



Fabrication and characterization of phosphorylated chitosan nanofiltration membranes with tunable surface charges and improved selectivities



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HIGHLIGHTS

- Novel nanofiltration membranes were fabricated with tunable surface charges.
- PCSs with modulated substituted degree of phosphate group were synthesized.
- FTIR and EDX analysis verified that it was introduced into the NFMs.
- Impacts on NFMs' permeation and selectivity performance were studied.
- NFM4 exhibits good chemical stability in the long-term operation.

ARTICLE INFO

Keywords:

Nanofiltration membrane
Phosphorylated chitosan
Degree of substitution
Tunable surface charge
Improved selectivity

ABSTRACT

Phosphorylated chitosan (PCS) with tailored amount of phosphate groups was synthesized, and novel composite nanofiltration membranes (NFMs) with tunable surface charges were prepared by coating PCS onto polyacrylonitrile (PAN) supporting layer and subsequently cross-linked by glutaraldehyde (GA). Chemical structures and compositions of PCS and NFMs, along with morphologies, surface charges, and performance of NFMs were represented by using FTIR, TG, ATR-IR, SEM-EDX, AFM, streaming potential analyzer, and cross-flow flat permeation test, respectively. The effect of different phosphorous abundance of PCS precursors on the surface charge and permselectivity of NFMs was investigated systematically. It was illustrated that the incorporation of phosphate group with high-substitute degree did enhance the surface charge and selectivity of NFM, respectively, while retaining its permeability. The resultant membrane showed a zeta potential of -77.6 mV at $1 \text{ mol}\cdot\text{m}^{-3}$ KCl electrolyte solution and pH 7.0, significantly more superior than that of the commercial DL membrane. For the feedwater ($\text{Na}_2\text{SO}_4 + \text{MgCl}_2$, $1.0 \text{ g}\cdot\text{L}^{-1}$), the mass ratio of $\text{SO}_4^{2-}/\text{Cl}^-$ and $\text{Mg}^{2+}/\text{Na}^+$ decreased from initial 0.5:1 in the feed to 1.58×10^{-2} and 0.254 in the permeate after filtration by the optimal NF membrane. Anionic dyes removal tests also confirmed the existence of negative charge characteristics from the prepared membranes, and pivotal role of the Donnan exclusion in separating performance. In addition, NFM4 exhibits good chemical stability in the long-term operation.

1. Introduction

Over the past few decades, great advances in nanofiltration (NF) membrane have encouraged the widespread use for many purposes, including wastewater reclamation, water softening, desalination, whey demineralization, dye purification and so forth [1–3]. NF membrane no longer hinges solely on steric hindrance exclusion, but also rather depends on electrostatic interactions and dielectric effects [4,5], which results that NF process is desirable because of its selective separation of one solute over another [6]. The unique separating performance of NF membrane mentioned above has been reported to closely relate to the

porous structure, charged groups and ionic selectivity for its ultra-thin active layer [7]. Among these characteristics, there is no doubt that the surface charge plays an integral role in applications of NF membrane separation technology. For instance, Daraei et al. prepared a negative charged NF membrane by surface grafting of poly(acrylic acid), with an acid blue (–) rejection more than 95% [8]. Therefore, it is of great interest to exploit new membrane materials or modify traditional used materials to develop novel NF membranes with tailored/tunable functionalized active layer assuring high surface charge density, high hydrophilicity, as well as enhanced perm-selectivity [9].

Currently, many studies have proven that the preparation of novel

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Nomenclature

A	the membrane area, m^2
$C_{f,i}$	concentration of solute i in the feed solution, $\text{mol}\cdot\text{m}^{-3}$
$C_{p,i}$	concentration of solute i in the permeate, $\text{mol}\cdot\text{m}^{-3}$
S_{anion}	ions selectivities of anion, –

S_{cation}	ions selectivities of cation, –
t	the permeation time, h^{-1}
V	the permeate volume, L
β	the slope of a ΔE_s - ΔP curve, $\text{mV}\cdot\text{kPa}^{-1}$
ΔE_s	the streaming potential drops, mV
ΔP	the flow pressure drops, kPa

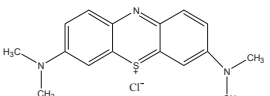
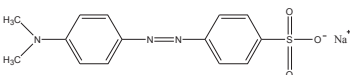
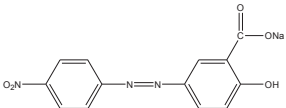
NF membrane with high surface charge density could be made by adding charged ion component to the membrane casting solution [10,11]. For example, Lin et al. informed that the fabrication of polyelectrolyte NF membranes with a $\text{Ni}(\text{OH})_2$ nanosheet layer allowed tunable surface charges, which could be regulated easily by the number of assembled layers [10]. Liu et al. found that modifying carbon nanotube with different charged polymers endowed the modified NF membranes possessing surface zeta potentials in the range of -40.81 to 17.46 mV at the pH of 7.0, and the antifouling data indicated that adjusting the surface charge could tune the interactions between the membrane surface and foulants, which could effectively suppress the irreversible fouling, resulting in 100% flux recovery [12]. Using the synthesized nano-MgO as positively charged precursor, a novel ceramic membrane was fabricated and exhibited high electrical performance [13]. Park et al. prepared a positively charged NF membrane that exhibited enhanced anti-fouling property by introducing a high-density positive charge derived from branched polyethyleneimine onto the selected membrane skin layer, and the corresponding zeta potential values suggested that the modified membrane had 19.52 mV of zeta potential, compared with -8.47 mV for the neat membrane under neutral condition [14]. All these findings confirmed that membrane surface charge density could be significantly enhanced after modification by grafting charged functional groups onto the membrane skin layer. Nevertheless, until recently, very few investigations dedicated to further understand the influence of charged ion component with different substitution degrees or abundance in the precursors on tunable surface charge density of NF membrane.

Chitosan (CS) is a cationic polysaccharide usually acquired from the deacetylation of chitin polymer and routinely applied in membrane preparation for its easy surface-functionalization and environmental benignancy properties [15]. In recent years, CS and its derivatives have been used more often as NF membrane materials to form thin active layers aimed at overcoming the permeability and selectivity trade-off [16,17]. Modification processes mainly focus on a series of substitution reactions of hydroxyls on C-3 and C-6 positions, amino group on C-2 position of CS monomers [18]. Miao et al. prepared amphoteric composite NF membranes by grafting sulphated group onto CS by hexamethylene diisocyanate or epichlorohydrin as cross-linker. At 18°C and 0.45 MPa, the rejections of $7.0\text{ mmol}\cdot\text{L}^{-1}$ K_2SO_4 , KCl solutions for both modified membranes were 90.5% and 37.6%, with permeate fluxes of 10.8 and $11.7\text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, 90.8% and 32.5%, with permeation fluxes of

22.9 and $58.4\text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively [19]. Gao et al. developed a new *O*-(carboxymethyl)-chitosan NF membrane through surface functionalization with graphene oxide (GO) nanosheets. This membrane performed salt rejections of 92.9% and 62.3% for a feed Na_2SO_4 and NaCl concentration of $1.0\text{ g}\cdot\text{L}^{-1}$, respectively, and the relevant permeate fluxes of 15.4 and $17.7\text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 1.0 MPa and ambient temperature, and displayed higher salt rejection including monovalent and divalent constituents than the pristine membrane and most of the commercial NF membranes [20]. These studies showed that the active layers of NF membranes synthesized from existing CS derivatives could yield high salt rejection rates and moderate permeate fluxes, while the relatively low selectivity for divalent ions over monovalent ions suggested potentially low efficiency of water softening or other water treatment.

So far, researches on novel NF membranes have mostly focused on improving the water flux and rejection rather than on ion selectivity [21]. Improved NF membrane selectivity will have a critical role in lowering energy consumption, eliminating the need for additional separation stages and adapting precise applications [22]. It has been shown that grafting high charged ion component to the functional layer could strength NF membrane surface charge and at the same time greatly alter the membrane selectivity [23]. Thus, as a notable high charge density polyelectrolyte, phosphorylated chitosan (PCS) appears to be one of the best candidate available to improve NF membrane surface performance substantially. The aim of this paper was to prepare a new kind of highly and tunable charged composite NF membrane from PCS with the flexibility of improving the membrane selectivity performance. Firstly, a series of the PCSs with modulated substituted degree of phosphate group, composition composed of CS and phosphorus pentoxide were synthesized. Secondly, their membranes were fabricated via surface coating on the polyacrylonitrile (PAN) supporting layer and chemical cross-linking reaction with glutaraldehyde (GA). Chemical compositions of PCSs and surface morphologies, properties of the active layers were characterized by FTIR, TG, ATR-IR, AFM, SEM and streaming potential analyzer. Finally, the regulation for preparation of PCS/PAN membranes with tunable surface charge and enhanced selectivity of divalent ions over monovalent ions and charged anionic dyes in standard conditions was discussed systematically, by manipulating of phosphorus content or substituted degree of phosphate group in the synthetic PCS precursors.

Table 1
Main structure features and characteristics of the anionic dyes adopted in this study.

Dye	Molecular structure	Molecular weight ($\text{g}\cdot\text{mol}^{-1}$)	Maximal absorption wave-length (λ_{max} , nm)
Methylene blue		319.9	664
Methyl orange		327.3	464
Alizarine yellow R		287.2	374

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