



Fabrication of novel heterogeneous cation exchange membrane by use of synthesized carbon nanotubes-co-copper nanolayer composite nanoparticles: Characterization, performance in desalination



A. Zandehnam^a, S. Mokhtari^a, S.M. Hosseini^{b,*}, M. Rabieyan^a

^a Thin Film Laboratory, Department of Physic, Faculty of Science, Arak University, Arak 38156-8-8349, Iran

^b Department of Chemical Engineering, Faculty of Engineering, Arak University, Arak 38156-8-8349, Iran

HIGHLIGHTS

- Novel PVC/MWCNT-co-Cu composite nanoparticle membranes were prepared.
- Selectivity was improved by an increase of composite nanoparticles content.
- Flux was declined by an increase in nanoparticles concentration and then increased.
- Electrical resistance was decreased sharply with the use of composite nanoparticles.
- Mechanical stability improved by use of MWCNT-co-Cu composite nanoparticles.

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ABSTRACT

In this research polyvinyl chloride/multi walled carbon nanotube-co-copper nanolayer composite nanoparticles heterogeneous cation exchange membranes were prepared by solution casting techniques. The MWCNT-co-Cu nanolayer composite nanoparticles were prepared by magnetron sputtering method. The effect of composite nanoparticle concentration on physico-chemical properties of membranes was studied. The SEM, TEM and XRD results showed uniform distribution and crystalline structure for the deposited Cu nanolayer on the MWCNTs' surface. SOM images also showed relatively uniform particle distribution for the membranes. The membrane potential, transport number, selectivity and electrical conductivity were improved by an increase of additive content in prepared membranes. Membrane average roughness was decreased slightly by an increase of additive concentration. Membrane ionic permeability and flux were decreased initially by an increase of additive ratio up to 0.5 wt.% and then showed an increasing trend by more additive concentration. Furthermore, mechanical stability of prepared membranes was improved by an increase of MWCNT-co-Cu nanolayer composite nanoparticle content in membrane matrix. Also, modified membrane containing 4 wt.% composite nanoparticles showed better electrochemical properties compared to other modified membranes, membrane containing pure MWCNTs and unmodified ones.

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1. Introduction

Nowadays, ion exchange membranes (IEMs) are being utilized as active separators in divers electrically driven processes such as electro-dialysis for desalting brackish waters, reconcentrating brine from seawater and production of table salt. IEMs also are efficient tools in resource recovery and food and pharmacy processing. Moreover, ion exchange membranes have been employed in environmental protection such as treating industrial and biological effluents processes [1–13].

In ion exchange membranes charged groups are attached to polymer backbone and freely permeable to opposite sign ions under an electrical field influence [12]. In such processes, ion interactions with membrane, water, and with each other occur in complex fashions. Knowledge of the physico/chemical properties of IEMs is important factor behind decisions about their applicability in separation processes [10,14–18].

Preparing IEMs with special physico-chemical characteristics may be as a vital step in future chemical and waste treatment application [2,10,19–21]. Variation of functional groups, selection of different polymeric matrices, polymer blending, use of various additives such as nanoparticles, alteration of cross-link density and surface modifications by nanolayer such silver nanolayer are important ways to obtain superior IEMs [3,5,10,14,15,22–28].

* Corresponding author. Tel.: +98 86 32625434; fax: +98 86 32625435.

E-mail addresses: Sayedmohsen_Hosseini@yahoo.com, S-Hosseini@Araku.ac.ir (S.M. Hosseini).

Preparing heterogeneous ion exchange membranes with appropriate physico-chemical properties for the application in ED processes related to water recovery and treatment was the primary target of the current research. For the purpose, PVC based/MWCNT-co-Cu nanolayer mixed matrix heterogeneous cation exchange membranes were prepared by solution casting techniques using cation exchange resin powder as functional group agent and tetrahydrofuran as solvent. PVC is a durable polymer with suitable biological and chemical resistance [29–31]. Also, a MWCNT-co-Cu nanolayer composite nanoparticle was employed as inorganic filler additive in membrane fabrication in order to improve the IEM physico-chemical properties. The *MWCNT-co-Cu nanolayer composite nanoparticles* were prepared by magnetron sputtering method. Utilizing of inorganic particles or fillers especially nano-materials/nanolayer into polymeric membranes such as ion exchange type has been examined in many applications to enhance the mechanical, thermal and chemical stabilities in severe conditions and also improve the separation properties of them as well as producing of antibacterial/antimicrobial membranes [9,14,23,32–36].

MWCNTs are new class of advanced materials with very interesting features and capacity such as superior electrical, mechanical and adsorption characteristics which also has been utilized in water treatment [23,32–34]. Copper nanolayer has also been gained much attention as multifunctional inorganic material because of superior electrical, thermal conductivity and natural anti-bacterial property [35,36].

It has been indicated that the MWCNT properties can be dramatically influenced by surface modification with inorganic materials such as metal/metal oxide nanoparticles based on the synergism between the component properties [37–41]. Different methods have been carried out in surface modification of MWCNTs by inorganic materials such as chemical reduction, radiation, electro-chemical deposition, ion beam assisted deposition, pulsed laser ablation, chemical vapor deposition and etc. [42–48].

No research was found by our literature survey to surface modification of MWCNTs by Cu nanolayer through magnetron sputtering technique/plasma treatment. The suitable adhesions of nanoparticles to substrate, uniformity, good and controllable deposition rate and high purity are some of advantages of this method [49].

Also, no report has considered incorporating *MWCNT-co-Cu nanolayer composite nanoparticles* into ion exchange membranes and the literature is silent on characteristics and functionality of mixed matrix PVC based/MWCNT-co-Cu nanolayer heterogeneous cation exchange membranes.

The effects of *MWCNT-co-Cu nanolayer composite nanoparticle* concentration in the casting solution on physico-chemical characteristics of prepared heterogeneous cation exchange membranes were studied. During this experiment, sodium chloride was employed as ionic solutions for the membrane characterization. The results are valuable for electro-membrane processes especially in electrodialysis process for water recovery and waste water treatment.

2. Materials and methods

2.1. Materials

Polyvinylchloride (PVC, grade S-7054, density: 490 g/L, viscosity: 105 cm²/S) supplied by Bandar Imam Petrochemical Company (BIPC), Iran, was used as binders. Tetrahydrofuran (THF, solubility: 20 °C, molar mass: 72.11 g/mol, density: 0.89 g/cm³) was employed as solvent. Multi walled carbon nano tubes (MWCNTs, functionalized type: COOH-MWCNT) with 10–20 nm outer diameter, 5–10 nm inner diameter, 0.5–2 μm length and 200 m²/g specific surface area was provided from NANO-RADBEHAN Company, Iran. Cation exchange resin (Ion exchanger Amberlyst® 15, strongly acidic cation exchanger, H⁺ form -4.7 meq/g dry weight) by Supelco was used in membrane preparation. All other chemicals were supplied by Merck. Throughout the experiment, distilled water was used.

2.2. Synthesis of MWCNT-co-Cu nanolayer composite nanoparticles

In order to fabricate the novel MWCNT-co-Cu nanolayer composite nanoparticles, copper was sputtered on MWCNTs (as substrate) in a vacuum reactor (with 10⁻⁶ mbar base pressure) by argon plasma treatment using magnetron sputtering method (planar magnetron sputtering model-12" MSPT, HIND high vacuum, Bangalore, India) at 90 W power (DC MAGNETRON SUPPLY POWER MODEL-PS-2000). Copper (Cu) with high purity (99.9% purity) and argon (research grade 99.9%) were utilized as target and plasma former in magnetron sputtering system respectively. The distance between substrate and Cu target (cathode, 12.5 cm diameter and 3 mm thickness) was kept 12 cm (optimal distance) in plasma reactor during the process to obtain a uniform film with good packing density. Copper nanoparticles with 0.5 nm/s was deposited on MWCNTs surface with constant thickness of 10 nm. The thickness of coating layer was adjusted by changing the deposition time. Before starting the actual experiment, the target was pre-sputtered for 10 min with a moveable shutter located in between the target and substrate. This shutter is also used to control the period of deposition exactly.

2.3. Preparation of nanocomposite cation exchange membranes

The heterogeneous cation exchange membranes were prepared by casting technique/phase inversion method. In order to undertake the membranes preparation, resin particles were dried in oven at 30 °C for 48 h and then pulverized into fine particles in a ball mill and sieved to the desired mesh size. The ion exchange resin with desired particle size (-300 + 400 mesh) was used in membrane fabrication. The preparation proceeded by dissolving the polymer binder into THF solvent ((THF: PVC) (v/w), (20:1)) in a glass reactor equipped with a mechanical stirrer (Model: Velp Scientifica Multi 6 stirrer) for more than 6 h. This was followed by dispersing a specific quantity of grinded resin particle as functional group agents ((Resin: PVC) (w/w), (1:1)) and MWCNT-co-Cu nanolayer composite particles as additive (0.0, 0.5, 1.0, 2.0, 4.0, 8.0 wt.%) in polymeric solution, respectively. The mixture was mixed vigorously at room temperature to obtain uniform particle distribution in the polymeric solution. In addition, for better dispersion of particles and breaking up their aggregates, the solution was sonicated for 2 h using an ultrasonic instrument (PARS NAHAND ENGINEERING CO, model: 11S, Power Supply: 220 VAC, Frequency: 28 kHz). Sonication of solid particles increases the viscosity of casting solution by reducing aggregation and sedimentation and reduces the evaporation rate of casting solvent. This improves the polymer chain relaxation as well as its conformation with particle surfaces and promotes the compatibility of particles and binder [50,51]. This reduces the amount of cracks and fissures between binder and particles and so improves the membrane selectivity. Moreover, excessive homogeneity and uniform distribution of resin particles on membrane surface and in the bulk of membrane matrix provide superior conducting regions in membrane and generate easy flow channels for counter-ion transportation. Also, the presence of more conducting region can strengthen the intensity of uniform electrical field around the membrane and decreases the concentration polarization phenomenon [52]. The mixing process was repeated for another 30 min using the mechanical stirrer. The mixture was then cast onto a clean and dry glass plate at 25 °C. The membranes were dried at ambient temperature (25 °C) for 10 min and then immersed in distilled water. As the final stage, the membranes were pretreated by immersing in 0.5 M NaCl solution for 48 h. The membrane thickness was measured by a digital caliper device (Electronic outside Micrometer, IP54 model OLR) around 60–70 μm.

2.4. Test cell

The electrochemical property measurements for the prepared membranes were carried out using the test cell [22,23]. The cell (Fig. 1)

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