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PAA grafting onto new acrylate-alumoxane/PES mixed matrix nano-enhanced membrane: Preparation, characterization and performance in dye removal

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HIGHLIGHTS

- ▶ Nano-sized acrylate-alumoxane was synthesized using acrylic acid and nanoboehmite.
- ▶ Boehmite and acrylate-alumoxane were added to PES casting dope.
- ▶ Grafting of PAA on acrylate-alumoxane/PES membrane results in high flux NF membrane.
- ▶ Grafted nanocomposite membrane shows superior dye removal and antifouling property.
- ▶ Grafting on nanocomposite membrane is a new way to obtain preferable modification.

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ABSTRACT

Nanoboehmite particles were modified by acrylic acid to produce new alumoxane nanoparticles. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were used to realize shape, size and functional groups of synthesized acrylate-alumoxane nanoparticles. The analyses declared that spherical acrylate-alumoxane nanoparticles were formed with hydroxyl and acrylate groups on their surface. Boehmite and acrylate-alumoxane were successfully introduced into polyethersulfone (PES) membrane matrix by the phase inversion method. Fabricated membranes were examined for water permeability, dye (acid blue 193) retention capability and fouling resistance against whey proteins. The field emission scanning electron microscopy (FE-SEM) images were used to estimate the changes in skin-layer morphology and bulk porosity of the prepared membranes. As a result, the directly arrayed finger-like macro-voids as well as bulk porosity were gained by adding acrylate-alumoxane nanoparticles compared to pristine PES membrane. However, different quantities of acrylate-alumoxane in the casting solution induced no noticeable alteration in the membranes bulk porosity. The membranes containing 1 wt.% of acrylate-alumoxane and 1 wt.% of nanoboehmite were selected to be grafted by polyacrylic acid (PAA). Comparison of grafting efficiency for pristine PES membrane and nanofiller blended membranes proved that acrylate-alumoxane offered more effective grafted membrane by providing polymerization initiation sites on mixed matrix membrane surface. In addition to high water permeability (around 19 kg/m^2 h bar), the acrylate-alumoxane mixed/PAA grafted membrane showed superior dye removal and fouling resistance. Atomic force microscopy (AFM) as well as water contact angle test was applied for investigation of membranes surface properties.

1. Introduction

Nanofiltration (NF) membranes as a growing technology in separation processes was mostly studied to be improved in antifouling properties as well as separation of the salts and the pollutants with molecular weights ranged between 100 and 1000 Da (e.g. dyes) [1–4]. This pursues using changes in the casting solution contents and preparation procedure, as well as applying additives, nanoparticles and grafting hydrophilic polymers [2,5–9].

The dye removal from effluents, as one of the important stages of water and waste water treatment, is mostly conducted by

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Nomenclature

List of symbols

AA	acrylic acid
AFM	atomic force microscopy
ATR-FTIR	attenuated total reflectance Fourier transform infrared spectroscopy
B_1	mixed matrix membrane with 1 wt.% nanoboehmite
$BAA_{0.5}$	mixed matrix membrane with 0.5 wt.% acrylate-alumoxane
BAA_1	mixed matrix membrane with 1 wt.% acrylate-alumoxane
BAA_2	mixed matrix membrane with 2 wt.% acrylate-alumoxane
BP	bulk porosity
C_f	dye concentration in feed (mg/l)
C_p	dye concentration in permeate (mg/l)
DMAc	N,N-dimethylacetamide
EG	ethylene glycol
FE-SEM	field emission scanning electron microscopy
FR	flux recovery (%)
FTIR	Fourier transform infrared spectroscopy
GB_1	PAA grafted B_1
$GBAA_1$	PAA grafted BAA_1
GPPES	PAA grafted PPES
J_w	water flux (kg/m^2 h)
$J_{w,1}$	initial water flux (kg/m^2 h)
$J_{w,2}$	after fouling water flux (kg/m^2 h)
J_{wh}	flux of whey solution (kg/m^2 h)
KPS	potassium persulfate
NF	nanofiltration
PAA	polyacrylic acid
PPES	pristine polyethersulfone membrane
PVP	polyvinylpyrrolidone
R	dye removal
R_{ir}	irreversible fouling ratio (%)
RO	reverse osmosis
R_r	reversible fouling ratio (%)
R_t	total fouling ratio (%)
S_a	average roughness (nm)
SEM	scanning electron microscopy
S_q	root mean square of the Z data (nm)
S_z	mean difference between highest peaks and lowest valleys (nm)
V_m	membrane pieces volume (cm^3)
W_d	dry membrane weight (g)
W_w	wet membrane weight (g)

reverse osmosis (RO) and nanofiltration processes; however, working at lower pressures rather than RO along with acceptable yield of dye retention are the commonly mentioned advantages of NF compared to RO processes [10–14]. Applying combined methods such as coagulation and NF [15] and ion exchange membranes with an adsorptive mechanism were studied in this regard [16]. Ceramic membranes prepared by $ZnAl_2O_3$–TiO_2 coated on raw clay were indicated high efficiency in dye removal and high permeate flux as reported [17]. Graft polymerization methods were utilized for production of high flux NF membranes with high efficiency in dye removal [4–6].

The other valuable attempt in membrane preparation is improving the antifouling properties and increasing the life time of the membranes. Addition of nanoparticles on the membrane surface (coating) or in their matrix (blending in casting solution or nonsolvent) [18], graft polymerization methods [6,19] and simultaneous use of these methods [20,21] are introduced as multiple ways to achieve membranes with more effective antifouling capability. Additionally, in the case of using nanofillers as additive in NF membranes, boehmite, organically modified clays, TiO_2, alumina, carbon nanotubes, etc., were reported to be effective in antifouling property, higher contaminant rejection and improved mechanical strength of the modified membranes [22–26].

γ-AlOOH (boehmite) nanoparticles mixed with casting solution were recently used to induce antifouling property to polyethersulfone (PES) membranes [22]. It was revealed that the extra hydroxyl groups of nanoboehmite was responsible for decreasing membrane fouling by increasing membrane hydrophilicity and changing surface roughness [22]. Immersion of casted membrane in nanoparticles-nonsolvent emulsion bath followed by thermal treatment for growing boehmite and gibbsite crystals was also carried out for embedding aluminum oxide nanoparticles in membrane matrix. The modified membrane showed decreased attachment of bacteria on the membrane surface (antibiofouling property) [27]; however, in this modification method (mixing a nanofiller), reduction of permeate flux might be observed with increase of nanofiller quantity because of nanoparticles agglomeration [22] which can be considered as a shortcoming of nanofillers addition into the membrane matrix [28].

Boehmite and modified boehmite nanoparticles are widely employed in fabrication of nanocomposites, metal doped aluminum oxide, catalysts, ceramic membranes and active coating layer on the membranes [29–33]. Boehmite nanoparticles can be modified using carboxylic acids because carboxyl group is able to be coordinated with aluminum as unidentate and bidentate ligands [32,34,35]. Modification of boehmite nanoparticles is carried out for changing the physical/chemical properties by targeted selection of a special carboxylic acid [34]. Although, there are several types of carboxylate modified boehmite nanoparticles (e.g. para hydroxybenzoate, salicylate, para aminobenzoate and fumarate) which contain the coordination of carboxyl group with the basic formula of $[Al(O)_x(OH)_y(O_2CR)_z]_n$ where $2x + y + z$ is equal to 3, x, y and z can include any integer or fraction values (for instance, x can be 0–1.5, y can be 0–3, z can be 0–3, and n can be 1–6 or greater) and R refers to C_1 to C_{14} hydrocarbons [29,36]. By our knowledge, acrylate modified boehmite (acrylate-alumoxane) has not been synthesized in any research regarding membrane preparation or modification.

In this study, a new procedure is presented for modification of PES membrane by mixing self-synthesized acrylate-alumoxane nanoparticles in the casting solution to achieve a support with linking sites for an effective grafting of polyacrylic acid on the membrane surface. Indeed, the main approach is to investigate the possibility of combination of graft polymerization and nanofiller addition for superior modification of PES NF membranes. The fabricated membranes are tested for water flux, acid blue 193 (831.68 Da) dye removal capability and antifouling properties. The scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR) and attenuated total reflectance FTIR (ATR-FTIR) are utilized for characterization of modified boehmite nanoparticles and nanocomposite NF membrane.