This is substantiated by the SEM observations of the beads (Figure 4.1(a) and (b)) which show that

the external pores are larger than the internal pores. Under such conditions, the overall mass transfer rate is generally governed by a linear driving force model, which is first order in nature.

After the external layers of the beads are saturated, the dye ions will penetrate into the inner parts of the beads. As AO-7 is a bulky molecule with a molecular weight of 350 and a molecular size of 1.25-1.27 nm [232], and the surface area of the beads is low ($\sim 60 \text{ m}^2/\text{g}$), so the rate limiting step is the pore and surface diffusion (or intraparticle diffusion). It is likely that the pore diffusion plays a major role because k_v shows a weak functional dependence on the feed concentration.

The dye adsorption mechanisms on CS are known to be complicated. They include ion-exchange, hydrophobic interaction, physical and chemical adsorption, etc. [32, 55] The adsorption kinetics revealed by batch experiments have shown great disparity depending on experimental conditions such as type of dyes, CS form, initial concentration, pH, and stirring rate, etc. The reported overall mass transfer mechanisms (rate) include: 1st order reaction [42], 2nd order reaction [55, 233], 1st order reaction at low concentration but 2nd order reaction at high concentration [234], and intraparticle diffusion [235-237].

The mass transfer mechanisms of our modified beads would be more complicated because of the displacement of SO_4^{2-} on amine groups and its subsequent back diffusion. The sorption and diffusion processes are largely multicomponent in nature which result in a *J*-shaped breakthrough curve and some overshoots in dye concentration in the effluents. However, the W-J model

provides a convenient tool for the simulation of such kinetic data with the two segmented approach.

4.10. Summary

The modification of CS beads using $(\text{NH}_4)_2\text{SO}_4$ significantly improved the adsorption capacity towards anionic dyes at pH 8.2, by shielding the protonated amine groups of CS with SO_4^{2-} groups for the following ion-exchange with dye anions. The adsorption efficiency was further improved when the modification was conducted in a packed column. The ion-exchange mechanism of dye adsorption on the modified CS beads was verified by FTIR analysis. The dye exhausted beads were efficiently regenerated and reused up to 20 times without significant loss of adsorption capacity. Fixed bed studies showed that the breakthrough curves on the modified beads were *J*-shaped in general with slight overshoot of the feed concentration in the effluents. The W-J equation was successfully used to model the breakthrough data with a two-segmented approach. The effects of the influent concentration and flow rate on the breakthrough behaviors and the kinetic parameters were investigated. It was found that, under the experimental conditions in this study, the overall mass transfer rate of dye adsorption was controlled by the film resistance in segment I and the intraparticle diffusion in segment II.

CHAPTER 5 CHARACTERISTICS OF CS MEMBRANE AND CS-POSS COMPOSITE MEMBRANES

5.1. Introduction

Incorporating inorganic fillers into a polymer matrix enables one to tune the structure and modify the properties of the resulting composite material. These modifications largely depend on the properties of the fillers and the polymer matrix, as well as the interactions between these two phases. Therefore, it is important to understand the structure-property relationship. Four types of POSS with different R vetex groups (OA, OAS, ONPS, and OAPS) have been incorporated with CS to fabricate CS-POSS composite membranes. The effects of POSS type and loading amount on the crystallinity, morphology, thermal stability, mechanical properties, as well as the swelling behavior of the composite membranes will be presented in this chapter. Moreover, the diffusion behavior of NaCl and riboflavin molecules in these composite membranes will be investigated.

5.2. Experimental

The CS and CS-POSS composite membranes were fabricated using solvent casting. POSS was incorporated into CS via solution blending as described in Section 3.4.1. After solvent evaporation and neutralization, the resulting membranes were characterized using FT-IR, XRD, SEM, TGA, tensile testing, swelling and diffusion experiments with details described in section 3.4.

5.3. FT-IR studies

FT-IR spectra of the POSS powders, CS membrane and CS-POSS composite membranes containing 9 wt.% POSS are shown in Figure 5.1. All the POSS show the characteristic peak of the Si-O stretching vibration at around 1090 cm^{-1} . However, the peak of the C-O stretching vibration of CS is also around 1092 cm^{-1} . The spectra of CS-OA, CS-OAS and CS-OAPS composite membranes are almost the same as the spectrum of CS membrane, because almost all the characteristic peaks of OA, OAS and OAPS POSS overlap with the peaks of CS. In the spectrum of CS-ONPS composite membrane, two characteristic peaks at 1350 and 1530 cm^{-1} from the stretching vibration of NO_2 groups of ONPS molecules appeared, as indicated by the arrows in Figure 5.1.

Figure 5.1. FT-IR spectra of POSS powders: (a) OA, (b) OAS, (c) ONPS, (d) OAPS; (e) CS membrane; and CS-POSS membranes containing 9 wt.% POSS: (f) CS-OA, (g) CS-OAS, (h) CS-ONPS, (i) CS-OAPS.

5.4. XRD studies

X-ray diffractograms of the POSS powders, CS membrane and CS-POSS composite membranes containing 9 wt.% POSS are shown in Figure 5.2. The CS membrane has two broad peaks around 10° and 20° , indicating the semi-crystalline nature of the polymer. After the incorporation of POSS, all the composite membranes show crystalline profiles very similar to the CS membrane regardless of the type and amount of POSS. For the CS-OA and CS-OAS composite membranes, their XRD patterns do not contain any characteristic sharp peaks of OA and OAS POSS. This suggests that OA and OAS are well-dispersed in the CS matrix. Although no characteristic peaks of ONPS and OAPS are found in the XRD profiles of the CS-ONPS and CS-OAPS composite membranes, it is difficult to determine the dispersion state of ONPS and OAPS in the membrane, as the XRD characteristic peaks of these two POSS are fairly broad.

Figure 5.2. XRD patterns of POSS powders: (a) OA, (b) OAS, (c) ONPS, (d) OAPS; (e) CS membrane; and CS-POSS membranes containing 9 wt.% POSS: (f) CS-OA, (g) CS-OAS, (h) CS-ONPS, (i) CS-OAPS.

5.5. Morphology

Figure 5.3 shows the SEM images of the surface and cross-section of the CS membrane. It is observed that the CS membrane is dense. No defect is found in the surface or cross section of the membrane from the SEM images.

Figure 5.3. SEM images of the CS membrane: (a) surface, (b) cross-section.

Figure 5.4 and 5.5 show the morphologies of the composite membranes containing OA and OAS, respectively. It is observed that with 1 to 9 wt.% loading of OA and OAS, the composite membranes have very smooth surfaces and cross-sections, which is similar to that of the CS membrane. This indicates that OA and OAS POSS were well dispersed in the CS matrix. Because OA and OAS are relatively hydrophilic, they have good compatibility with the CS matrix.

In the CS-ONPS composite membranes (as shown in Figure 5.6), aggregations of ONPS with the size larger than 10 µm are observed, and the number of these aggregations increases with increased loading of ONPS. At 5 wt.% or higher loadings, severe phase separation occurred and some defects or pinholes can be observed in the composite membranes. As shown in Figure 5.7,

in the composite membranes containing OAPS, particles with size of less than 1 μm are observed which may be due to the agglomeration of OAPS. With increasing content of OAPS, the number of these particles increases. With up to 9 wt.% loading, the OAPS particles are still homogeneously distributed within the membranes. The formation of aggregations of hydrophobic OAPS and ONPS in membranes is probably due to their poor compatibility with the hydrophilic CS matrix, particularly ONPS.

The observations from SEM images suggest that the dispersion of the POSS fillers in the CS matrix is substantially dependent on the hydrophilic/hydrophobic nature of the fillers.

Figure 5.4. SEM images of the CS-OA composite membranes: (a) surface of 1 wt.% loading, (b) cross-section of 1 wt.% loading, (c) surface of 5 wt.% loading, (d) cross-section of 5 wt.% loading, (e) surface of 9 wt.% loading, (f) cross-section of 9 wt.% loading.

Figure 5.5. SEM images of the CS-OAS composite membranes: (a) surface of 1 wt.% loading, (b) cross-section of 1 wt.% loading, (c) surface of 5 wt.% loading, (d) cross-section of 5 wt.% loading, (e) surface of 9 wt.% loading, (f) cross-section of 9 wt.% loading.

Figure 5.6. SEM images of the CS-ONPS composite membranes: (a) surface of 1 wt.% loading, (b) cross-section of 1 wt.% loading, (c) surface of 5 wt.% loading, (d) cross-section of 5 wt.% loading, (e) surface of 9 wt.% loading, (f) cross-section of 9 wt.% loading.

Figure 5.7. SEM images of the CS-OAPS composite membranes: (a) surface of 1 wt.% loading, (b) cross-section of 1 wt.% loading, (c) surface of 5 wt.% loading, (d) cross-section of 5 wt.% loading, (e) surface of 9 wt.% loading, (f) cross-section of 9 wt.% loading.

5.6. TGA studies

The TGA curves in Figure 5.8 show that the four types of POSS have very different thermal degradation profiles. Among them, OAPS has the greatest thermal stability with an initial thermal decomposition temperature, T_d , at around 415 °C, while OA has the poorest stability with the lowest char yield of 26%.

Figure 5.8. TGA curves of POSS.

However, despite the large differences in the thermal stability of different POSS, all the CS-POSS composite membranes containing 9 wt.% POSS display very similar degradation behavior to that of the CS membrane as shown in Figure 5.9. This indicates that the degradation mechanism of the CS matrix was not significantly altered by the presence of POSS fillers. However, compared to the CS membrane, all the composite membranes show slightly lower T_d and higher char yield. The reduction of T_d is ascribed to the poor stability of the

organic R vertex groups of POSS. However, the remaining inorganic Si-O frameworks of POSS, which are thermally robust, may form protective layers on the composite membranes preventing further degradation. This would contribute to the increased char yield in the CS-POSS composite membranes [238].

Figure 5.9. TGA curves of the CS membrane and CS-POSS composite membranes containing 9 wt.% POSS.

5.7. Mechanical properties

Table 5.1 shows the mechanical properties of the CS membrane and CS-POSS composite membranes. Compared to the CS membrane, the Young's modulus of all the composite membranes is reduced regardless of the type and amount of POSS loading. For example, the reduction on modulus is around 23%, 50%, 56%, and 65% for the composite membranes containing 9 wt.% of OA, OAS, ONPS and OAPS respectively, compared to the CS membrane.

Baldi et al. [239] proposed that when POSS with the structure of siliceous hard-core surrounded by hydrocarbon soft shell were dispersed in the polymer matrix, they would act as soft, rubber-like particles which were unable to reinforce stiffness. They also pointed out that the reduction effect on the modulus depended on the thickness of the soft shell determined by the length of the organic R groups of POSS molecules.

It is also observed in Table 5.1 that the addition of OA and OAS has little impact on the tensile strength of the composite membranes, while the introduction of ONPS and OAPS decreases the strength. It is known that tensile strength is influenced by the stress transfer between the fillers and the matrix [240]. Hydrophobic POSS molecules, which tend to form aggregates and have very poor interfacial adhesion with the matrix, can cause inefficient stress transfer.

The incorporation of hydrophilic POSS or hydrophobic POSS also has very different effects on the elongation at break of the composite membranes. With 9 wt.% loading of OA and OAS, the elongation at break of the composite membranes increases by 49% and 71%, respectively. However, the addition of 9 wt.% ONPS and OAPS results in a decrease of 42% and 9% on the elongation at break, respectively, compared to the CS membrane. These differences are attributed to the different interactions of different POSS with the CS matrix. For the composite membranes containing hydrophilic POSS, the non-chemical interactions such as hydrogen bonding and van der Waals forces provide strong interfacial adhesion between hydrophilic POSS and CS, which enhance the ability of the composite membranes to resist deformation. On the other hand, the interactions between hydrophilic POSS molecules and CS may also lead to

a loose packing structure of polymer – the so called plasticization effect [241] – resulting in increased mobility of polymer chains. In contrast, hydrophobic POSS molecules, which form aggregates in the CS matrix, not only hinder the stress transfer, but also increase the number of defects [193] thus making the composites membranes more brittle.

In summary, the composite membranes containing hydrophilic POSS become less stiff and more ductile without loss of strength, while the composite membranes containing hydrophobic POSS have worse overall mechanical properties compared to the CS membrane. Unlike other nano-fillers such as nano-clay and carbon nanotubes which tend to increase the modulus and strength of polymers via reinforcement mechanism [220, 242], POSS can either embrittle materials or act as plasticizers depending on the interactions between POSS and polymers. When POSS are grafted to the polymer chain or copolymerized with other monomers, nano-dispersion of POSS molecules in the matrix is facilitated by the strong covalent bonds between POSS and the polymer. Therefore, the nano-scale reinforcement on the polymer matrix is significant [243-244]. Furthermore, POSS may act as crosslinking agents between polymer chains and hence reduce ductility by increasing the crosslinking density [95]. However, when POSS are blended with polymer as in this study, the modification effects on polymer mechanical properties are largely dependent on the physical interactions between POSS and the polymer matrix. Kopesky et al. [107] have reported that trisilanol-phenyl-POSS could better retain the modulus and yield stress of PMMA compared to methacryl-POSS owing to the formation of hydrogen bond between the hydroxyl groups of trisilanol-phenyl-POSS and the ester groups of PMMA. Because of the

specific core-shell molecular structure of POSS, the R groups, which mediate the interactions between POSS molecules and polymer, play a significant role on the effects of POSS fillers to the polymer. In general, the modification effects of POSS fillers on polymer are multi-faceted depending on the complex interactions between POSS and the polymer.

Table 5.1. Mechanical properties of the CS membrane and CS-POSS composite membranes.

Membranes	Young's modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)
CS	43.2 $\pm$ 4.8	15.5 $\pm$ 3.0	59.1 $\pm$ 5.3
CS-OA			
1 wt. %	23.4 $\pm$ 0.8	14.2 $\pm$ 2.7	52.2 $\pm$ 4.5
5 wt. %	25.2 $\pm$ 2.4	18.2 $\pm$ 3.4	62.2 $\pm$ 6.7
9 wt. %	33.2 $\pm$ 2.0	23.1 $\pm$ 2.3	60.9 $\pm$ 3.1
CS-OAS			
1 wt. %	23.7 $\pm$ 2.8	14.1 $\pm$ 6.4	49.6 $\pm$ 9.4
5 wt. %	23.7 $\pm$ 0.7	25.6 $\pm$ 2.4	59.7 $\pm$ 3.0
9 wt. %	21.7 $\pm$ 1.4	26.5 $\pm$ 4.2	50.3 $\pm$ 7.1
CS-ONPS			
1 wt. %	22.3 $\pm$ 2.9	17.4 $\pm$ 2.5	47.7 $\pm$ 6.5
5 wt. %	17.5 $\pm$ 2.8	14.1 $\pm$ 4.7	33.0 $\pm$ 6.3
9 wt. %	18.9 $\pm$ 2.6	9.0 $\pm$ 4.2	33.9 $\pm$ 3.6
CS-OAPS			
1 wt. %	26.7 $\pm$ 1.7	13.9 $\pm$ 5.3	50.2 $\pm$ 2.9
5 wt. %	24.8 $\pm$ 0.7	13.5 $\pm$ 3.4	40.2 $\pm$ 3.4
9 wt. %	15.2 $\pm$ 0.9	14.0 $\pm$ 4.6	34.0 $\pm$ 6.4

5.8. Swelling characteristics of membranes in water

Figure 5.10. DS% of the CS membrane and CS-POSS composite membranes in de-ionized water.

Figure 5.10 shows the effects of the type and loading amount of POSS on the DS% of the CS membrane and CS-POSS composite membranes in de-ionized water. Generally, the DS% of the CS-POSS composite membranes is lower than the CS membrane. For the composite membranes containing hydrophobic OAPS and ONPS, the DS% gradually decreases with increasing POSS content. For the composite membranes containing hydrophilic OA and OAS, the DS% first decreases, then increases with increasing POSS loading. However, even for the composite membranes with the highest OA and OAS loadings (9wt.%), the DS% is still lower than the CS membrane. It is known that the swelling of a membrane in water depends on the chemical composition, microstructure,

incorporated moiety and degree of crystallinity of the membrane. XRD data (Figure 5.2) have shown that there was little change in the degree of crystallinity of membranes when POSS were incorporated. Therefore, the swelling behavior of the composite membranes is mainly influenced by the properties of POSS. As expected, the incorporation of hydrophobic POSS reduces the hydrophilicity of membranes, thus decreasing the water affinity. The decrease in the DS% of composite membranes containing hydrophilic POSS is likely due to the reduction of water absorption sites owing to the competition between POSS and water for such sites in the CS matrix.

5.9. Permeability of NaCl and riboflavin

Figure 5.11(a) and (b) show that during the time range of the permeability experiment, the concentrations of NaCl and riboflavin in the receiving compartment increase linearly with time. Hence, Fick's law can be applied and Eq. (3.6) and (3.7) can be used to determine the permeability coefficient. Figure 5.12 (a) and (b) show the permeability coefficients of NaCl and riboflavin in the CS-POSS composite membranes, respectively. For the CS-OA and CS-ONPS composite membranes, at only 1 wt.% loading, the permeability coefficient increases by 18% and 16% respectively, compared to that of the CS membrane. However, as the amount of embedded OA and ONPS further increases, the permeability coefficient decreases. With increasing amount of OAPS in the membrane, the permeability coefficient increases and a maximum value is reached when the OAPS loading is 5 wt.%. For the CS-OAS composite membranes, the permeability coefficient is almost unchanged when the loading

is low (1 and 5 wt.%), whereas an increase of around 6.8% is obtained at 9 wt.% OAS loading.

Figure 5.11. Variations of the concentration of (a) NaCl and (b) riboflavin in the receiving compartment with time.

Figure 5.12. Permeability coefficients of (a) NaCl and (b) riboflavin in the CS membrane and CS-POSS composite membranes.

Figure 5.12(b) shows the permeability coefficient of riboflavin in the CS-POSS composite membranes. It is observed that the variation of the permeability coefficients of riboflavin in these membranes is similar to that of

NaCl (Figure 5.12(a)). For CS-OA composite membranes, the permeability coefficient reaches a maximum value at 1 wt.% loading, then decreases with increasing OA. In CS-OAPS composite membranes, the permeability coefficient reaches a maximum value at 5 wt.% loading. In CS-OAS and CS-ONPS composite membranes, the permeability coefficient decreases monotonically with increasing ONPS and OAS content. However, except for the composites containing 1 wt.% and 5 wt.% OA, the permeability coefficients of riboflavin in all the other composite membranes are lower than those in the CS membrane, which is different from the NaCl permeability in these membranes.

It is known that the permeability of a solute in a hydrogel membrane is substantially influenced by the size of the solute, the degree of hydration of the membrane and the interactions between the solute and the membrane (ionic, hydrophilic/hydrophobic interactions, etc.). Riboflavin, which has a pK_a of 10.2, is positively charged at pH 7.0. Therefore, riboflavin and Na^+ ions are likely to favor negatively charged membranes such as CS-OA and CS-ONPS composite membranes which contain negatively charged OA and ONPS. However, CS-OA and CS-OAS composite membranes have relatively high DS% in water owing to the hydrophilic nature of OA and OAS. Therefore, the permeability of riboflavin and NaCl in the composite membranes is dependent on the synergetic effects of the electrostatic interactions and the hydration of the membranes.

5.10. Partition coefficient and diffusion coefficient of riboflavin

Based on the free volume theory, the permeability of a solute in a membrane comprises of the sorption of the solute into the membrane and the diffusion within the membrane [107]. Therefore, adsorption experiments were carried out to investigate the interactions between riboflavin and membranes.

Table 5.2. Partition coefficients and diffusion coefficients of riboflavin in the CS membrane and CS-POSS composite membranes containing 9 wt. % POSS.

Membranes	Partition coefficient	Diffusion coefficient ($\times 10^{12}$, m^2/s)
CS	24.4	2.1
CS-OA	44.4	1.0
CS-OAS	30.3	1.3
CS-ONPS	15.8	2.7
CS-OAPS	21.2	2.2

Table 5.2 shows the partition coefficient and diffusion coefficient of riboflavin for the CS membrane and CS-POSS composite membranes containing 9 wt.% POSS calculated from Eq. (3.8) and (3.9) respectively. It is observed that the partition coefficients of the CS and CS-POSS membranes are much larger than unity. This phenomenon has been reported for PVA and CS membranes [245-246] and was attributed to the presence of bound water that connected the solute to the membrane. The enrichment of riboflavin in these

membranes is likely due to the good affinity of the CS matrix toward riboflavin. Furthermore, the partition coefficient of riboflavin decreases in the order: CS-OA > CS-OAS > CS > CS-OAPS > CS-ONPS. Because of the hydrophilic nature of riboflavin, it is expected that high affinity and good distribution of riboflavin can be obtained in the membranes containing hydrophilic OA and OAS. It is also worth noting that CS-OA has much higher affinity to riboflavin than CS-OAS, which can be attributed to the electrostatic attraction between the negative charged OA and the positively charged riboflavin. However, the hydrophobic nature of CS-OAPS and CS-ONPS composite membrane makes it difficult for riboflavin molecules to get close enough to the polymer chains for electrostatic interactions to play a role. Therefore, the higher partition coefficient of riboflavin in CS-OAPS compared to CS-ONPS is attributed to the greater DS% of CS-OAPS. Because riboflavin is soluble in water, more water inside the membranes provides more accommodations for riboflavin.

As shown in Table 5.2, the diffusion coefficient of riboflavin decreases in the order: CS-ONPS > CS-OAPS > CS > CS-OAS > CS-OA, which is opposite to that of the partition coefficient. Based on the free volume theory, the diffusion of a solute in polymer membrane depends on the probability of a solute to find a mesh formed by the polymer network which has a volume with at least the diameter of the solute. The interactions between the solute and the polymer make it hard for the solute to leave the present site and shift to the next one, but also offer more opportunities for the solute to find other sites [247]. The former effect decreases the probability of the solute to diffuse while the latter increases this probability. Our results suggest that the former effect is predominant in the studied membranes. Therefore, the adsorption of riboflavin

in the membranes reduces the interfacial velocity, causing riboflavin molecules to take a long time to be transported through the membranes [248]. Hence, riboflavin would have a low diffusion rate in hydrophilic membranes with high partitioning effect.

5.11. Summary

The incorporation of POSS into CS was found to significantly affect the structures and properties of the composite materials. The modifications of POSS on the membranes were largely dependent on the R groups and the hydrophilic/hydrophobic nature of POSS. Phase separation was only observed in the composite membranes containing hydrophobic POSS (ONPS and OAPS). The thermal stability of all the CS-POSS composite membranes was improved. With the POSS embedded in CS, significant loss in modulus was observed, while the effects on the elongation at break and tensile strength depended on the type of POSS. The diffusion permeability of NaCl and riboflavin in the composite membranes was influenced by the interactions between the solutes and the membranes, as well as the hydration of the membranes.

CHAPTER 6 PERVAPORATION PERFORMANCE OF CS MEMBRANE AND CS-POSS COMPOSITE MEMBRANES

6.1. Introduction

The structure and properties of the CS-POSS composite membranes have been found to be significantly modified by the POSS fillers. These modifications will certainly affect the pervaporation performance of these composite membranes, because the membrane is the key to determine the separation efficiency of pervaporation. In this chapter, the effects of POSS type and loading amount on the sorption behavior and the pervaporation performance for EtOH dehydration will be presented. Moreover, the effects of feed concentration on the pervaporation and diffusion behavior of the membranes will be analyzed. The dependence of flux on temperature will be evaluated by the Arrhenius equation and the apparent activation energy for permeation will be estimated.

6.2. Experiments

The swelling and sorption experiments of the CS membrane and CS-POSS composite membranes were carried out in various EtOH aqueous solutions following the procedure given in Section 3.6. The pervaporation experiments of these membranes were conducted using the set-up described in section 3.5 with the water fraction in the feed varying from 5 to 30 wt.%, and temperature from 30 to 60 °C. The permeate concentration was analyzed by GC with the operating

procedure & parameters given in section 3.5. The separation factor, flux and PSI were calculated using Eq. (3.10), (3.11) and (3.12), respectively.

6.3. Swelling and sorption characteristics of membranes in EtOH solutions

6.3.1. Degree of swelling

The DS% of the CS membrane and CS-POSS composite membranes containing 5 wt.% POSS in various EtOH aqueous solutions at 30 °C are shown in Figure 6.1. When the fraction of water in the feed increases, the DS% of all the membranes increases. As a hydrophilic polymer, CS contains a large number of hydroxyl and amine groups which can interact strongerly with water molecules [195]. As the water fraction increases in the feed solution, more water molecules enter and interact with the membranes thus causing increasing swelling.

However, the effects of POSS on the swelling behavior of the membranes are complex. The interactions among the three components (i.e. CS, POSS and water) are largely affected by the increased water content in the feed. Figure 6.1 shows that when water fraction in the feed increases from 5 to 15 wt.%, the increase on DS% of the CS/POSS composite membranes is slower than the increase of the CS membrane. However, when water fraction in the feed increases from 15 to 30 wt.%, the increase on DS% of the CS-POSS membranes is faster than that of the CS membrane. This may be a result from a competition of the interactions between POSS and CS, and the interactions

between water and CS. When water fraction in the feed is low, the interactions between POSS and CS are dominant which may reduce the interactions between water and CS. However, when water fraction in the feed increases to 15 wt.%, the interactions between water and CS become stronger and may suppress the interactions between POSS and CS. Therefore, phase separation between CS and POSS may occur and generate some large voids allowing more water to enter.

Among the four types of composite membranes, CS-ONPS displays the highest DS% while CS-OAPS has the lowest one in the entire range of feed composition. The differences in the DS% between these two composite membranes become more significant with the increased water fraction in the feed. It is expected that the incorporation of hydrophobic POSS would decrease the hydrophilicity of the CS membrane, thus decreasing the DS%. However, the presence of defects or large voids at the interface of ONPS and the CS matrix resulting from the incompatibility between these two phases may be responsible for the high swelling. The incorporation of hydrophilic OA and OAS would improve the hydrophilicity of the membranes, thus increasing the DS%.

Figure 6.1. Variations of DS% of the CS membrane and CS-POSS composite membranes containing 5 wt.% POSS with feed concentration at 30 °C.

6.3.2. Sorption selectivity and diffusion selectivity

Based on the sorption data, the sorption selectivity and diffusion selectivity of the CS membrane and CS-OA, CS-OAPS composite membranes at different feed concentrations were calculated using Eq. (3.14) and Eq. (3.15), respectively. As shown in Figure 6.2(a) and (b), the diffusion selectivity of membranes is generally higher than the sorption selectivity, particularly when water fraction in the feed is lower than 15 wt.%. This indicates that the overall selectivity is mainly governed by the selective diffusion process.

The sorption selectivity shows a complicated dependence pattern on the feed concentration. The sorption selectivity of all the membranes demonstrates a trend that it first increases, reaches a maximum value, and then decreases as the fraction of water in the feed decreases. It has been shown in Figure 6.1 that, the

DS% of membrane would decrease with the decreased water fraction in the feed. This results in the reductions of the free volume of membranes. Thereby, the penetration of large EtOH molecules is more constrained, which explains the initial increased sorption selectivity. However, when water fraction in the feed is too low (e.g. 5 wt.%), the sorption selectivity is reduced because very few water molecules are available to be adsorbed into the membrane. Furthermore, compared to the CS-OA and CS-OAPS membranes, the CS membrane shows higher sorption selectivity when water fraction in the feed is 15 wt.% and above. However, when water fraction in the feed is lower than 15 wt.%, the sorption selectivity of the CS-OA and CS-OAPS membranes becomes higher than the CS membrane. This may be a result of the competition between the interactions between POSS and CS, and the interactions between water and CS as discussed in section 6.3.1. When water fraction in the feed is low (< 15 wt.%), the interactions between POSS and CS are strong, which may restrain the free volume and limit the penetration of large EtOH molecules. When water fraction in the feed exceeds 15 wt.%, the water adsorption is lower in the composite membrane compared to the CS membrane due to the competition of POSS.

Figure 6.2. Variations of (a) sorption selectivity and (b) diffusion selectivity of the CS membrane and CS-OA, CS-OAPS composite membranes containing 5 wt.% POSS with feed concentration at 30 °C.

As shown in Figure 6.2(b), the diffusion selectivity of all the membranes decreases with increased water fraction in feed owing to increased DS% (Figure 6.1). Moreover, the CS membrane shows generally lower diffusion selectivity compared to the CS-OA and CS-OAPS composite membranes. This indicates

that the presence of POSS in the CS matrix can possibly compact the membrane and restrict the excessive increase on the free volume size due to the swelling. Therefore, the transport flux of EtOH molecules in the composite membranes is reduced compared to that in the native CS membrane.

6.4. Effects of POSS loading on pervaporation performance

Figure 6.3 shows the effects of the type and amount of POSS loading on the pervaporation performance of membranes for the dehydration of EtOH solution containing 10 wt.% water at 30 °C. It is seen in Figure 6.3(a) that with only 1 wt.% of POSS loading, the separation factor of the composite membranes is greatly improved compared to the CS membrane. However, at higher POSS loading, the composite membranes displayed different behaviors depending on the type of POSS. The separation factor of CS-ONPS composite membrane decreases monotonically with increasing POSS content. Whereas, the separation factors of CS-OA, CS-OAS, and CS-OAPS composite membranes reach maximum values at 5 wt.% loading, then decrease at 9 wt.% loading. Figure 6.3(b) shows that the incorporation of POSS reduces the flux of the membranes. The flux of CS-ONPS composite membranes reaches a lowest value at 1 wt.% ONPS loading, then it increases with increasing ONPS content, with the value exceeding that of the CS membrane at 9 wt.% loading. The lowest flux values of the CS-OA, CS-OAS, and CS-OAPS composite membranes are observed at 5 wt.% POSS loadings. The trend observed in the flux of the composite membranes is exactly opposite to that observed in the separation factor. This is the so-called “trade-off” phenomenon [114].

Figure 6.3. Effects of POSS on pervaporation performance (water fraction in the feed: 10 wt.%, temperature: 30 °C): (a) separation factor, (b) flux.

As observed by SEM (Figure 5.6 & 5.7), hydrophobic ONPS and OAPS formed macro-aggregates in membranes due to the incompatibility between these two POSS and the CS matrix. If the hydrophobic ONPS and OAPS particles are homogeneously dispersed in the polymer matrix, they may constrain the polymer segmental mobility and reduce the size of free volume, thereby enhancing the selectivity of the composite membranes. However,

overloading of these hydrophobic POSS will cause reductions in selectivity due to the non-selective voids generated from the serious agglomeration of hydrophobic POSS and phase separation. In this study, it is seen that the limits of ONPS and OAPS loading are 1 wt.% and 5 wt.%, respectively. With the incorporation of hydrophilic OAS and OA, the selectivity of the membrane is also enhanced which is attributed to the increased hydrophilicity of the composite membranes. However, with small molecular size of POSS (1-3 nm in diameter [90]), they may be embedded in the polymer network as barriers to the diffusants, thus causing reductions in flux. Furthermore, since OA carries negative charge, it may interact electrostatically with the amine group of CS, and cause the amorphous region of CS to be more compact. This explains the high separation factor for the composite membrane containing 5 wt.% OA.

6.5. Effects of feed concentration on pervaporation performance

The overall pervaporation performance of the CS and the CS-POSS membranes containing 5 wt.% POSS in the feed solutions with 5 to 30 wt.% water at 30 °C are summarized in Table 6.1. Generally, the water fraction in the permeate decreases with increasing water fraction in the feed. However, some exceptions are observed when the water fraction increases from 5 to 10 wt%, and from 15 to 20 wt.%, which is a result from the synergistic effects of the sorption and diffusion selectivity. CS-POSS composite membranes show improved PSI compared to the CS membrane in the same feed solution. Particularly, the PSI value of CS-OAS membrane is 2.8 times of that of the CS membrane with 5 wt.% water in the feed, while CS-OAPS membrane displays a PSI value 3.3 times of that of the CS membrane with 10 wt.% water in the feed.

Table 6.1. Pervaporation data of the CS and CS-POSS membranes containing 5 wt.% POSS in various feed solutions at 30 °C.

Water fraction in feed (wt.%)	Water fraction in permeate (wt.%)	Separation factor, α	Flux, J (g/m² h)	PSI
CS				
5	92	207	13	2609
10	88	65	51	3294
15	85	32	136	4286
20	85	23	185	4053
30	79	9	398	3097
CS-OA				
5	94	321	8	2495
10	97	306	28	8516
15	85	33	139	4451
20	85	23	229	5037
30	83	11	402	4007
CS-OAS				
5	98	953	8	7409
10	96	199	36	7213
15	87	36	125	4405
20	86	25	176	4215
30	83	11	362	3632
CS-ONPS				
5	95	324	14	4599
10	93	128	41	5263
15	84	30	134	3820
20	83	19	261	4810
30	78	8	599	4432
CS-OAPS				
5	96	402	10	3980
10	98	373	29	10842
15	85	36	141	4888
20	85	23	280	6258
30	85	13	480	5637

As shown in Figure 6.4(a), the separation factor of all the membranes decreases with increasing water fraction in the feed. This phenomenon has been widely observed in hydrophilic membranes and can be explained by the so-called “plasticizing” effect [249]. As the feed water fraction increases, the mobility of the polymer chains increases and results in an increase in free volume [250]. Therefore, the transport of large EtOH molecules becomes easier, which compromises the selectivity of the membranes. When water fraction in the feed is 5 wt.%, CS-OAS composite membrane shows the highest separation factor among all the membranes. This can be attributed to the positively charged OAS molecules which have high affinity towards the polar water molecules. However, this effect becomes insignificant as the water permeation increases rapidly with increasing water fraction in the feed due to the high DS%. The composite membrane containing cationic OAPS also has good selectivity and maintains it even in the feed with high water fraction. The presence of hydrophobic OAPS particles inside the membrane can restrain the mobility of polymer chains at high water concentration, thus reducing the plasticization.

Figure 6.4(b) shows that the permeation flux of all the membranes increases with increasing water fraction. This can be attributed to the increased DS% of membranes. The composite membranes containing hydrophilic OA and OAS have comparable flux with the CS membrane in the entire concentration range of the feed. The composite membranes containing hydrophobic ONPS and OAPS have similar flux to the CS membranes when water fraction in the feed is below 15 wt.%, but show much greater flux when water fraction in the feed exceeds 20 wt.%. This is consistent with the variation in the DS% as shown in Figure 6.1. With increased water fraction in the feed, the enhanced interactions

between water and CS matrix are likely to aggravate the phase separation between the CS matrix and hydrophobic POSS. Hence, large cracks at the interface of CS matrix and hydrophobic POSS particles would appear inducing the high permeation flux.

Figure 6.4. Effects of water fraction in the feed on the pervaporation performance of the CS membrane and CS-POSS composite membranes containing 5 wt.% POSS at 30 °C: (a) separation factor, (b) flux.

6.6. Diffusion coefficient

The solution-diffusion model [251] is widely used to describe the mass transport mechanism in pervaporation. In this model, the solubility and diffusivity of the penetrating molecules in membrane are the key factors determining the selectivity and flux. Hence, it is necessary to evaluate the diffusion coefficient during the mass transport process. As the thermodynamic equilibrium is believed to be reached instantly at the feed-membrane interface [195], Fick's first law can be used to describe the permeation behavior of the components in membrane:

$$J_i = -D_i \frac{dC_i}{dl} \quad (6.1)$$

where J_i is the permeation flux of component i ($\text{g/m}^2 \text{ h}$), D_i is the diffusion coefficient (m^2/s), C_i is the concentration (g/m^3), and l is the diffusion path (m). The concentration profile along the membrane is assumed to be linear. The concentration of component i in the permeate side can be considered to zero, as the permeate is promptly removed at the permeate side of the membrane. Thus, D_i can be estimated by:

$$D_i = \frac{J_i \delta}{C_{ms,i}} \quad (6.2)$$

where δ is the membrane thickness (m), $C_{ms,i}$ is the concentration of component i at the membrane surface in contact with the feed, which can be obtained by the sorption experiment. The diffusion coefficients of water (D_w) and EtOH (D_e) in the CS membrane and the CS-OA, CS-OAPS composite membranes containing 5 wt.% POSS at 30 °C are shown in Table 6.2. It is observed that D_w and D_e in all the membranes increase with increasing water fraction in the feed. However, the increase in D_e is much faster than the increase in D_w . For example,

when the water fraction increases from 5 wt.% to 30 wt.%, D_w of the CS membranes increases around 4 times, while D_e increases more than 200 times. Therefore, the value of D_w/D_e , which is another expression of the diffusion selectivity, decreases with increasing water fraction in the feed. This is consistent with the result shown in Figure 6.2(b). In an ideal permeation, the transport of one component is independent on other components, therefore, constant selectivity can be obtained irrespective of feed composition. However, in a membrane which can be plasticized by one component in the feed, coupled transport of penetrating molecules is frequently observed [252]. Therefore, in this study, the transport of smaller water molecules which have a higher diffusion coefficient in the membranes would be slow down by the transport of larger EtOH molecules with a lower diffusion coefficient. The diffusion of coupled molecules is enhanced by the increased DS%, and the coupling effect increases with the increased water fraction in the feed [253].

Table 6.2. Diffusion coefficients of water and EtOH in the CS membrane and CS-OA, CS-OAPS composite membranes containing 5 wt.% POSS in various feed solutions at 30 °C.

Water fraction in the feed (wt. %)	$D_w \times 10^{13} \text{ (m}^2\text{/s)}$			$D_e \times 10^{13} \text{ (m}^2\text{/s)}$		
	CS	CS-OA	CS- OAPS	CS	CS-OA	CS- OAPS
5	6.8	4.6	3.6	0.1	0.08	0.07
10	9.1	5.0	5.9	0.8	0.2	0.2
15	20.0	36.2	25.1	4.2	4.9	5.4
20	20.8	51.9	89.3	5.9	7.4	7.8
30	36.7	73.8	104.9	20.3	17.6	19.1

6.7. Effects of temperature on pervaporation performance

To investigate the influence of operating temperature, the pervaporation of the CS membrane and CS-POSS composite membranes containing 5 wt.% POSS were conducted at four temperatures from 30 to 60 °C, with the water fraction in the feed maintained at 10 wt.%. The overall performance of the membranes are summarized in Table 6.3. It is shown that at the same temperature, all the composite membranes present higher PSI compared to CS membrane. Furthermore, all the composite membranes show the highest values of PSI at 30 °C among the tested temperatures owing to the high separation

factor at low temperature. The lowest values of PSI for the CS-POSS composite membranes are found at 40 °C, then it increases with the increased temperature which can be ascribed to the increased flux.

As shown in Figure 6.5, the separation factor of all the membranes decreases while the flux increases with increasing temperature. As reported in many papers [156, 200, 254], with increasing temperature, the thermal mobility of the polymer segments is enhanced resulting in increase in free volume. Hence, the diffusion coefficient of the permeating molecules increases, but the selectivity decreases. Furthermore, the increase in driving force owing to the increased partial vapor pressure in the feed side, as well as the decrease in the viscosity of the feed solution with increasing temperature would also contribute to the large increase in flux [255].

Table 6.3. Pervaporation data of the CS and CS-POSS membranes containing 5 wt.% POSS at different temperatures in the feed containing 10 wt.% water.

Temperature (°C)	Water fraction in permeate (wt.%)	Separation factor, α	Flux, J, (g/m ² h)	PSI
CS				
30	88	65	51	3294
40	82	40	101	3919
50	78	31	149	4464
60	75	26	251	6383
CS-OA				
30	97	306	28	8516
40	85	53	82	4196
50	81	37	146	5314
60	76	28	242	6629
CS-OAS				
30	96	199	36	7213
40	87	61	90	5349
50	83	42	152	6291
60	77	30	228	6632
CS-ONPS				
30	93	128	41	5263
40	81	38	93	3402
50	76	28	162	4375
60	74	26	257	6408
CS-OAPS				
30	98	373	29	10842
40	84	49	87	4140
50	78	32	171	5376
60	76	28	273	7319

Figure 6.5. Effects of temperature on the pervaporation performance of the CS membrane and CS-POSS composite membranes containing 5 wt.% POSS in the feed with 10 wt.% water: (a) separation factor, (b) flux.

The temperature dependence of flux can be interpreted by Arrhenius relationship [256]:

$$X_i = X_0 \exp\left(\frac{-E_i}{RT}\right) \quad (6.3)$$

where X_i represent permeation (total permation, J_p , permeation of water, J_{we} , and permeation of EtOH, J_{pe}), or diffusion (D), X_0 is a constant, E_i is the apparent activation energy of permeating component i (kJ/mol), R is the gas constant, and T is the temperature in Kalvin. Arrhenius plots of the total permeation, J , in the membranes are shown in Figure 6.6 as an example. The linear relationship between $\ln J$ and $1/T$ indicates the applicability of Arrhenius equation. Simialr linear relationships were also obtained between $\ln D$ and $1/T$. Therefore, the apparent activation energies of the diffusion (E_{diff}) and permeation including total permeation (E_p), permeation of water (E_{pw}) and EtOH (E_{pe}) of membranes were estimated and listed in Table 6.4.

Figure 6.6. Arrhenius plot of $\ln J$ vs $1/T$.

Generally, the apparent activation energy of water permeation (E_W) is lower than that of EtOH permeation (E_E) in all the membranes as shown in Table 6.4. This indicates that more energy is needed for the EtOH transport which is due to the larger molecular size of EtOH and the hydrophilic nature of the membrane matrix. Furthermore, with the incorporation of POSS, all the values

of E increased, which may explain the reductions on flux of the CS-POSS composite membranes. CS-OAS and CS-ONPS composite membranes have comparable E_W values with that of the CS membranes, but much higher E_E values. CS-OA and CS-OAPS composite membranes have both increased E_W and E_E , however, the increases in E_E are more significant. Therefore, the differences between E_E and E_W of the composite membranes, particularly CS-OA and CS-OAPS, are much greater than that of the CS membrane. This suggests that the transport of EtOH has been strongly hindered in the CS-OA and CS-OAPS composite membranes resulting in the high water selectivity.

Table 6.4. Apparent Arrhenius activation energies of permeation and diffusion in the CS membrane and CS-POSS composite membranes containing 5 wt.% POSS.

Membran	E_p	E_{pw}	E_{pe}	$E_{pe} - E_{pw}$	E_{diff}	ΔH_s
es	(kJ/mol)	(kJ/mol)	(kJ/mol)		(kJ/mol)	(kJ/mol)
CS	38.7	43.3	63.7	20.4	44.4	-5.7
CS-OA	59.5	52.8	116.3	63.5	69.1	-9.6
CS-OAS	50.9	45.0	96.0	51.0	56.2	-5.3
CS-ONPS	50.8	44.4	87.7	43.3	51.3	-0.5
CS-OAPS	62.2	55.1	124.8	69.7	65.8	-3.6

Heat of sorption ΔH_s (kJ/mol) can be calculated as:

$$\Delta H_s = E_p - E_D \quad (6.2)$$

The value of ΔH_s reflects the contributions of Langmuir's type and Henry's type of sorption. Henry's sorption is an endothermic process involving the formation of site and the dissolution of species into the site; while Langmuir's sorption, a hole-filling mechanism occurring in the existing sites, is an exothermic process. The ΔH_s values listed in Table 6.4 are negative for all the membranes revealing that the sorption process in the studied membranes is exothermic. Therefore, the Langmuir's sorption was predominant [257].

6.8. Comparison of pervaporation performance

As listed in Table 2.2, various CS-filler composite membranes have been investigated on the application of pervaporation, including CS membranes filled with zeolite, silane, clay, CNT, etc. For EtOH dehydration, a novel of CS-modified zeolite composite membrane showed a separation factor of 274 and a flux of 278 g/(m² h) at 80 °C when the feed concentration is 90% [198]; With the same feed concentration, CS membranes filled with silica nanoparticles exhibited a separation factor of 919 and a flux of 410 g/(m² h) at 70 °C [213]; and a CS membrane crosslinked by APTEOS had a separation factor of 597 and a flux of 887 g/(m² h) in pervaporation of 85 wt.% EtOH at 50 °C [208]. However, to our knowledge, there is no report on the CS-POSS composite membranes used for pervaporation so far. Generally, the performance of CS-POSS composite membranes in our study is comparable with that of other CS-filler composite membranes. According to some reports [198], intensifying the interactions between fillers and matrix is very likely to enhance the interfacial properties and eliminate the non-selective voids of the composite membranes, resulting in improvements on the pervaporation performance. Due to the unique

structure of POSS (inorganic frame and organic vertex groups), it is feasible to manipulate the interactions between POSS and CS via changing R vertex group of POSS. Therefore, it is hopefully that high pervaporation performance can be obtained if stronger interactions (such as covalent bond) can be formed between CS chains and R vertex groups of POSS.

6.9. Summary

The pervaporation performance for EtOH dehydration of the CS membrane and CS-POSS composite membranes were investigated. It was found that a small amount of POSS loading (1 wt.%) was able to significantly improve the selectivity of the membrane. However, overloading of POSS would cause reductions in selectivity. The composite membranes containing 5 wt.% POSS showed high selectivity when water fraction in the feed is low (5 to 10 wt.%) due to the limited transport of EtOH. The dependence of permeation flux on temperature was fitted by the Arrhenius relationship and the apparent activation energy for permeation was obtained. The CS-POSS composite membranes, particularly CS-OA and CS-OAPS, exhibited much higher activation energies for EtOH permeation compared to that of the CS membrane, which is responsible for the much greater water selectivity of these two composite membranes.

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusions

CS-based hydrogel beads and composite membranes have been successfully developed, characterized, and investigated for dye adsorption and pervaporation separation applications, respectively. The modifications of native CS beads using $(\text{NH}_4)_2\text{SO}_4$ significantly improved the adsorption capacity towards anionic dyes (AO-7 and AR-18) in aqueous solutions at pH 8.2. The mechanism of adsorption was verified by FTIR results. It was found that the proposed modification technique could effectively shield the protonated amine groups of CS to assist the ion-exchange with dye molecules and thereby resulted in the high adsorption capacity at basic conditions. The dye exhausted beads could be efficiently regenerated and reused at least up to 20 times without loss of adsorption capacity. Fixed bed studies showed that the breakthrough curves on the modified beads are *J*-shaped in general and can be modeled with a two-segmented W-J model. The low cost, high adsorption capacity, and excellent regenerative capability make the modified CS beads promising adsorbents for the recovery of dyes from industrial wastewater.

POSS with different R groups (OA, OAS, ONPS and OAPS) were incorporated into CS matrix to form composite membranes. The morphologies, thermal stability, mechanical properties, swelling and diffusion behaviors of these membranes were thoroughly investigated. Hydrophobic POSS (ONPS and OAPS) formed aggregations in the membranes due to their poor compatibility with the CS matrix, while hydrophilic POSS (OA and OAS) were found to be

well dispersed in CS. The thermal decomposition of all the CS-POSS composite membranes was retarded contributing to the improved thermal stability. With the incorporation of POSS, significant loss in modulus was observed, whereas the effects on the strength elongation at break varied with the type of POSS depending on the interfacial interactions between POSS and CS. The diffusion permeability of NaCl and riboflavin in the CS-POSS composite membranes was found to be affected by the interactions between the solutes and the membranes, as well as the hydration of the membranes. Membranes containing hydrophilic POSS (OA and OAS) displayed higher partition coefficients, but lower diffusion coefficients of riboflavin, compared to that of the membranes containing hydrophobic POSS (ONPS and OAPS). In short, with the incorporation of a small amount of POSS, the structure and properties of CS membrane can be modified and the modifications are largely dependent on the structure and properties of POSS.

The developed CS-POSS composite membranes were tested for the pervaporation dehydration of EtOH aqueous solutions. The sorption and pervaporation performance of the composite membranes were influenced by the type and content of POSS, or more fundamentally, by the interactions between POSS and CS. Incorporation with a small amount of POSS was able to significantly improve the water selectivity (separation factor) of the membranes. The composite membranes containing 5 wt.% POSS showed high selectivity when water fraction in the feed is low (5 to 10 wt.%) due to the low diffusion coefficient of EtOH. Arrhenius relationship was used to describe the dependence of the permeation flux on temperature and to derive the apparent activation energy. The composite membranes, particularly CS-OA and CS-

OAPS, exhibited much higher activation energies for EtOH permeation compared to the CS membrane, indicating the limited transport of EtOH in the composite membranes. The CS-POSS composite membranes with high selectivity and tunable properties possess high potential in separation applications.

7.2. Recommendations for future studies

As the versatile polymer and the low-cost adsorbent, CS is finding increasing applications in the fields of purification and separation. To further explore the potential of the technologies developed in this project, the following future studies are recommended for the CS-based adsorbents:

- (1) Studying the adsorption of other types of dyes using the $(\text{NH}_4)_2\text{SO}_4$ modified CS beads, such as the reactive dyes and direct dyes.
- (2) Investigating other factors influencing the adsorption efficiency of the modified CS beads, e.g. temperature, ionic strength, other dyes or components in the solution.
- (3) Conducting the adsorption in real industrial wastewater to evaluate the feasibility of the modified CS beads for practical applications.

For the CS-based composite membranes, the following aspects may be considered in future studies:

- (1) Applying the CS-POSS composite membranes for the pervaporation of other solvent systems, such as the mixtures of MeOH/MTBE, and benzene/cyclohexane.

- (2) Since the properties and performance of the CS-POSS composite membranes are largely dependent on the structure of POSS and the interactions between POSS and CS, POSS molecules with some other functional groups, particularly those strongly interact (e.g. via covalent bond) with CS, can be selected as the fillers to form composites with CS. The strong interactions can reinforce the nano-dispersion of POSS in the CS matrix, hence effectively modifying the properties of the resulting composite materials.
- (3) Incorporating some other inorganic (nano)fillers, such as CNT, clay, metal oxides, graphene, etc. into CS, and combining with other membrane fabrication techniques (such as crosslinking, polymer blending, multi-layered) to improve the pervaporation efficiency.
- (4) Developing mathematical models on the mass transport of pervaporation for the organic-inorganic composite membranes considering the effects of the embedded inorganic fillers.

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1. Xu, D.; Hein, S.; Loo, S. L.; Wang K., The fixed-bed study of dye removal on chitosan beads at high pH. *Industrial & Engineering Chemistry Research* (2008), 47, 8796-8800.
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1. Xu, D.; Wang, K., Pervaporatgion dehydration of ethanol using chitosan-POSS composite membranes, *The International Symposium on Exploring the Frontiers of Chemical and Biomedical Engineering*, Singapore, May 2010.