

Synthesis of surface-treated NaX nanocrystals

The surface-treated zeolite nanocrystals (ST-NaX-NCs) were synthesized by the hydrothermal method reported in our previous works^{1,2}. In this process, at first, 2.67 g of NaOH was dissolved into 25 g of DI-water. Next, 1.21 g of NaAlO₂ was added to the solution and continuously stirred pending a colorless solution was obtained. Then, 1.715 g of fumed silica was sluggishly added to the solution, and the solution was mixed (24 h) until a smooth gel was obtained. Later, the prepared gel was grown inside the microwave (90°C, 3 h), and NaX nanocrystals were synthesized.

1.5 g of synthesis nanocrystals were added to 225 mL of DI-water and stirred at (25°C, 2 h), and sonicated (1 h). Then, 1.925 g of chloroacetic acid (ClCH₂COOH) was gradually added to the suspension while agitating on a magnetic stirrer. After reflux (100°C, 8 h), primary, the suspension blend was cooled to ambient temperature, and next washed using a laboratory tabletop centrifuge (10 min, 6000 rpm) with DI-water until it reaches normal pH. After washing for 4 times, it was dried (80°C, 12 h).

Preparation of mixed matrix composite membranes

The mixed matrix composite membranes (MMCMs) containing ST-NaX-NCs were prepared through the solution casting and solvent evaporation techniques^{1,2}.

For fabrication of PES support-layer, first, the PES granules (16 %wt) dissolved in the DMF solvent (84 %wt), and the obtained polymer solution was agitated on a heater stirrer for 24h. Next, a layer of bubble-free PES solution was cast on flat glass. Afterwards, the glass plate was immediately immersed in a DI-water bath. After 24 h, the formed PES membranes were dried for one day at ambient temperature.

For the preparation of selective layer solutions, first, zeolite nanocrystals were mixed in water/ethanol (30/70 wt/wt) solvent under agitating (25°C, 4h) and sonicating (1h) to gain a smooth suspension. Second, PEBAX-1657 copolymer granules were dissolved in water/ethanol (30/70 wt/wt) solvent mixture under stirring (70°C, 4h) and refluxing to obtain a homogeneous PEBAX solution (10 %wt). Third, in 4 steps and each time 1/4 of the PEBAX solution was blended with nanocrystals suspension, stirred for 30 min and sonicated for 15 min. Later, the obtained dope solution was stirred (1h) and sonicated (30min) as the final homogenization step.

To fabricate MMCMs, the PES support-layer was fixed on a flat glass via removable tape, and then using a casing-knife, a layer of selective-layer solution was cast on the PES support layer. The resulting films are then conditioned in an oven at 35 °C for 24 h to form the MMCMs.

Characterization of ST-NaX-NCs and MMCMs

The crystalline structure and crystal size of the ST-NaX-NCs particles were scrutinized by X-Ray Diffraction instrument (XRD, Equinox 3000, Inel, France) by CuK α radiation of $\lambda=1.5419$ Å at 45 kV, 40 mA, 25 °C and angle diffraction (2θ) from 5 to 40° with 0.03° (2θ) min⁻¹ scanning speed.

The morphology of synthesized ST-NaX particles was evaluated using Field Emission Scanning Electron Microscopy (FESEM, S-4700, Hitachi, NJ, USA).

The Brunauer-Emmett-Teller (BET) analysis of the ST-NaX-NCs was executed on Quantachrome Autosorb-1 analyzer (USA) via operating N₂ adsorption-desorption isotherms at 77 K. Before testing, the particles were degassed under vacuum at 120 °C and 10⁻⁴ Pa for 12 h.

The chemical structures of nanoparticles and MMCMs were perused using Fourier Transforms Infra-Red (FTIR, Nicolet Instrument, USA) from 400–4000 cm⁻¹.

The accurate surface and cross-sectional morphology of the MMCMs were surveyed using Scanning Electron Microscope device (SEM, AIS2300C, Seron Technology's, South Korea). The presence of filler in the membrane matrix was certified via Energy-Dispersive X-ray spectroscopy (EDX) analysis with a FESEM (S-4700, Hitachi, NJ, USA).

The determination of the degree crystallinity of MMCMs was conducted by differential scanning calorimeter (DSC) instrument (Mettler-Toledo Inc., Switzerland). The samples were heated in the temperature range of -80 to 250 °C under argon atmosphere with the rate of 10°C/min in two cycles. The crystallinity of the fabricated membranes was estimated based on the method presented in our previous report¹.

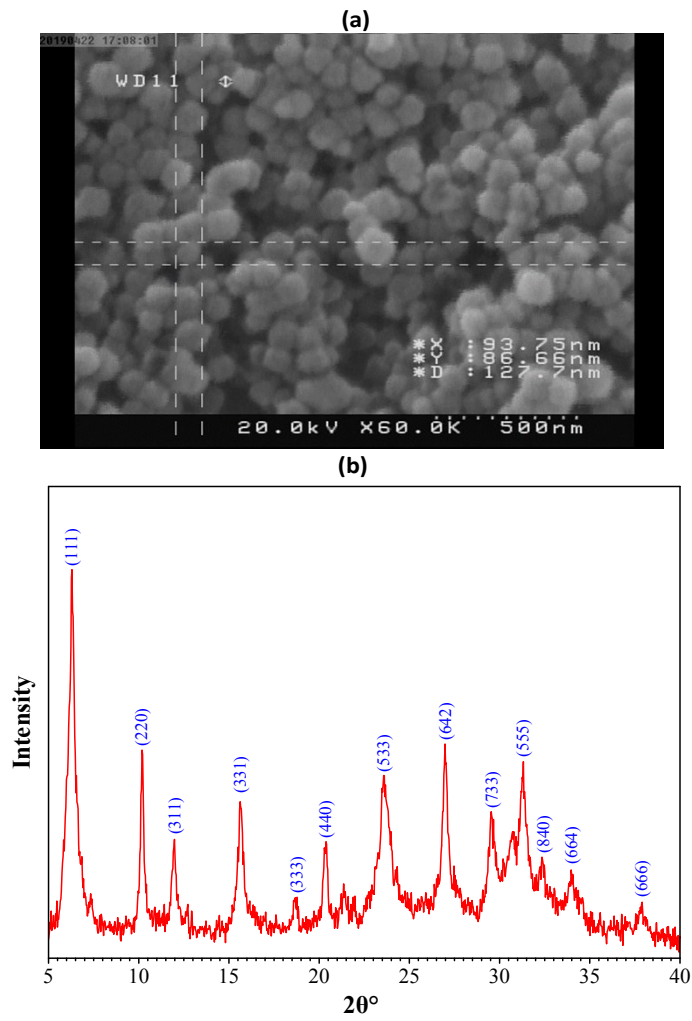


Fig. S1: The FESEM image (a), and XRD pattern (b) of the prepared ST-NaX-NCs.

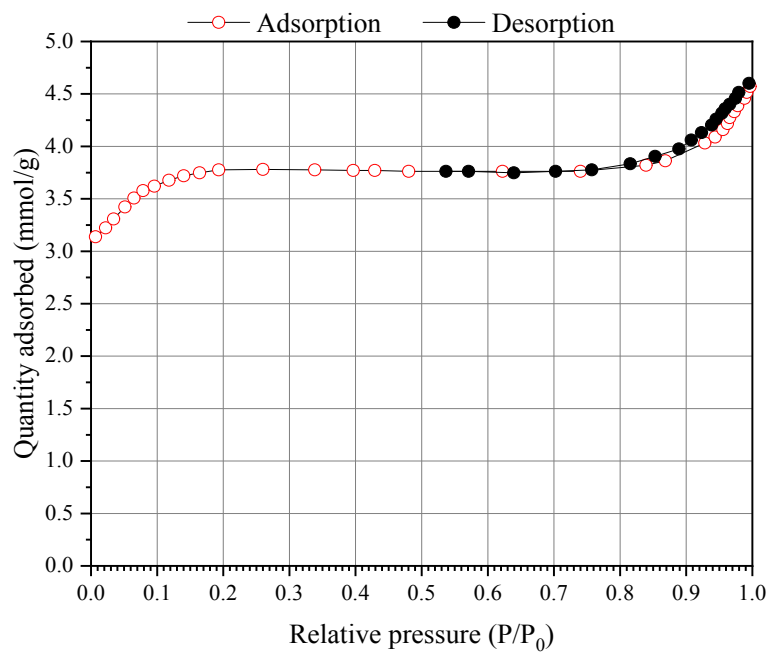


Fig. S2: The adsorption and desorption isotherms of the surface-treated nano-NaX zeolite.

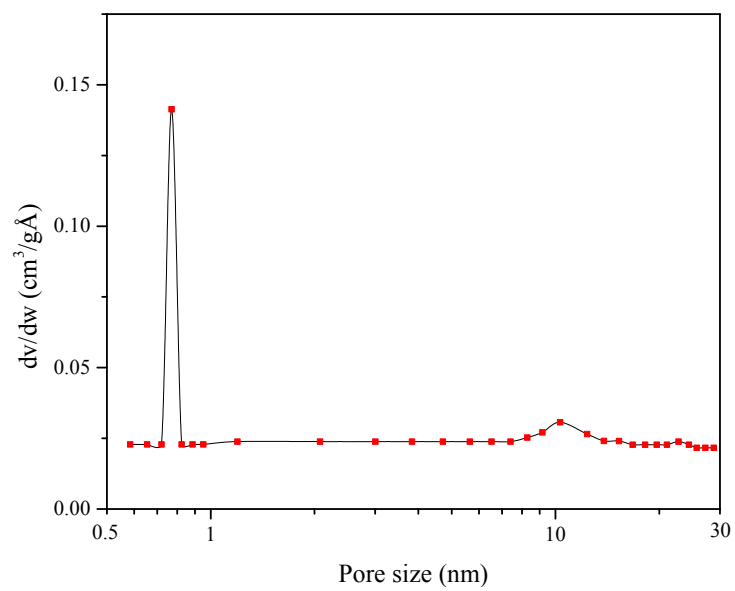


Fig. S3: The pore size distribution of the surface-treated nano-NaX zeolite.

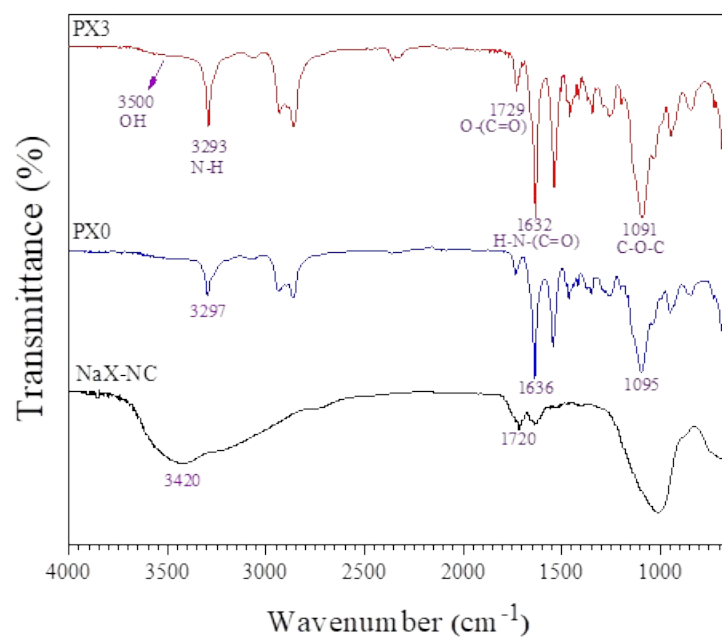
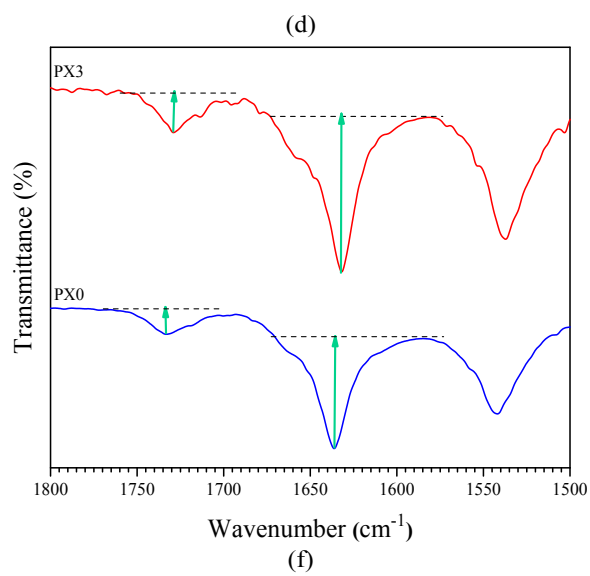
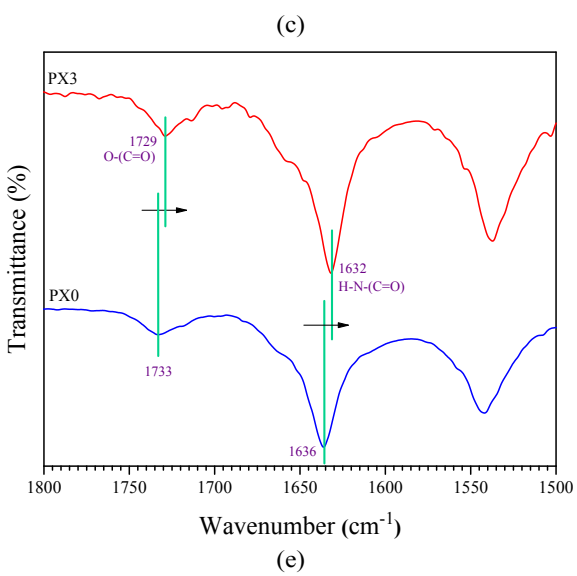
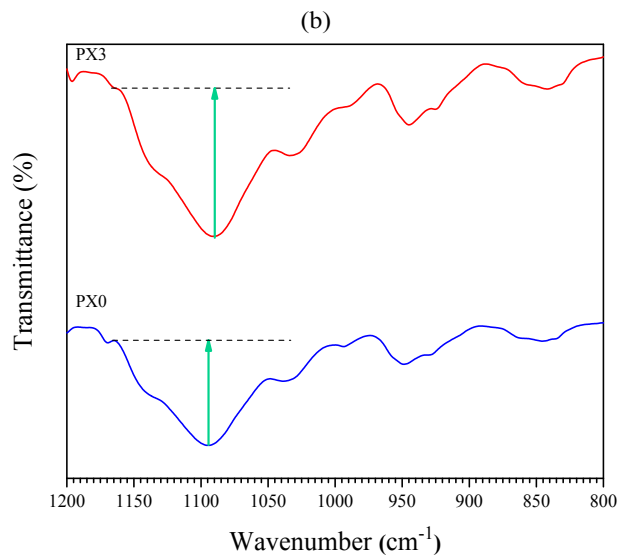
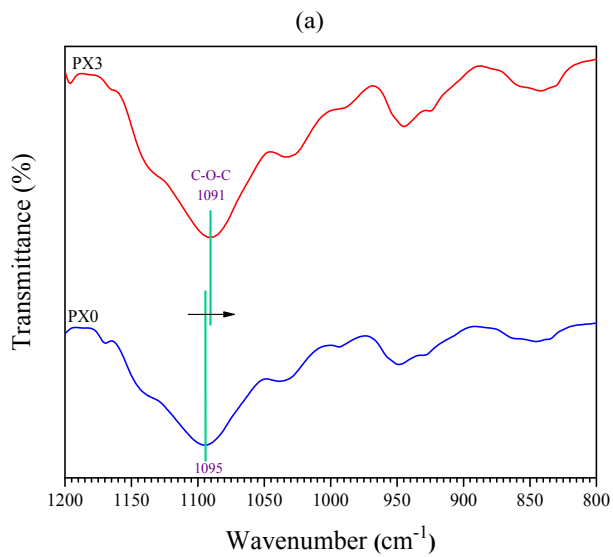


Fig. S4: The FTIR spectra of the ST-NaX-NCs and PX0 and PX3 membranes.



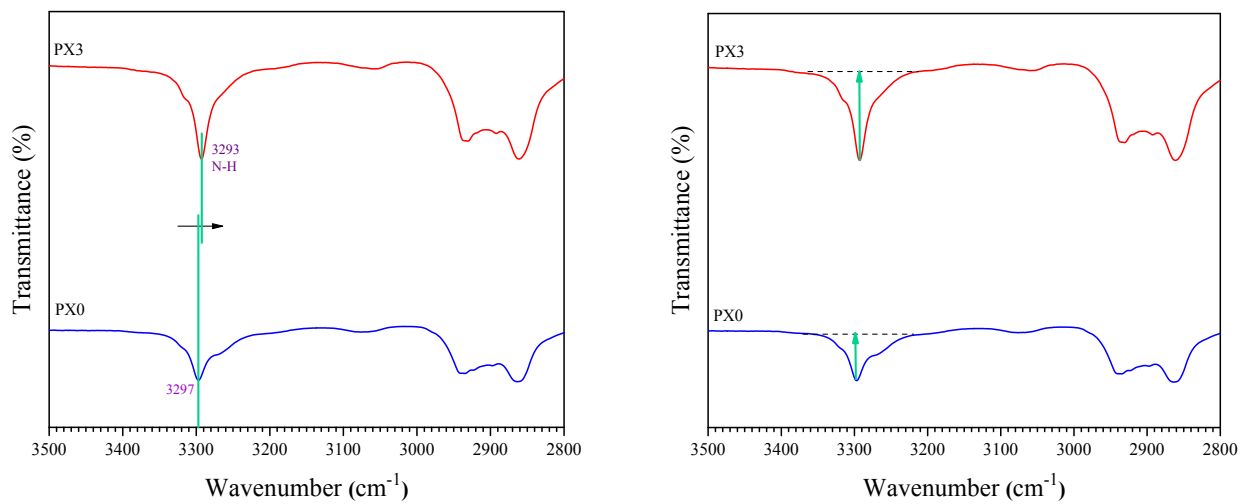


Fig. S5: The comparison of the FTIR spectra of PX0 and PX3 membranes at 800-1200, 1500-1800 and 2800-3500 cm⁻¹. (Left graphs related to peak shift and right graphs related to peak intensity variations).

References

1. M. S. Maleh and A. Raisi, *RSC Advances*, 2019, **9**, 15542-15553.
2. M. S. Maleh and A. Raisi, *Chemical Engineering Research Design*, 2019, **147**, 545-560.