Abstract

Low temperature plasma treatment using pulsed direct current discharge of nitrogen and ammonia gases was employed to enhance hydrophilicity of the polyacrylonitrile co-polymer membrane surface. Carbon dioxide and nitrogen plasma of radio frequency discharge were also used to modify the surface of the membrane. The enhancement of hydrophilicity of the plasma modified membrane surface was evaluated by measuring the contact angle. The membranes were characterized in terms of morphology, structure, wettability and performance. Properties and functional groups on the surface of polyacrylonitrile co-polymer membranes were investigated by scanning electron microscopy, atomic force microscopy and x-ray photoelectron spectroscopy. Influence of various plasma operating conditions, namely, pulsed voltage, duty cycle, power and exposure time on improvement of permeability and hydrophilicity of the membrane was investigated. Hydrophilicity of the nitrogen plasma treated membranes was more at higher exposure time and power for radio frequency discharge. Permeability of pulsed direct current nitrogen plasma treated membrane was enhanced by 47% and it was retained upto 70 days. Surface etching due to plasma treatment was confirmed by weight loss of the treated membranes. About 78% increase in average pore size was obtained using radio frequency carbon dioxide plasma treatment due to surface etching. In case of ammonia plasma treatment, the pore size remains same but the hydrophilicity was improved significantly. The ammonia plasma treated membranes were used for separation of oil-water emulsion. It was found that the anti-fouling property of membrane improved remarkably after plasma treatment by enhancement of permeate flux without significant changes in oil rejection. About 32% increase in permeate flux of the treated membrane was obtained due to superior efficacy for augmenting anti-fouling characteristics. On the other hand, for pulsed DC discharge nitrogen plasma results in surface etching leading to increase in average pore size thereby lowering the rejection of 200 kDa polyethylene glycol to about 70%. Low temperature RF plasma is preferred due to uniform distribution of plasma inside the reactor providing good functionalization rates with less gas breakdown voltage. The RF nitrogen plasma treatment (70 W, 8 min) rendered the modified PAN surface to be the most hydrophilic ($8^\circ \pm 2^\circ$). Radio frequency discharge of nitrogen plasma was more superior to the carbon dioxide plasma in conferring greater wettability, higher functionality and lower weight loss of the PAN membranes. The pore enlargement due to plasma etching is the only dominating factor in enhancing permeability (70%) of RF carbon dioxide modified (70 W, 6 min) membrane throughout the ageing period of 100 days. The combined effect of pore enlargement and hydrophilicity leads to increase in permeability of the RF nitrogen modified membrane for the initial 20 days of aging. After 20 days of the ageing period, the permeability of treated PAN only depends on pore enlargement due to plasma etching. Hydrophilicity of radio frequency carbon dioxide plasma modified membrane was enhanced by 22% and it was maintained upto 100 days. The pulsed DC ammonia plasma treatment is better than the nitrogen plasma of RF and DC discharge that incorporates various hydrophilic functional groups on the surface with insignificant weight loss and pore enlargement due to marginal etching. As compared to DC discharge of nitrogen and ammonia plasma, the carbon dioxide RF plasma has a high etching rate resulting in the significant weight loss of the membrane. The RF nitrogen plasma modified surfaces appear to retain their functionality better than the pulsed DC discharge of nitrogen plasma-treated samples. Oxygen and nitrogen functional groups were identified to be responsible for surface hydrophilicity.

Keywords: Polyacrylonitrile co-polymer membrane; plasma treatment; hydrophilicity; permeability; contact angle.