# ABSTRACT

This study primarily investigates the crystallization of low- and intermediate- silica zeolites from natural aluminosilicate precursors: bentonite, kaolinite, and volcanic ash for oil-water separation applications. This study addresses the need for sustainable environmental remediation materials through transformation of natural minerals into higher-value and structurally tunable crystalline zeolite frameworks. Through the systematic variation of crystallization temperatures (90-150°) and initial gel silicon-to-aluminum ratio (SAR), the crystallization pathways and structural evolution were mapped.

Structural evaluation was done via X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Fourier Transform Infrared (FTIR) spectroscopy to reveal crystallization kinetics that are parameter-dependent. Alumina-rich environments (gel SAR = 1) were found to yield single-phase products, faujasite (FAU) from bentonite and sodalite (SOD) from kaolinite and volcanic ash. In contrast, silica-rich environments (gel SAR = 3) followed a kinetic transformation sequence dictated by the Ostwald rule of stages that progressing through increasingly dense frameworks: FAU-phase to SOD-phase to ANA-phase (analcime) zeolite frameworks. The structural relationship between FAU and SOD wherein both contain sodalite-cage secondary building units support the structural building block mechanism of crystallization. Meanwhile, the crystallization of ANA phase at higher thermal energy required complete dissolution materials to Si-O and Al-O tetrahedra. Textural characterization conducted via BET showed that kaolinite-derived FAU-phase zeolite achieved the highest surface area ($226.2\text{m}^2/\text{g}$).

The potential for oil-water separation was evaluated through wicking kinetics and equilibrium adsorption studies. Functional evaluation using the Lucas-Washburn model identified a kinetic gap between water and oil transport in several products. The engineered zeolites have shown superhydrophilic behavior with effective dynamic water contact angles reaching $< 0\,^{\circ}$ and wicking constants ($K_{\text{water}}$) as high as $84.4\ \text{mm}^2/\text{s}$ (B150S1). In contrast, the high viscosity of the engine oil used in this study restricted its oil transport rate to $K_{oil}$ ¡ 0.4 $mm^2/s$ leading to an water-oil selectivity index (SI) reaching 825 for the B150S3 (ANA) product. The good selectivity index for oil-water for the B150S3 product produces an underwater oleophobic material that can act as a shield to reject petroleum components especially in marine environments. The research also categorized the products into materials of two functional roles depending on their wicking kinetics and equilibrium adsorption characteristics: water-selective membranes (VA120S1) and high-capacity oil sponges (K120S3, $AC_{oil}$ = 9.50 g/g).

The practical utility of the zeolites was demonstrated through the fabrication of carrageenan-based composite films. Mechanical testing through ASTM D882 showed that FAU-type zeolites provide the highest mechanical reinforcement to the film increasing the ultimate tensile strength (UTS) to 1.4 MPa, while volcanic-ash derived zeolites exhibited good flexibility with maximum tensile strain (MTS) exceeding 0.55 mm/mm. A Pearson correlation analysis showed a high positive correlation ($r = 0.986$) between BET surface area and UTS for the bentonite series, and high negative correlation ($r = -0.999$) between the BET surface area and MTS for the volcanic ash series.

These findings establish that low-cost natural precursors can be precisely tuned to either high-flux selective membranes or high-capacity oil sponges, providing a sustainable and tunable toolkit for environmental remediation of marine oil spills and industrial oil-water separation.

Keywords: zeolite synthesis, bentonite, kaolinite, volcanic ash, petroleum sorption, oil-water separation, composite films