Thermodynamic and kinetic study of the adsorption of dyes on modified graphene oxides

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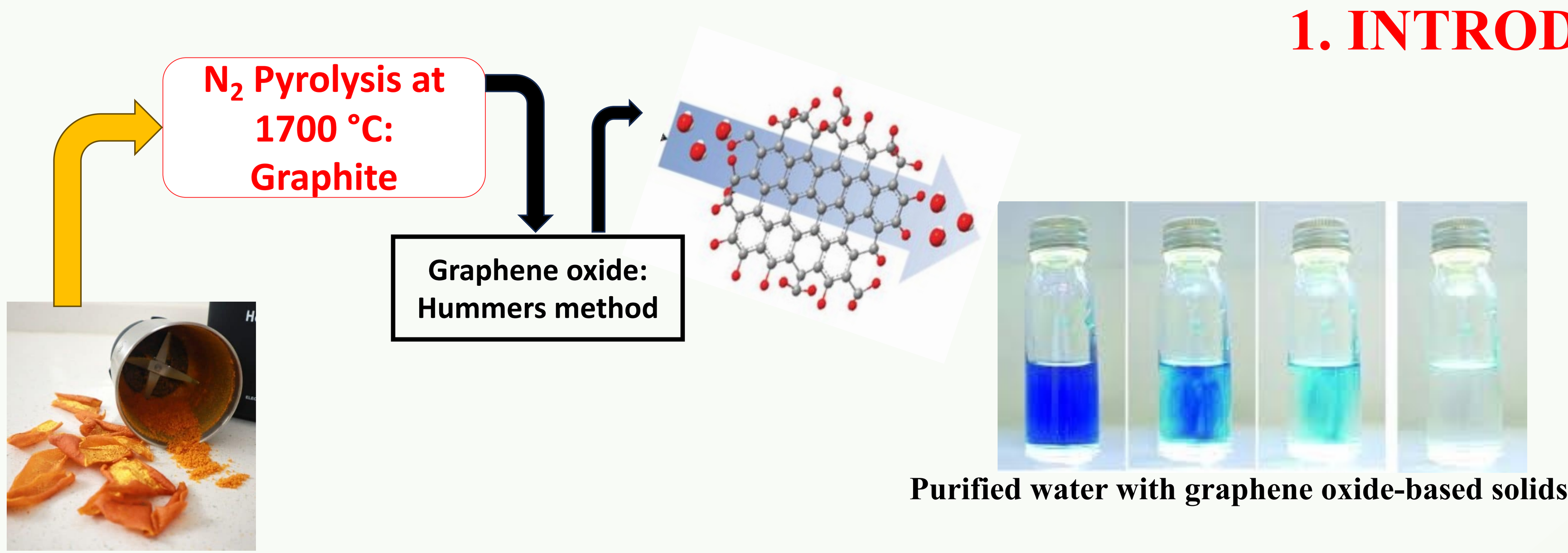
1. INTRODUCTION



Purified water with graphene oxide-based solids

- ✓ Industrial activity leads to widespread discharge of organic compounds, posing environmental risks.
- ✓ Current treatment methods face scalability and cost challenges.
- ✓ Adsorption, including metal-organic frameworks and activated carbon, offers promise.
- ✓ This study investigates adsorption mechanisms of dyes on various materials to advance wastewater treatment.

2. METHODOLOGY AND MATERIALS

Graphene Oxide (GO) Synthesis and Oxidation State Variation

✓ *GO Synthesis Using Modified Hummers' Method:*

- This study presents a novel approach to derive graphene oxide from mandarin peels. Peels undergo drying, cleaning, pyrolysis, and exfoliation to yield graphite. $KMnO_4$ is gradually added to the graphite, $NaNO_3$, and H_2SO_4 mixture. After reaction completion and washing, centrifugation separates the precipitate, yielding graphene oxide powder.
- *Graphene Oxide (GO) Synthesis with Varied Oxidation Degree: GOHOS and GOLOS*

✓ *GOHOS Synthesis:*

- A Pyrex glass reactor is employed, combining sulfuric acid, graphite, and $NaNO_3$ under cryostat conditions. $KMnO_4$ (3.5 M)is incrementally added over 6 hours, followed by heating and stirring. The solution undergoes transfer, and H_2O_2 addition eliminates excess $KMnO_4$. Ultracentrifugation produces GOHOS.

✓ *GOLOS Synthesis*:

- Similar to GOHOS, with adjusted parameters. Graphite, sulfuric acid, and $NaNO_3$ are stirred for dispersion. $KMnO_4$ (1.5 M) is gradually introduced over 6 hours, followed by transfer to deionized water and H_2O_2 addition. After settling, GOLOS is obtained.

✓ *Purification Process:*

- Both GOHOS and GOLOS undergo purification with acid washes and rinses to remove impurities. The resulting precipitate undergoes further washing with deionized water before drying for analysis.

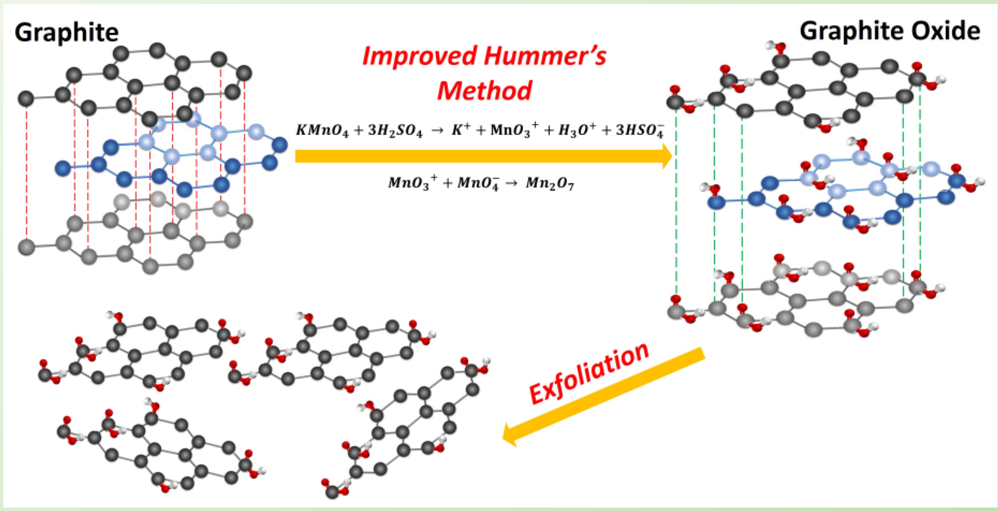


Fig 1. Hummers Method for obtain GO

- To achieve effective activation of cashew shells, the oils are initially extracted by mixing with hexane and drying. It was subsequently impregnated with H_3PO_4, and carbonized under an inert atmosphere at 400°C for 3 hours, followed by exhaustive washing and drying for 48 hours, to be labeled as ACNS.
- With XRD and nitrogen adsorption determine the textural properties. UV-Vis analyzes dye concentrations. Kinetic models evaluate adsorption rates. Thermodynamic modeling investigates the nature of the adsorption process.

3a. RESULTS

- The Freundlich model provided the best fit for MO and MB adsorption, with R^2 consistently > 0.99, corroborated by Figure 2 and Figure 3. This suggests multilayer adsorption, with heterogeneous surfaces.
- Both dyes exhibited similar adsorption isotherms, indicating their weak acid and anionic character. GOHOS showed the highest adsorption capacity, followed by GOLOS, ACCN, and GO.
- The adsorption process involves physical and chemical mechanisms, including Van der Waals forces, electrostatic forces, and hydrogen bonding, facilitated by the porous structure of ACNS.
- GO samples, with their developed BET surface, exhibit favorable interactions for dye adsorption, primarily through physical interactions and potential chemical bonding facilitated by surface functional groups.
- Overall, graphene oxide demonstrates greater selectivity and adsorption capacity compared to activated carbon due to its specific surface properties and two-dimensional structure.

3b. RESULTS

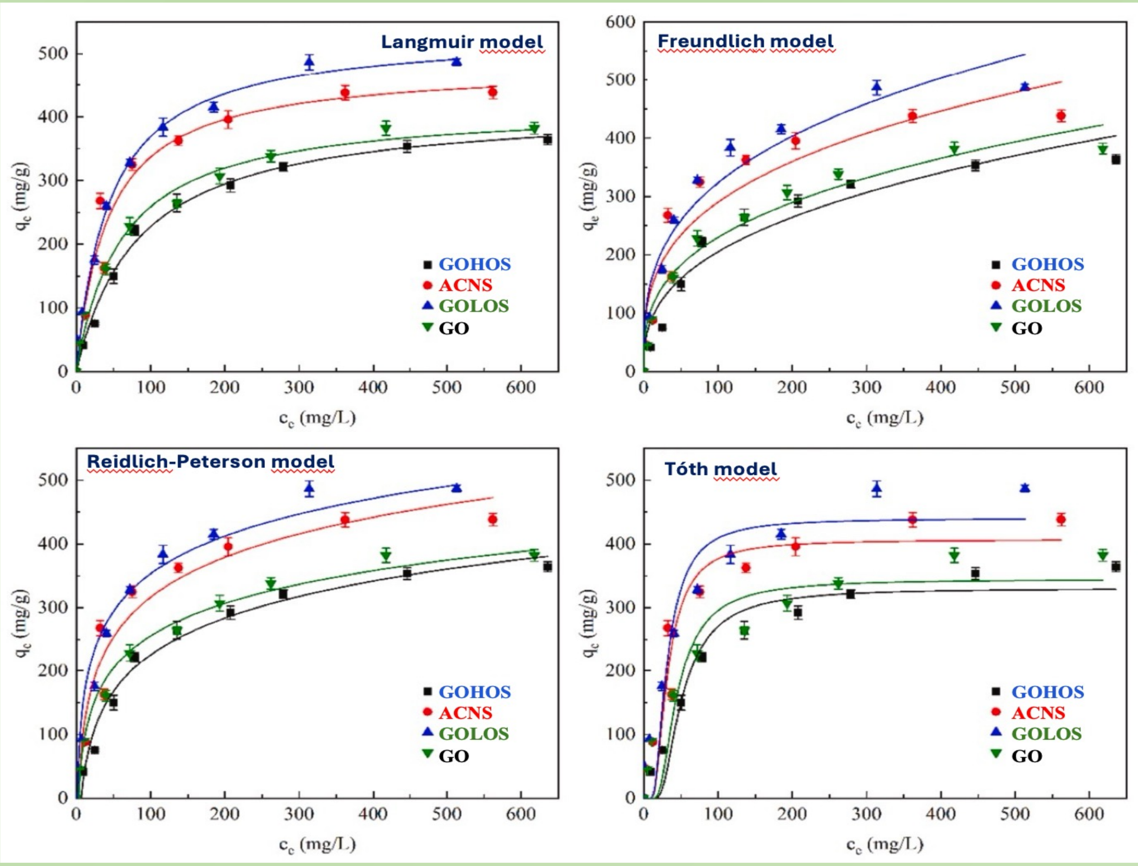


Fig 3. Fitting of the experimental data of the adsorption of the Methylene Blue on each of the adsorbates, with the different models used in this work

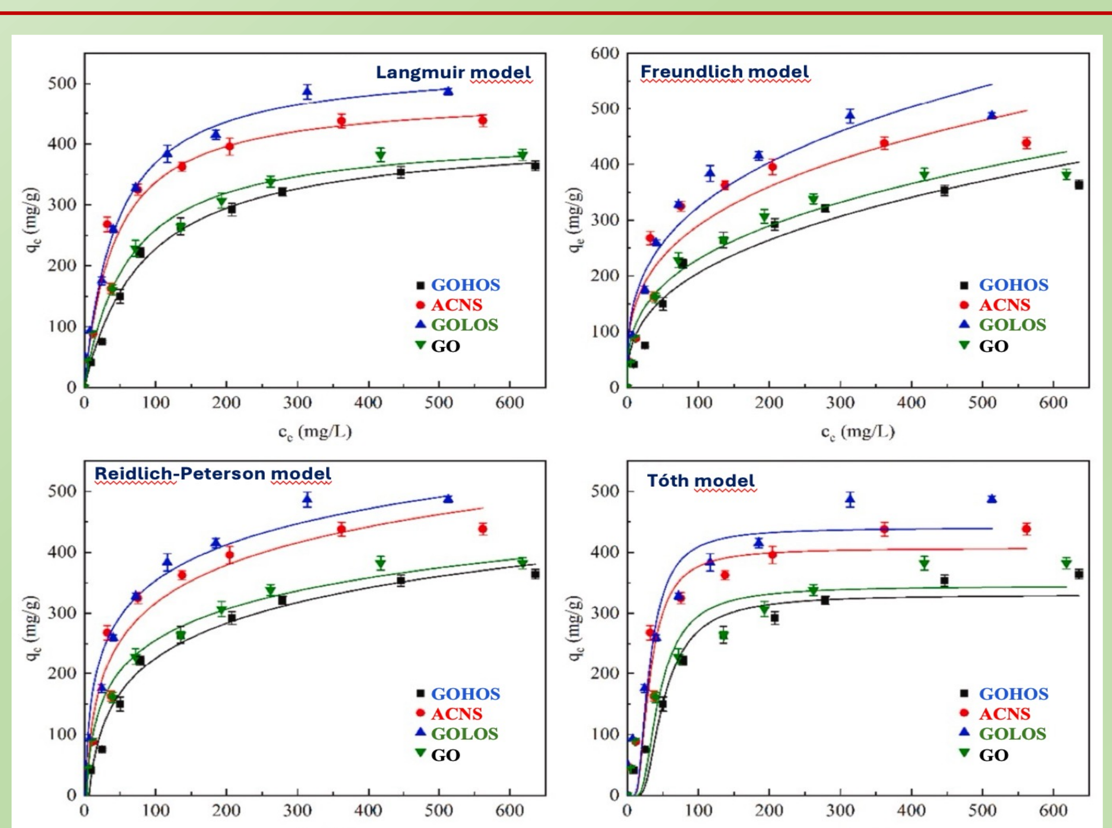


Fig 2. Fitting of the experimental data of the adsorption of the Methyl Orange on each of the adsorbates, with the different models used in this work

4. CONCLUSIONS

- Four municipal waste-derived adsorbents were studied for Methyl Orange and Methylene Blue adsorption.
- Freundlich models fit well, showing higher capacities than reported. GOHOS had the highest MO adsorption (215.3 mg/g), while GO had the lowest (78.3 mg/g), indicating electrostatic and physical-chemical adsorption mechanisms.
- Thermodynamic studies favor spontaneous adsorption. ACNS, derived from Cashew nut shells, showed promising adsorption capacities comparable to GOHOS.

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