Regenerable Graphene Wool for the Removal of Selected Polycyclic Aromatic Hydrocarbons from Contaminated Water

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Abstract: A novel graphene wool (GW) material was used as adsorbent for the removal of phenanthrene (PHEN) and pyrene (PYR) from aqueous solution. Adsorption kinetics, adsorption isotherms, thermodynamics of adsorption and effect of pH, ionic strength, and temperature on the adsorption of PHEN and PYR onto GW were comprehensively investigated. Isothermal and kinetic experimental data were fit to Langmuir, Freundlich, Temkin, Sips and Dubinin-Radushkevish (D-R) models, as well as pseudo-first-order and pseudo-second-order kinetic models. The adsorption kinetic data best fit the pseudo-second-order kinetic model for PHEN and PYR sorption with R^2 value >0.999, whilst the Sips model best fit isotherm data. Kinetic data revealed that 24 h of contact between adsorbent and PAHs was sufficient for maximum adsorption, where the Langmuir maximum adsorption capacity of GW for PHEN and PYR was 5 and 20 mg g^{-1} and the optimum removal efficiency was 99.9% and 99.1%, respectively. Thermodynamic experiments revealed that adsorption processes were endothermic and spontaneous. Desorption experiments indicated that irreversible sorption occurred with a hysteresis index greater than zero for both PAHs. The high adsorption capacity and potential reusability of GW makes it a very attractive material for removal of hydrophobic organic micro-pollutants from water.

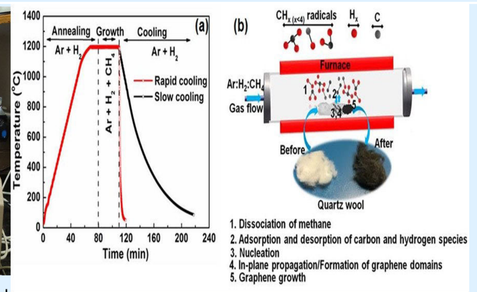
INTRODUCTION

- The adsorption process has been identified as a suitable, simple and effective remediation approach for the removal of several pollutants from water without chemical transformation. Carbonaceous or carbon-based materials have been reported to be effective for the removal of PAHs, however, most of the adsorbents present several challenges including difficulties regarding regeneration and reusability of spent adsorbent.
- The overall goal of this work was to apply a novel, regenerable graphene wool material for the removal of phenanthrene and pyrene from water (Adeola and Forbes, 2019). The role of environmental or process variables such as pH, temperature, ionic strength/TDS of the solution and initial concentration of PAHs on the sorptive removal of the compounds was studied to establish the optimum conditions for effective use of graphene wool for water treatment.

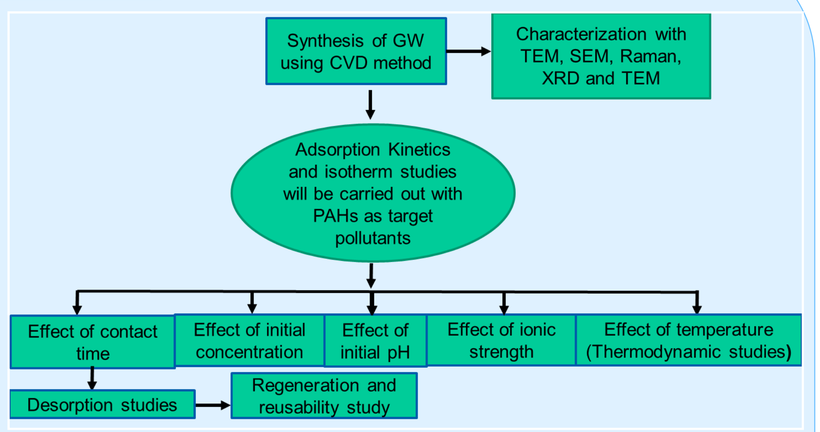
EXPERIMENTAL

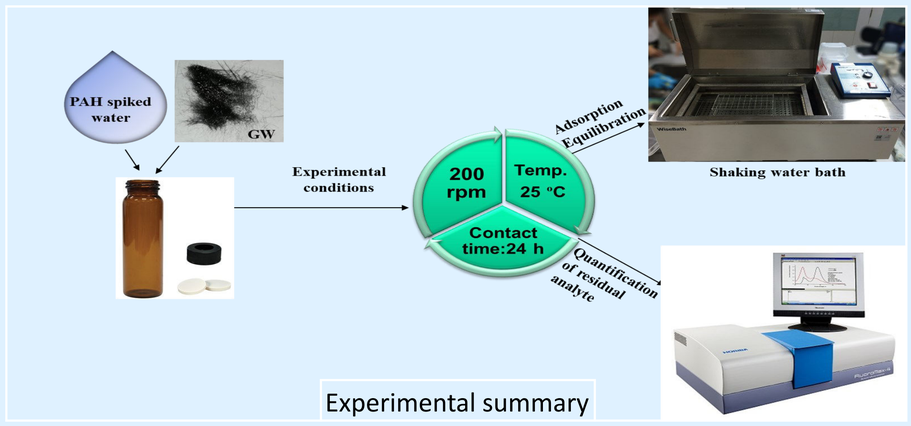
Chemical vapor deposition instrument used in our laboratory with optimized flow rates of argon, hydrogen and methane gas (500: 500: 100 sccm) respectively.

(Schoonraad et al., 2020)



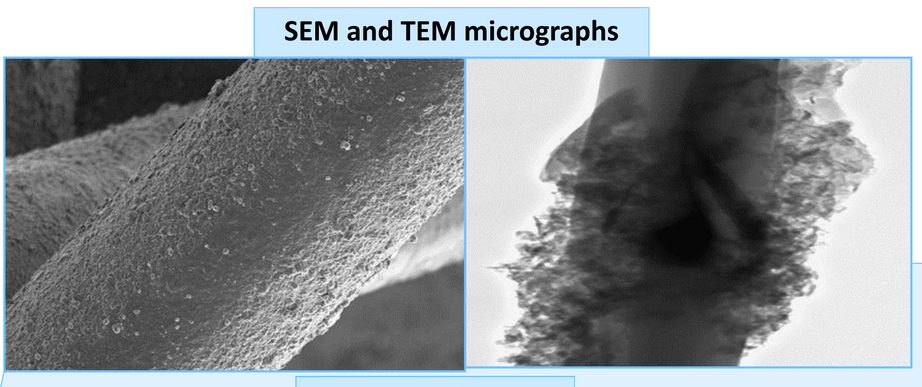
(a) Temperature profile of the CVD process as measured by a series of thermocouples and (b) schematic of the non-catalytic direct growth mechanism of CVD graphene on quartz wool substrate.



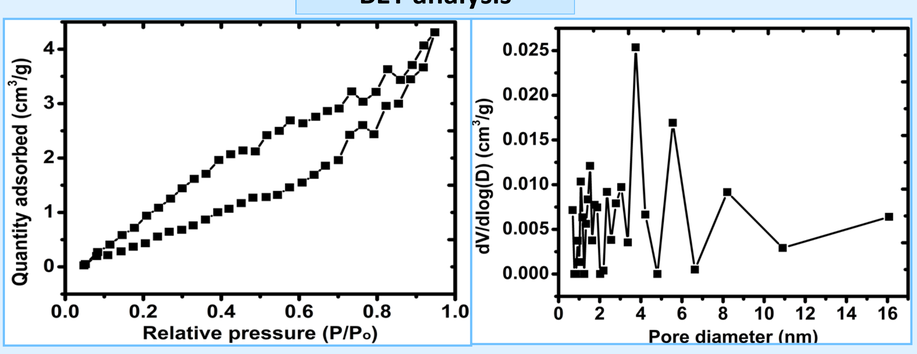


Experimental summary

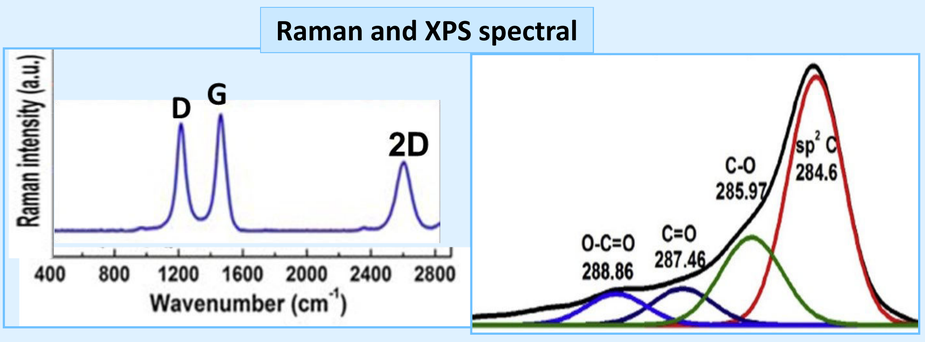
SEM and TEM micrographs



BET analysis

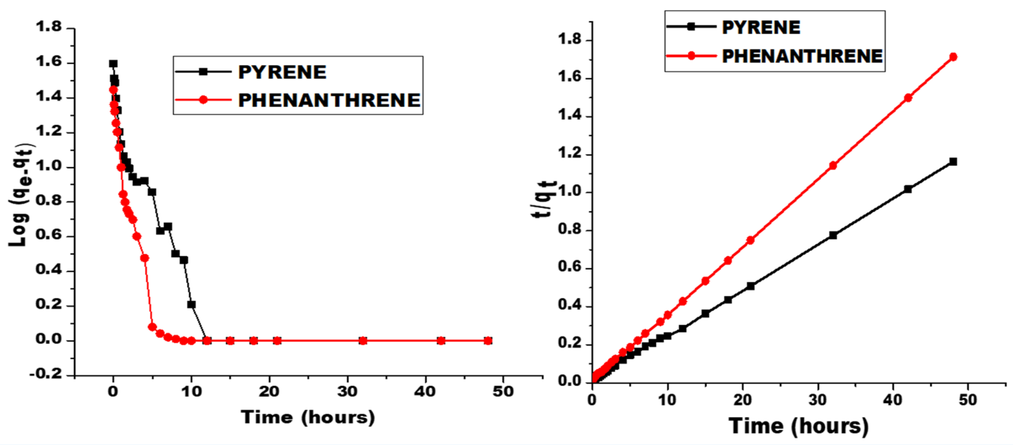


Raman and XPS spectral



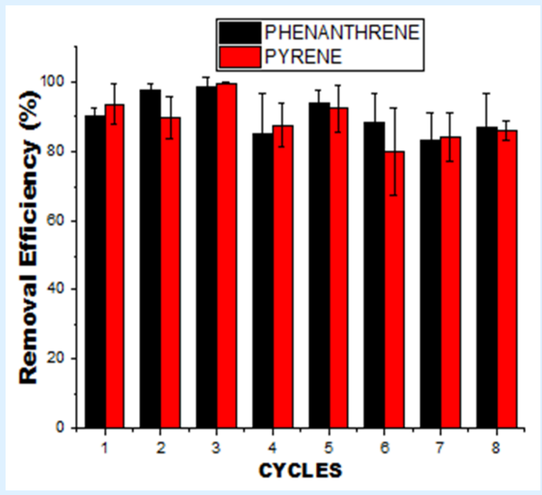
RESULTS

PAH Kinetic results



Core findings: *Better R^2 value (linearity) suggest that the pseudo-second-order kinetic model best describes the adsorption of the PAHs. This also implies chemisorption*

Regeneration and reuse



Core findings: *High reusability after several cycles of regeneration.*

PAH Isotherm results

Table 2: Coefficients of sorption isotherm for phenanthrene and pyrene removal by graphene wool (GW)

Isotherm model	Parameter	PAHs	
		Phenanthrene	Pyrene
Dubinin-Radushkevish	R^2	0.9812	0.9920
Freundlich	R^2	0.9906	0.9685
Langmuir	Maximum adsorption capacity q_{max} (mg g^{-1})	5.0	20.0 → *Pyrene was better adsorbed*
	R^2	0.9793	0.9635
Sips (Freundlich-Langmuir)	N	0.46	0.54
	R^2	0.9956	0.9984 → *Sips best fit adsorption data, which implies that localized adsorption controlled the adsorption process.*
Temkin	R^2	0.9414	0.9872

Table 3: Thermodynamic parameters for adsorption of phenanthrene (PHEN) and pyrene (PYR) onto graphene wool (GW)

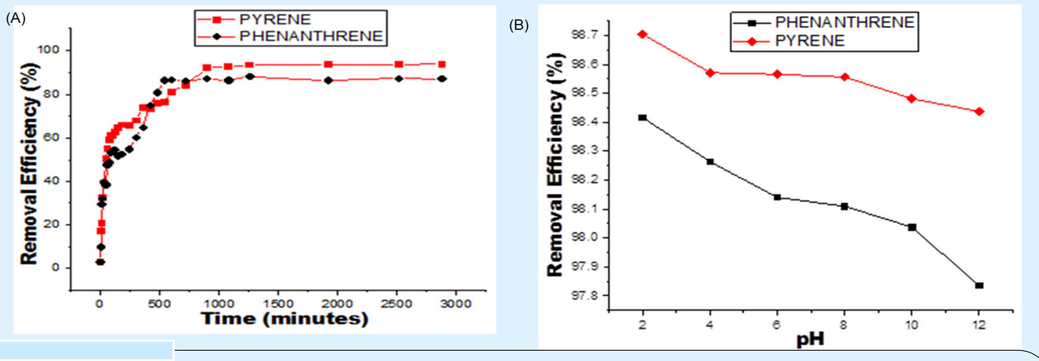
Temperature (K)	PHEN			PYR		
	ΔG° (cal/mol)	ΔH° (cal/mol)	ΔS° (cal/mol.K)	ΔG° (cal/mol)	ΔH° (cal/mol)	ΔS° (cal/mol.K)
25°C	-2752.78			-6810.76		
35°C	-3226.58	11,865.7	47.46	-7941.66	28,020.9	113.09
45°C	-3701.18			-9072.56		

ΔG° is more negative, Implies better feasibility

Core findings:

- *ΔH° is positive, which implies spontaneous endothermic reaction.*
- *GW was reusable over several cycles.*

Effect of contact time and solution pH



Core findings:

- *Adsorption equilibrium is reached after 600 min for PHEN and 900 min for PYR due to site saturation (10 —15 hr is sufficient for optimum adsorption).*
- *Acidic pH conditions favours adsorption of PAHs due to surface protonation which slight enhanced adsorption*

CONCLUSION

The study revealed that PAHs can be removed from polluted water successfully using GW and that this material may be employed in water treatment plants (WTPs) as a polishing tool (Adeola and Forbes, 2019).

REFERENCES

- Adedapo. Adeola, Patricia B. C. Forbes (2019). Optimisation of the sorption of selected polycyclic aromatic hydrocarbons by regenerable graphene wool. Water Science & Technology 80 (10), 1931-1943.
- Schoonraad G.-L., Madito M. J., Manyala N. and Forbes P. (2020). Synthesis and optimisation of a novel graphene wool material by atmospheric pressure chemical vapour deposition. Journal of Materials Science 55, 545-64.

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RAND WATER