ABSTRACT

This study presents a multidisciplinary investigation into transforming crude-derived heavy fractions into functional carbon-based materials, with emphasis on microwave-assisted reduced graphene oxide (rGO-M) for environmental remediation. The research integrates crude oil analysis, material synthesis, and performance evaluation, offering methodological innovations and industrial implications.

A major contribution was refining a Thin-Layer Chromatography–Flame Ionization Detection (TLC-FID) method for accurate quantification of SARA (Saturates, Aromatics, Resins, Asphaltenes) fractions. Derived response coefficients enabled reproducible analysis, overcoming limitations of conventional protocols. Validation against ASTM D6560, IP 391, and HTSD confirmed robustness. Compatibility thresholds—Crude Incompatibility Index (CII < 1.0) and P-value > 1.45—were established as reliable indicators of stability, providing refiners with predictive tools for blending outcomes, fouling control, and process optimization.

Characterization of Aromatic, Resin, and Asphaltene (ARA) fractions from three crude types—LCO (Light, 33.4°API), MCO (Medium, 21.4°API), and EHCO (Extra Heavy, 9.5°API)—offered insights into molecular complexity. FTIR, GPC, ^{1}H/^{13}C NMR, and elemental analysis revealed increasing aromaticity, molecular weight, heteroatom content, and polydispersity from light to heavy crudes. These findings confirmed that heavier fractions possess more complex architectures influencing refining and material conversion.

ARA fractions were then subjected to three-stage heat treatment (pyrolysis) to yield high-purity carbon materials—green, calcined, and graphitized carbons. XRD and Raman spectroscopy confirmed structural evolution from amorphous to ordered graphitic states. Declining d-spacing (~3.5 Å → ~3.37 Å), increasing crystallite size, and lower ID/IG ratios evidenced graphitic order. Elemental analysis showed enrichment in carbon content, reaching ~99.99% in graphitized samples, while TGA validated improved thermal stability. Importantly, carbon products from different fractions exhibited negligible property differences, indicating that heat treatment homogenizes feedstock variations.

In parallel, graphene-based materials—graphene oxide (GO), thermally reduced graphene oxide (rGO), and rGO-M—were synthesized and characterized using XRD, Raman, FTIR, FESEM, HRTEM, BET, elemental analysis, and TGA. GO exhibited expanded interlayer spacing and high oxygen content due to functional groups (hydroxyl, epoxide, carboxyl). Reduction restored graphitic networks. While rGO showed partial recovery, rGO-M delivered superior performance: higher C/O ratio (310.26), reduced d-spacing (3.3960 Å), enhanced crystallinity, and greater thermal stability. FESEM and BET indicated rGO-M possessed meso–macroporous morphology, improving accessibility and surface interaction, essential for adsorption. Raman revealed a higher ID/IG ratio (1.52), indicating a well-developed graphitic framework with retained active sites, ideal for pollutant capture.

Environmental applications were evaluated through wastewater treatment and oil spill remediation. In batch adsorption studies using alkaline industrial wastewater (pH 13.8, TOC 22.74 ppm, hardness 170 ppm), rGO-M outperformed thermally reduced rGO in removing TOC, calcium, magnesium, and total hardness. At 1.0 g/L dosage, rGO-M achieved 80% reduction in hardness and 60% TOC removal, compared to 70% and 55% by rGO. Its adsorption capacity was 136 mg/g for hardness and 13.65 mg/g for TOC. At 1.5 g/L dosage, efficiencies increased to 85% and 61%. These results were attributed to high surface area, residual functional groups, and crumpled-sheet morphology enhancing pollutant interactions.

In simulated oil spill studies, rGO-M showed remarkable performance. It achieved oil adsorption capacity of 190 mg/g and 95% removal within 30 minutes, versus 120 mg/g and 60% by rGO. Kinetic studies revealed rapid uptake, with 40% removal in the first minute and 85% within five minutes. Hydrophobicity, ionophilicity, and porous architecture facilitated selective and efficient oil adsorption, highlighting rGO-M as a promising sorbent for emergency clean-up.

The synthesis of rGO-M was optimized using Design Expert software with a Box–Behnken Design (BBD), evaluating microwave power, exposure time, and reducing agent concentration. A quadratic regression model ($R^2 = 0.9749$, adjusted $R^2 = 0.9426$) demonstrated strong predictive accuracy. ANOVA confirmed significance of all three factors and the interaction between exposure time and reducing agent concentration. Response surface and contour plots identified optimal conditions for pollutant removal, reinforcing process reproducibility and scalability.

Mechanistic studies revealed that GO’s polar and dielectric nature enables selective microwave absorption at 2.45 GHz, producing rapid heating and efficient oxygen group removal. This restored the sp^2 carbon network while minimizing defects. Uniform energy distribution and reduced reaction time made microwave reduction more efficient and scalable than conventional thermal methods, aligning with literature reports.

In summary, this thesis develops an integrated framework for valorizing petroleum fractions into advanced carbon materials, emphasizing the industrial relevance of analytical methods and synthesized products. The successful development of rGO-M underscores its potential as a multifunctional material for environmental applications, combining high adsorption capacity, rapid kinetics, thermal stability, and structural robustness. This work demonstrates a scalable, eco-friendly, and cost-effective pathway for mitigating pollution while valorizing petroleum by-products. Future studies could extend applications into energy storage, catalysis, and coatings, opening promising directions for sustainable carbon technologies.