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Graphene Industrial Forum &2DM 2020

The ARC Research Hub for Graphene Enabled Industry Transformation

Multithiol Functionalized Graphene Bio-Sponge for Efficient Removal of Heavy Metal Ions in Water

THE UNIVERSITY of ADELAIDE

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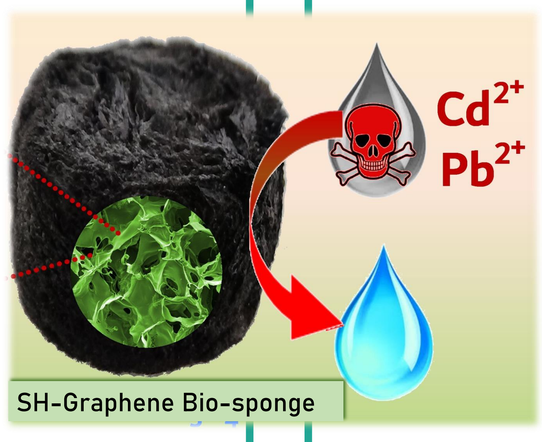
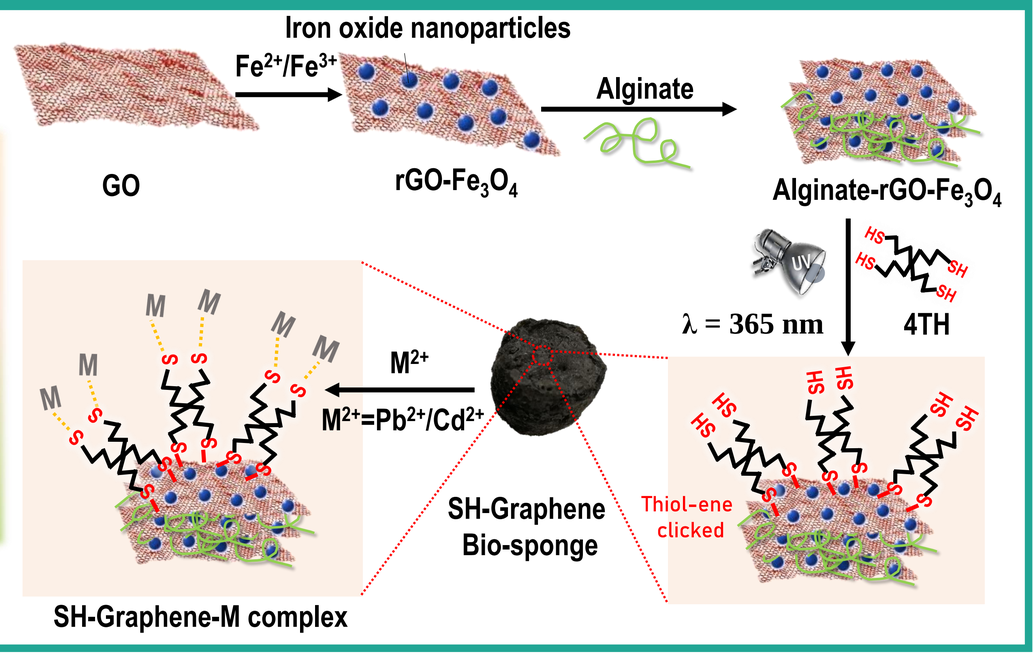
BACKGROUND & MOTIVATIONS

- Efficient and sustainable water purification technologies are still highly sought-after owing to the uncontrollable widespread of heavy metals in water bodies.
- This work presents a green and scalable UV thiol-ene click approach to develop multithiol-functionalized graphene (SH-Graphene)bio-sponge for efficient removal of heavy metal ions (Pb and Cd) in water towards meeting global clean water demand
- The aims of this work are to:
  1. design a robust adsorbent with strong affinity, high regenerability, and high selectivity towards heavy metal ions adsorption
  2. develop an energy- efficient, environmentally-friendly & scalable functionalization method for preparing highly efficient graphene-based adsorbent

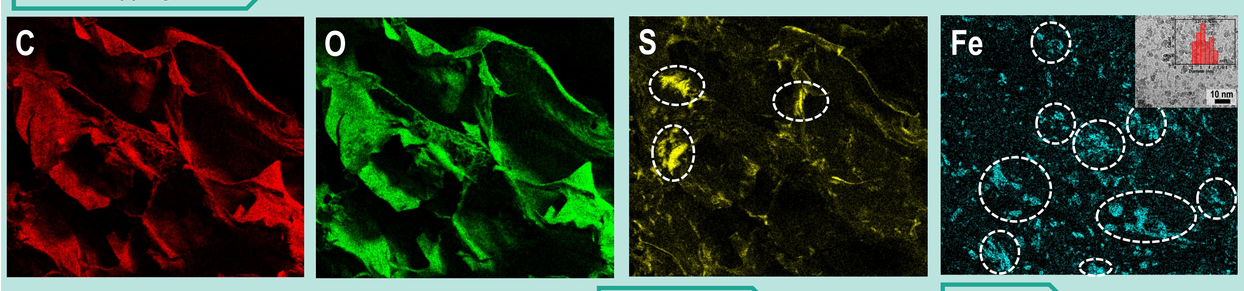


CONCEPT & METHODOLOGY [1]



MATERIALS CHARACTERIZATION

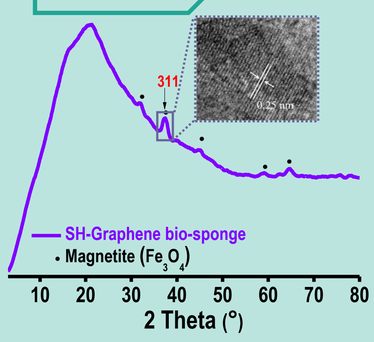
EDX Mapping & TEM



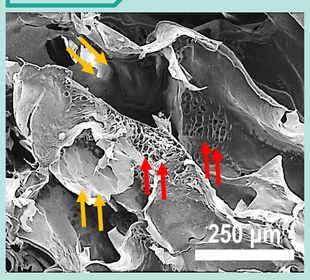
Microstructural Properties

- TEM: 2-5 nm Fe_3O_4 nanoparticles dispersed on rGO sheet
- SEM: Presence of macropores and micropores structure in 4TH-rGO-Fe_3O_4/Alg for enhanced pollutants removal
- EDX Mapping: Highly concentrated regions of S and Fe did not overlap→ no covalent interaction between iron & thiol group
- XRD & HRTEM: (311) plane detected on XRD diffractogram for magnetite (Fe_3O_4) is evidenced with lattice fringe found on HRTEM

XRD & HRTEM



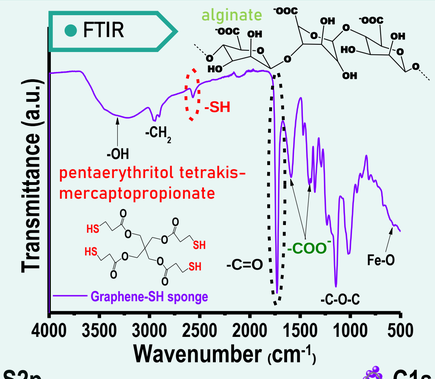
SEM



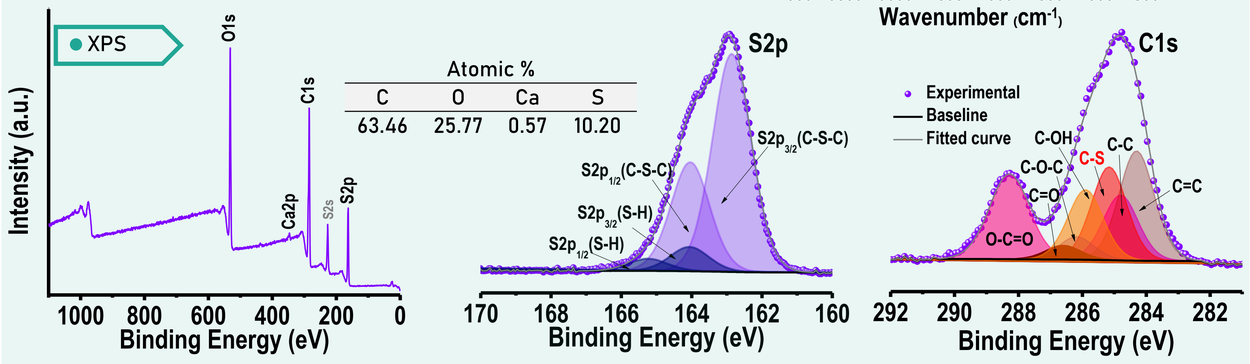
Chemical Properties

- FTIR: Presence of -SH, -COO (4TH precursor); -COO-, -OH (Alg precursor), Fe-O (Fe_3O_4 precursor), -C-O-C, -OH (GO) indicates successful modification of GO
- XPS: Presence of C-S bond and multiple oxygen species on deconvulted C1s spectrum; High S loading (10.20 at%) of combined-SH and C-S-C species detected verified successful functionalization of GO

FTIR

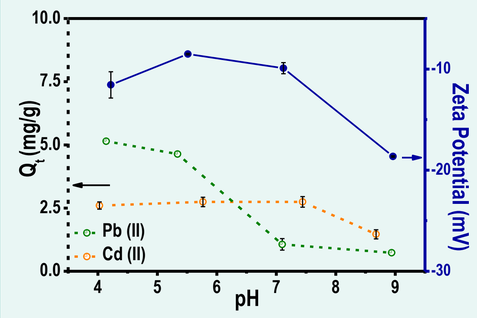


XPS

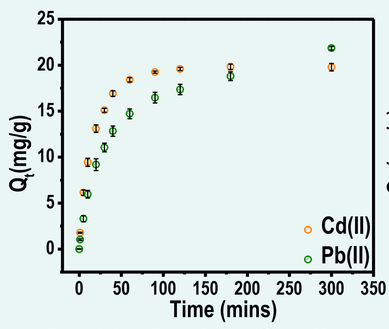


METAL IONS ADSORPTION

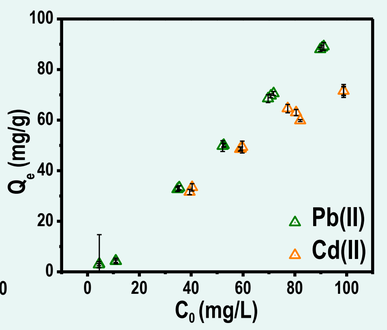
pH & Zeta Potential studies



Kinetic study



Isotherm study



Interaction Mechanism Studies

- pH & Zeta Potential Studies : Negatively charged surface of SH-Graphene bio-sponge over pH 4-9; Good affinity towards adsorption of heavy metal ions, Pb (II) and Cd (II) ions
- Kinetic: Equilibrium uptake of metal ions attained at 1st hour; follows pseudo 2nd order kinetic model (R^2>0.99)→ chemisorption is rate controlling step, primary adsorption mechanism involves e- sharing and exchange
- Isotherm: Maximum adsorption capacity (101.01 mg/g for Pb (II), 102.99 mg/g for Cd (II)), follows Langmuir isotherm model (R^2>0.97)→ monolayer coverage of metal ions on the surface of SH-Graphene Bio-sponge

Regeneration study

Selectivity study

Real sample assessment

Performance Testings

- Regeneration study: Excellent stability and recyclability with only 0.015 mg/L Pb(II) detected after 5 recurring cycles conforming US EPA maximum contaminant level (MCL) of drinking water for lead [2]
- Selectivity study: Outstanding selectivity towards Pb(II) and Cd(II), surpassed activated carbon
- Real sample assessment: Good binding affinity towards Pb(II) and Cd(II) using metal ions-spiked sea water sample, outperformed control and commercial adsorbent

CONCLUSIONS & FUTURE OUTLOOK

- SH-Graphene bio-sponge with high density of S was successfully developed via sustainable and energy efficient photoinduced thiol-ene click approach for effective immobilization of heavy metals in water..
- SH-Graphene bio-sponge **exhibited highly regenerative, selective, efficient Pb(II) & Cd(II) adsorption** and surpassed commercial adsorbent
- UV-directed thiol-ene click approach paves a promising scalable strategy to develop advanced water purification technology to address overwhelming global water demand
- Future research direction will focus on the translation of **this lab scale water purification technology for wastewater treatment in field application**

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[1] Yap, P. L.; Auyoong, Y. L.; Hassan, K.; Farivar, F.; Tran, D. N. H.; Ma, J.; Losic, D. *Chem. Eng. J.* 2020, *395*, 124965.

[2] US EPA *National primary drinking water regulations*, EPA-816-F-09-004 Search PubMed, 2009.

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