Phenazine Porous polymers for Radioactive Iodine Capture

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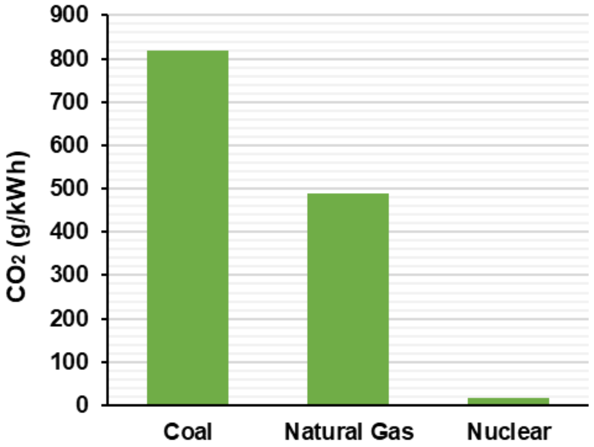
Nuclear Energy as a source of energy

1 kg of 4%-enriched fuel grade uranium = equivalent to the combustion of nearly 100 tons of high-grade coal or 60 tons of oil.

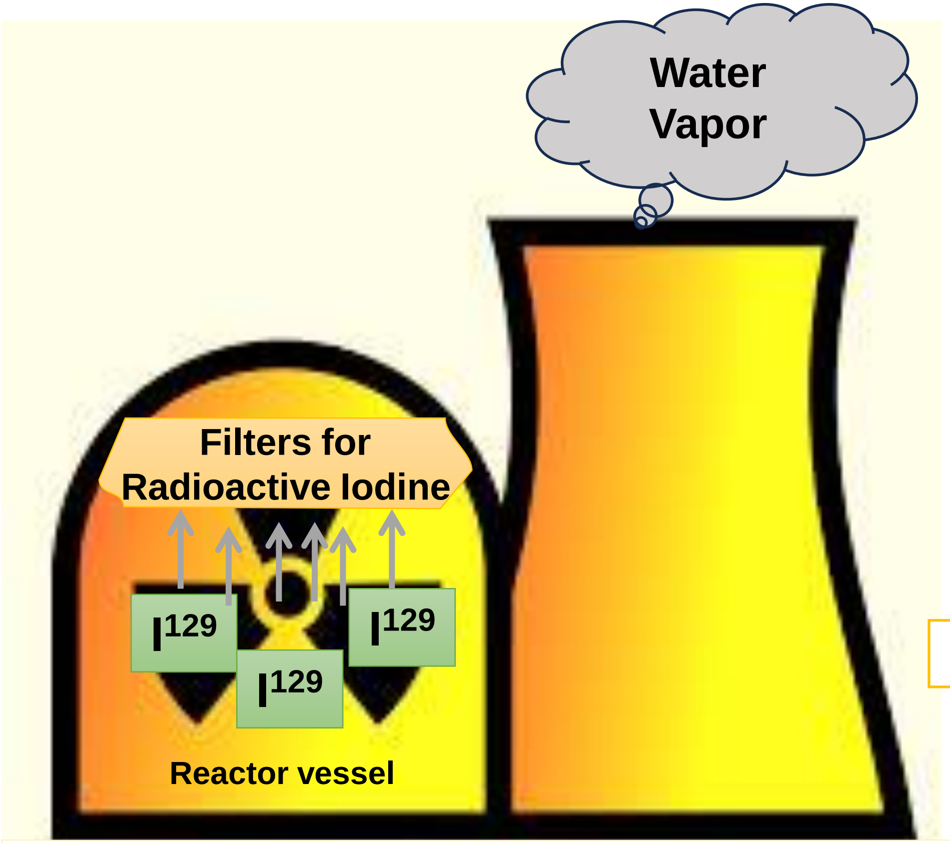
Small land footprint



Disadvantages:
Release of radioactive Nucleotides:
^{3}H, ^{85}Kr, ^{127}Xe, and ^{129}I,

- Kurisingal, J. F., H. Yun and C. S. Hong (2023). Journal of Hazardous Materials 458: 131835.
- Pan, T., K. Yang, X. Dong and Y. Han (2023). Journal of Materials Chemistry A 11(11): 5460-5475.

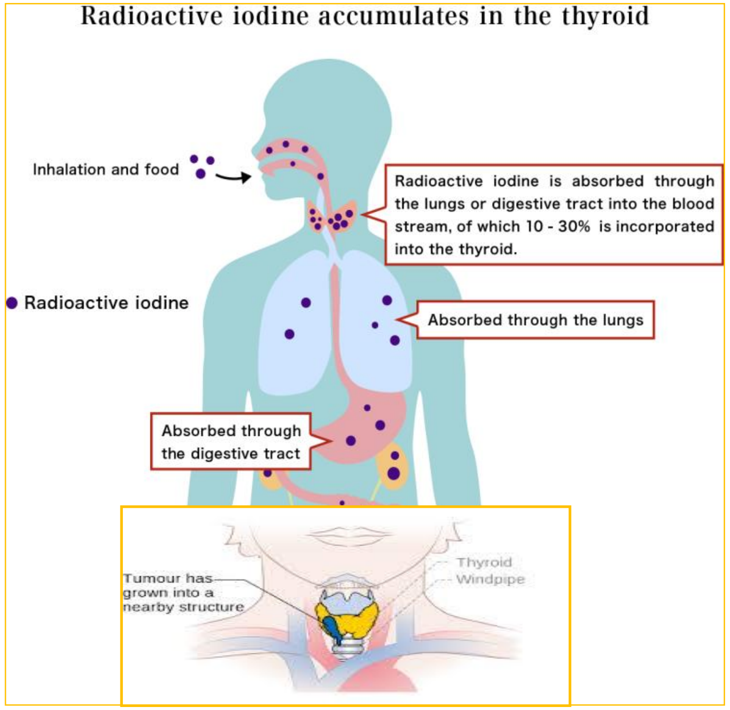
Radioactive iodine release in nuclear plants and their Effect



- I^{129}, Volatile; $t_{1/2}$: 1.57 *10^{-7} Years.
- I^{131}, Volatile; $t_{1/2}$: 8 days.

Release to the Environment

Causes Thyroid Cancer and effects metabolic processes

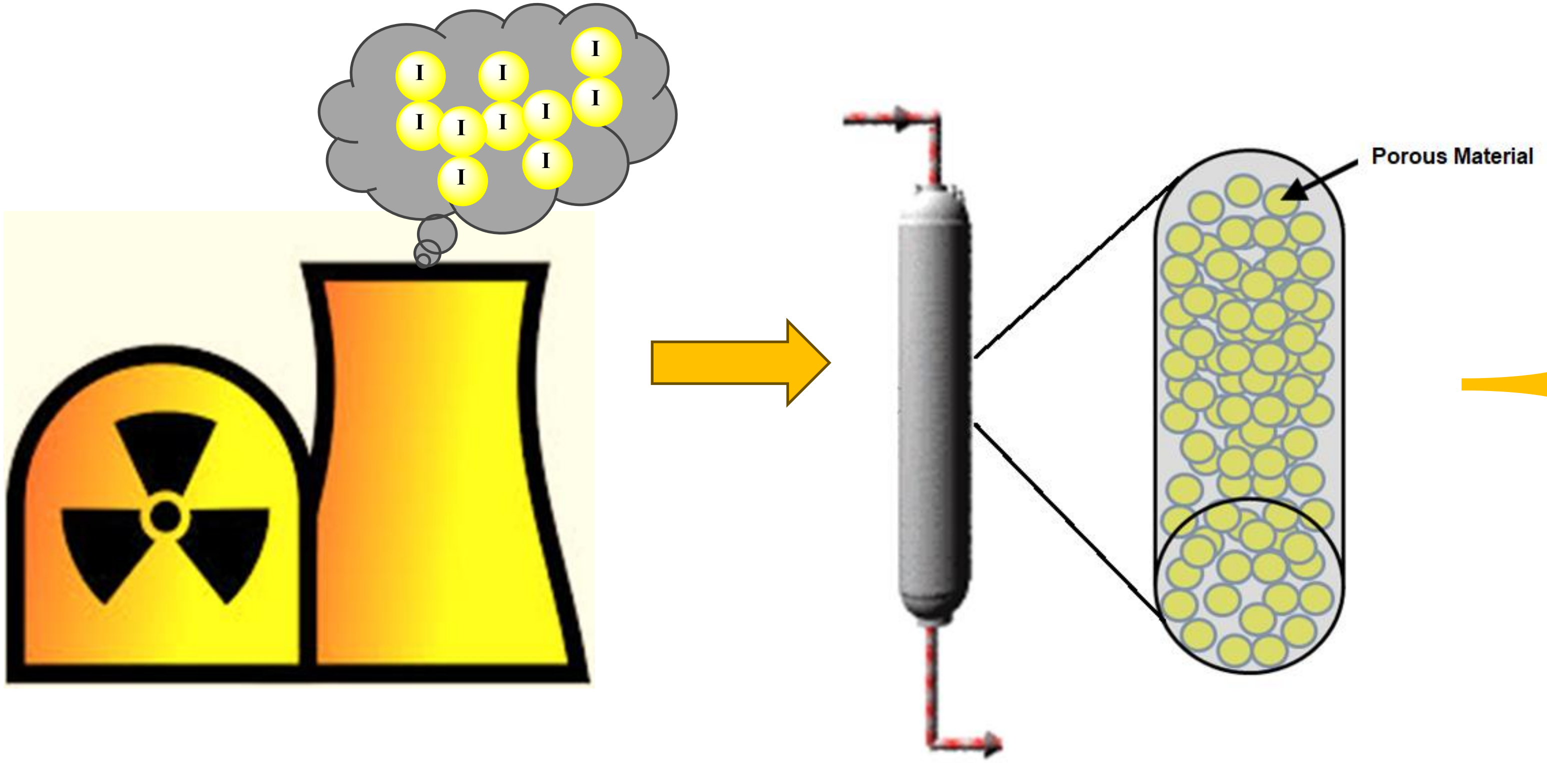


Radioactive Iodine Released by:

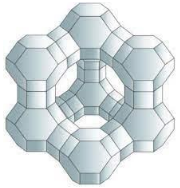
1. Aqueous reprocessing of used nuclear fuels.
2. Severe nuclear accidents (Chernobyl 1986, Fukushima 2011).
3. Emission of Gaseous radionucleotides released in the off-gas stream.

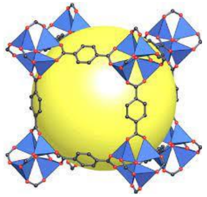
- Huve, J., et al; (2018). RSC Advances 8(51): 29248-29273.
- Kurisingal, J. F., et al; (2023). Journal of Hazardous Materials 458: 131835.

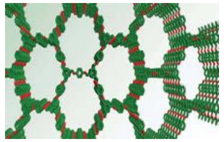
Porous materials for radioactive iodine capture

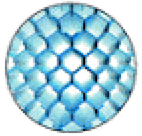



Activated Carbon


Zeolites


MOFs

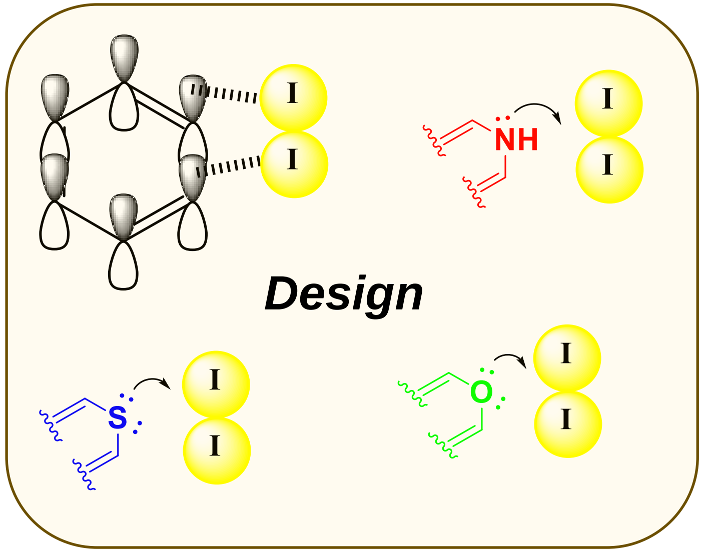

COFs

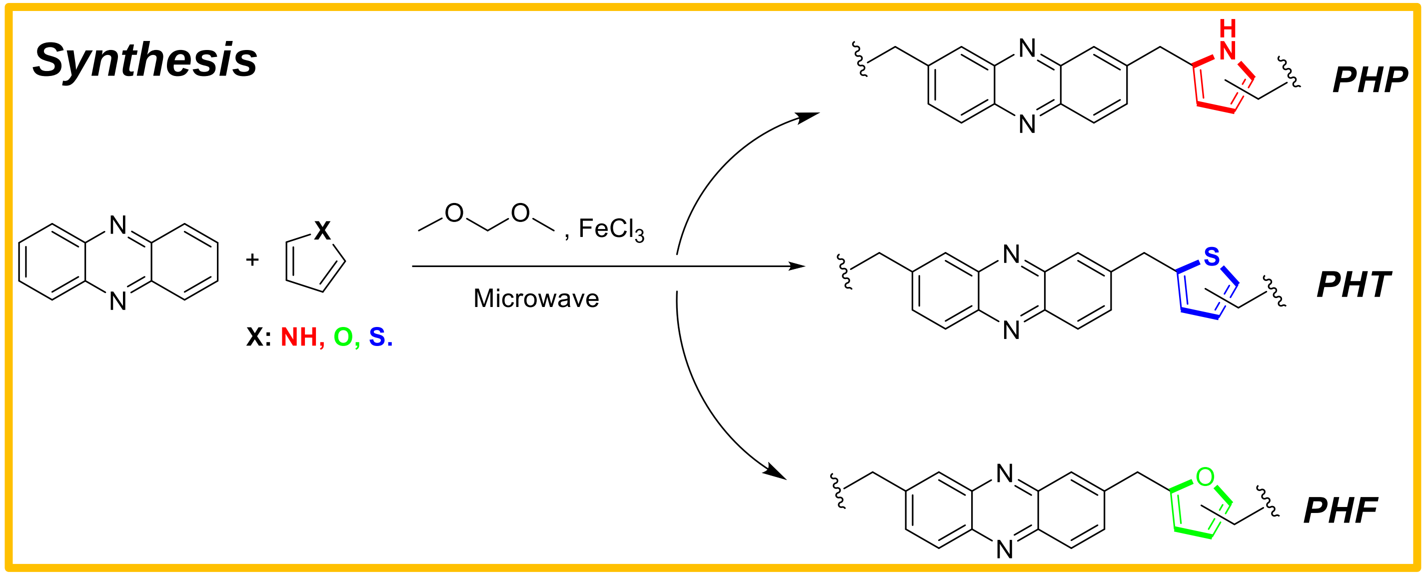

POPs

- Pan, X., et al; (2020). Microporous and Mesoporous Materials **300: 110161.**
- Xie, W., et al; (2019). Materials Horizons **6(8): 1571-1595.**
- Huve, J., et al; (2018). RSC Advances **8(51): 29248-29273.**

Phenazine-based porous polymers

Design and Synthesis:





EXPERIMENTAL

<u>One pot reaction:</u>

Phenazine (1.8g, 0.01 mol) in 50 ml of DMF in a microwave vessel (Easyprep). Pyrrole (2.01g, 0.03 mol) and dimethoxymethane (4.6g, 0.01 mol) were then added to the mixture and stirred until a homogenous solution was obtained. Anhydrous $FeCl_3$ (9.7g, 0.06 mol) were dissolved in the mixture.

Microwave vessel
Flushed with N_2 and heated at
90°C for 30 minutes

Washing:
Methanol-Ammonia-water-methanol.

Dried under vacuum at 70°C until constant weight is acheived

- Li, X., Y. Peng and Q. Jia (2020). <u>Separation and Purification Technology **236: 116260.**</u>
- O. C. S. Al Hamouz, et al (2022). <u>Journal of Industrial and Engineering Chemistry</u> 113: 215-225.

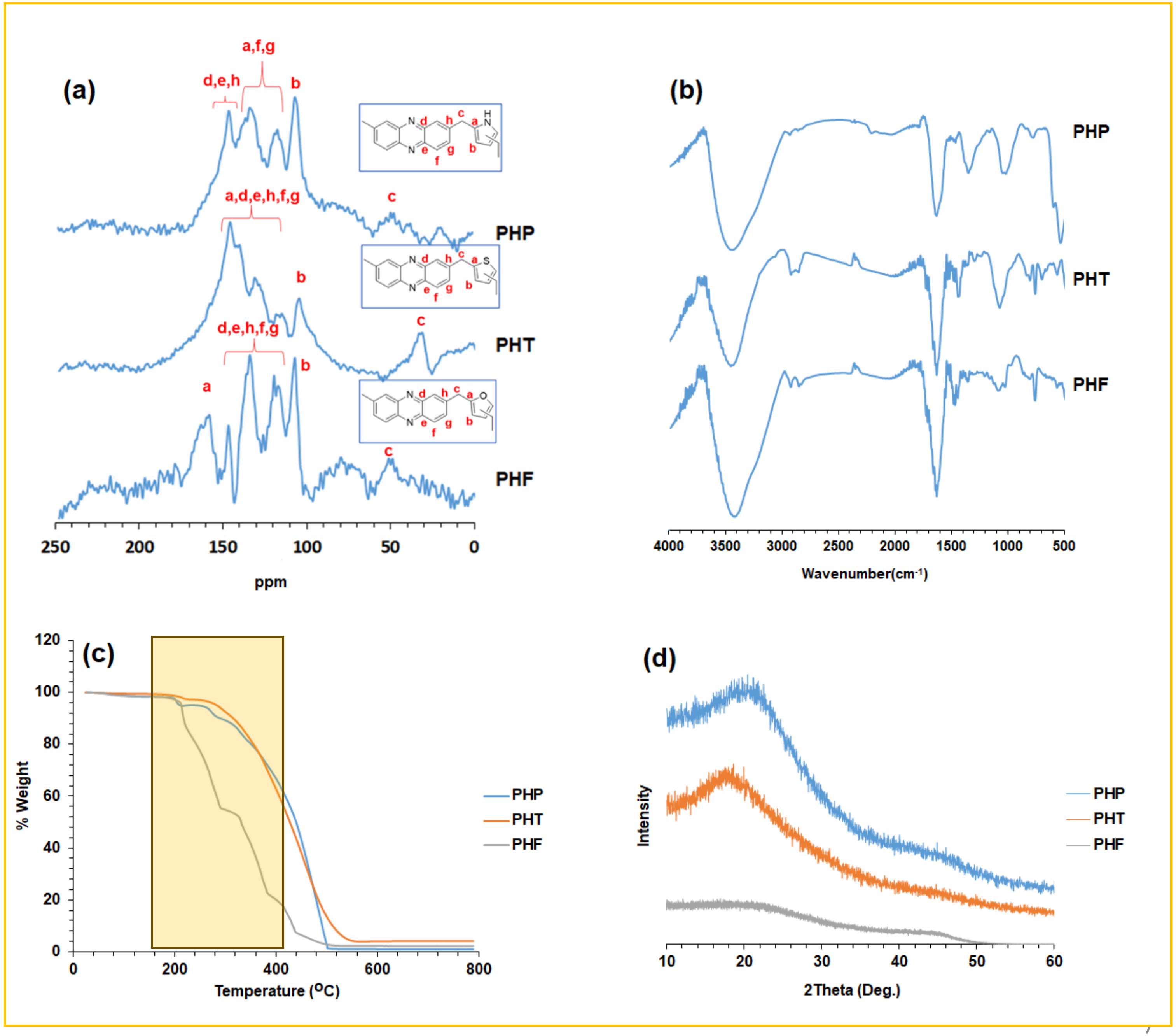
Characterization

(a) Solid ^{13}C-NMR-CPMAS spectra of the synthesized polymers **PHP**, **PHT** and **PHF**.

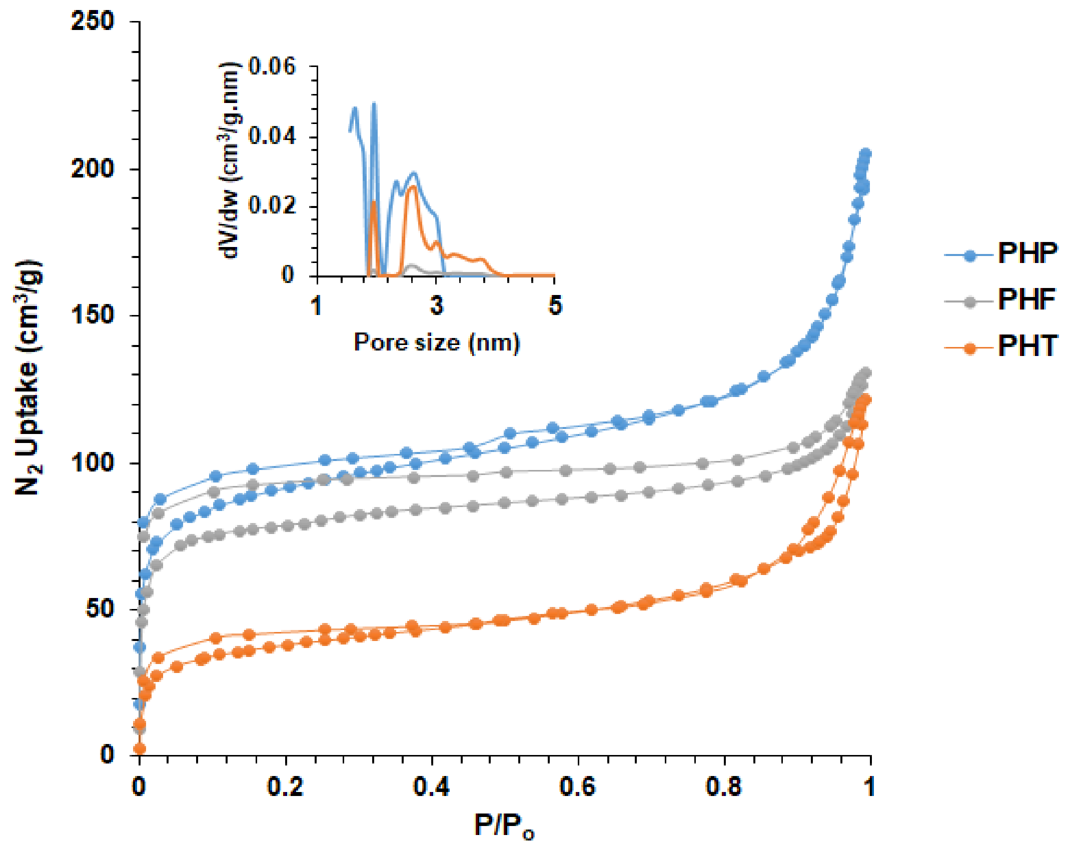
(b) FT-IR spectra of the synthesized polymers **PHP**, **PHT** and **PHF**.

(c) TGA thermograms of the synthesized polymers **PHP**, **PHT** and **PHF**.

(d) PXRD patterns of the synthesized polymers **PHP**, **PHT** and **PHF**.



Surface Area and Porosity:



N_2 adsorption/desorption isotherm, and NLDFT pore size distribution curve of the synthesized polymers **PHP**, **PHT** and **PHF.**

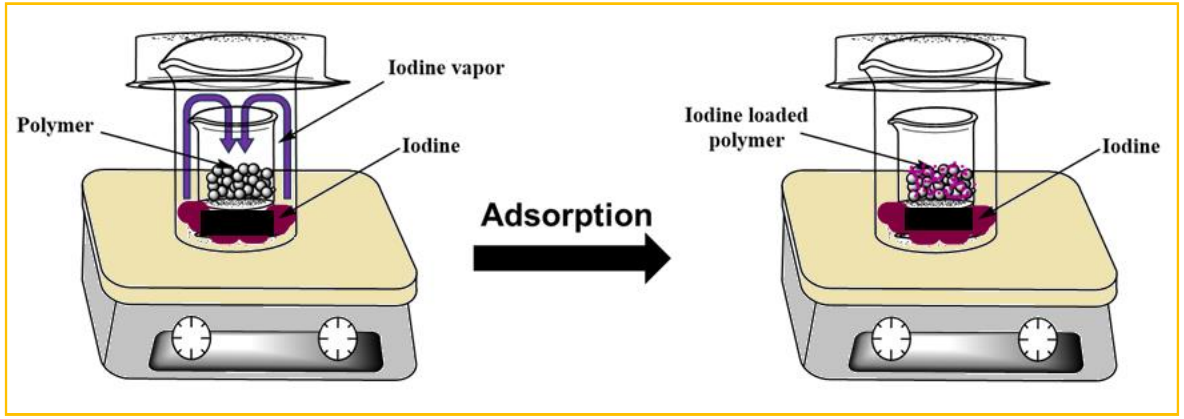
Surface area:

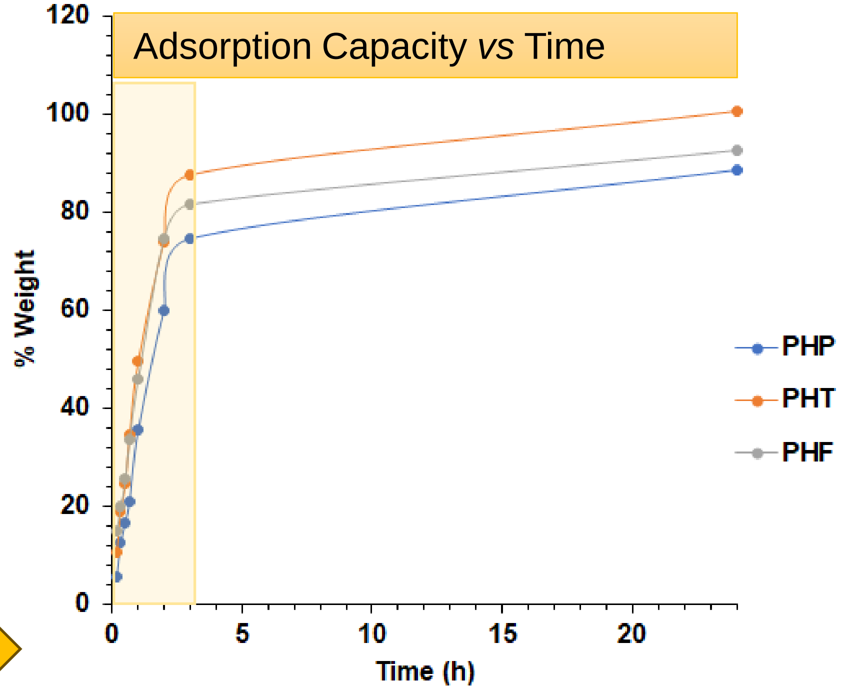
- PHP: 380 m^2/g.
- PHF: 280 m^2/g.
- PHT: 170 m^2/g.

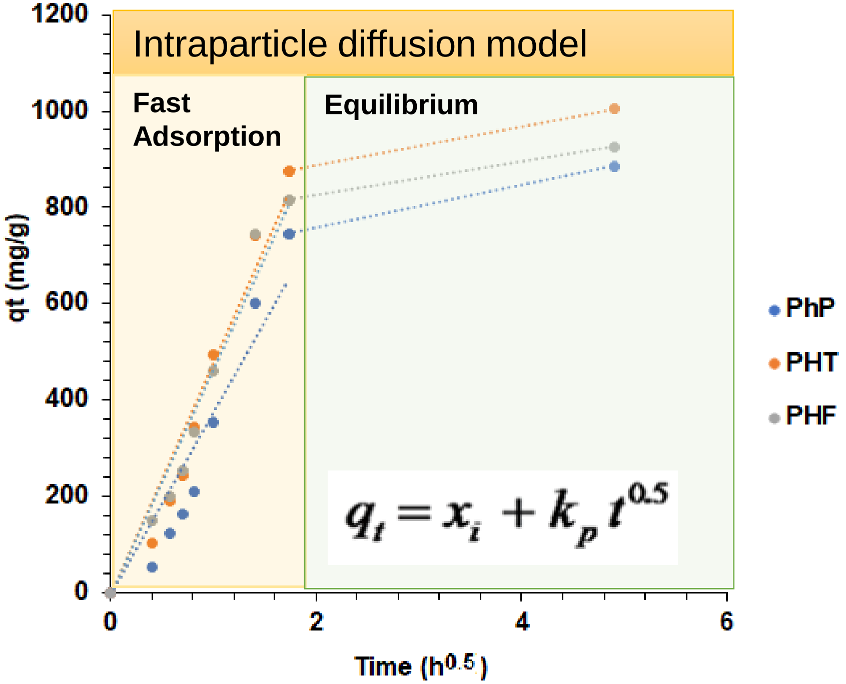
Adsorption of Iodine Vapor

Adsorption of Volatile Iodine

Experimental: 75ºC, 1 atm.







$$q_t = x_i + k_p t^{0.5}$$

<u>% Removal:</u>

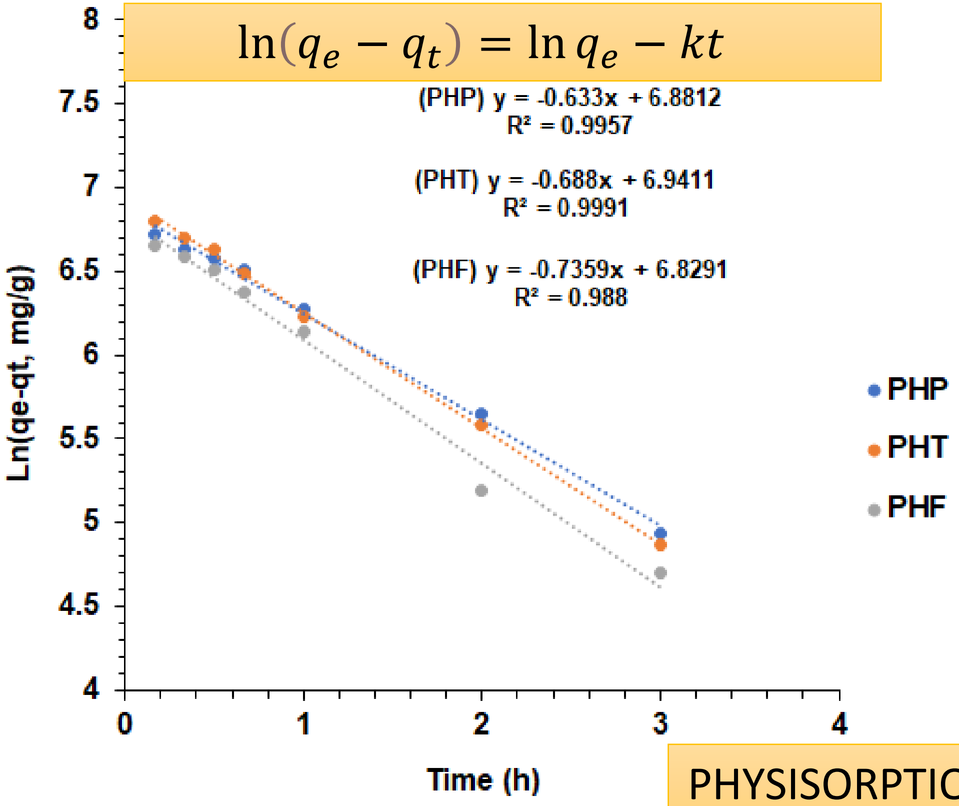
$$\% \, wt. = \frac{(m_f - m_i)}{m_i} \times 100\%$$

m_f: mass of polymer loaded with iodine.
m_i: mass of polymer.

Adsorption of Kinetics:

Pseudo first-order kinetic model

$$\ln(q_e - q_t) = \ln q_e - kt$$

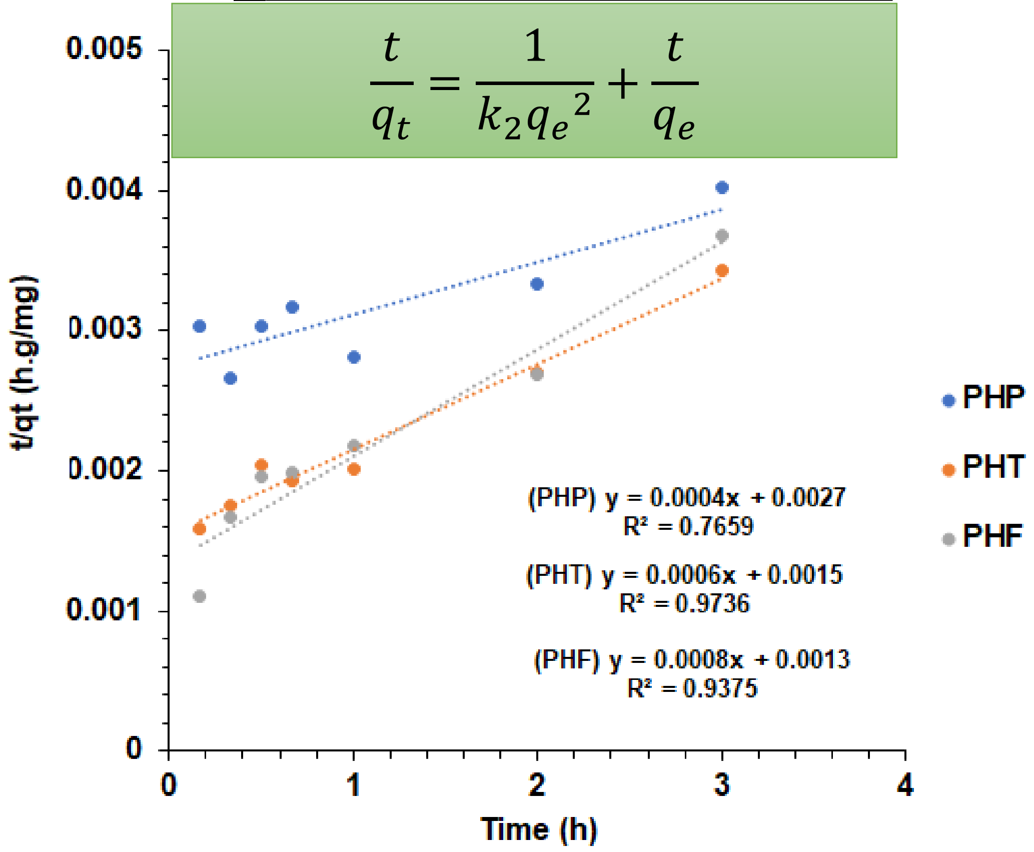


PHYSISORPTION

Pseudo first-order kinetic model parameters of the adsorption of volatile iodine by the porous polymers PHP, PHF and PHT.					
Model	Polymer	Constants			
		$q_{e(exp)}$	$q_{e(calc.)}$	k	R^2
Pseudo first-order	PHP	885.0	974.0	0.6330	0.9957
	PHT	1005	1034	0.6880	0.9991
	PHF	925.0	924.0	0.7360	0.9880

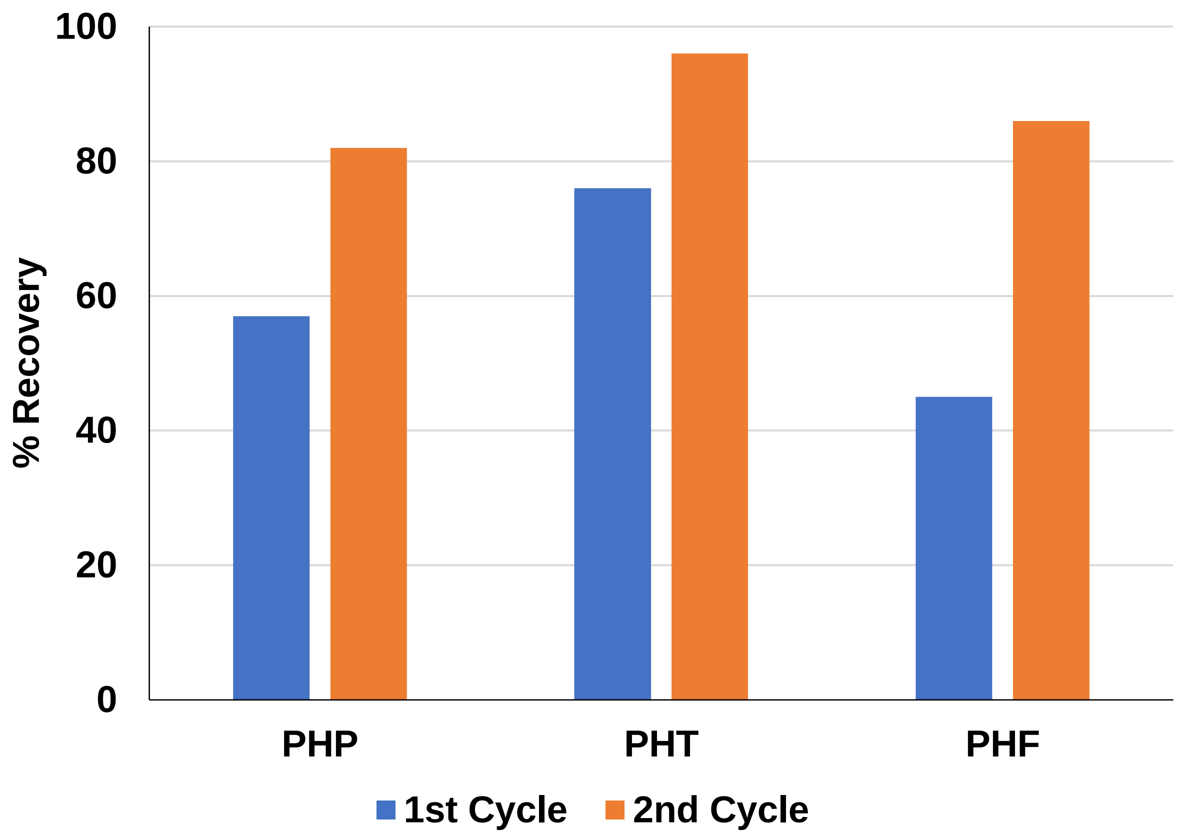
Pseudo second-order kinetic

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e}$$



pseudo second-order kinetic model parameters of the adsorption of volatile iodine by the porous polymers PHP, PHF and PHT.					
Model	Polymer	Constants			
		$q_{e(exp)}$	$q_{e(calc.)}$	k	R^2
Pseudo second-order	PHP	885.0	2500	5.930×10^{-5}	0.7659
	PHT	1005	1667	2.390×10^{-4}	0.9736
	PHF	925.0	1250	4.920×10^{-4}	0.9375

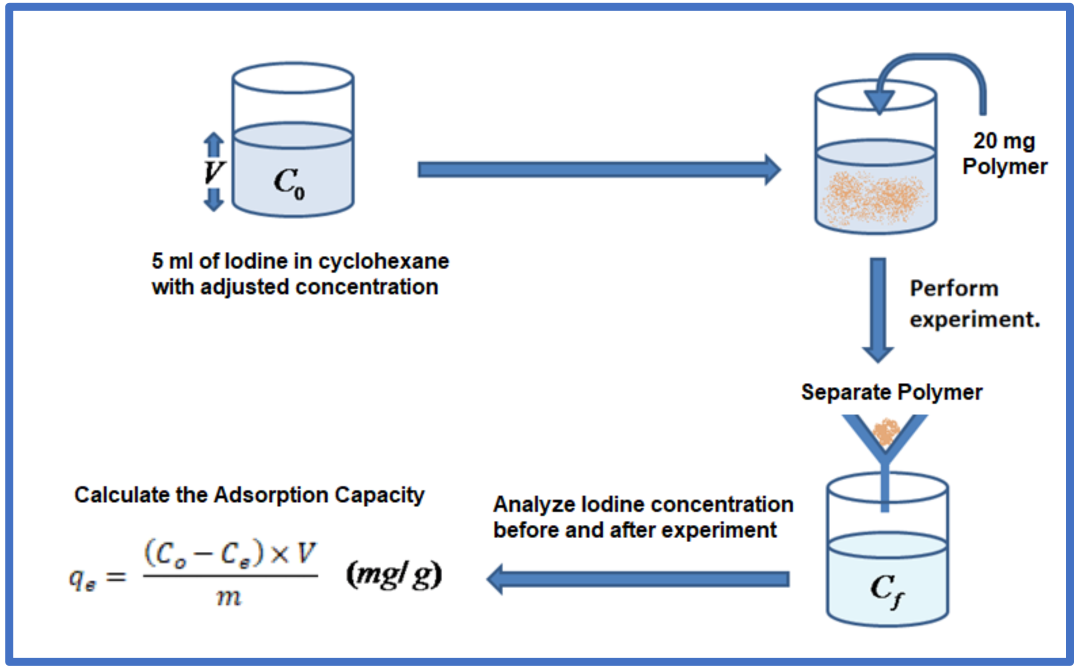
Regeneration of Phenazine based polymers

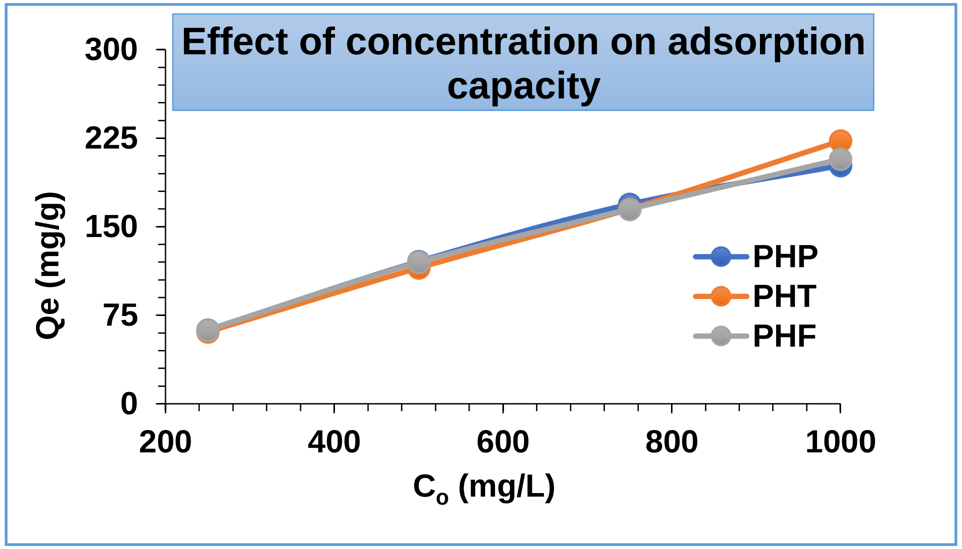


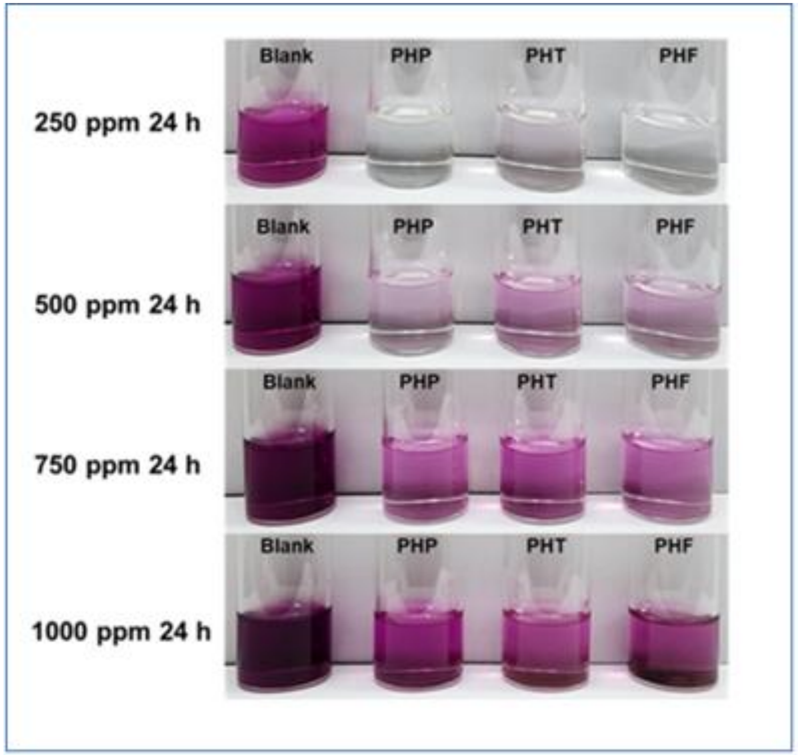
Regeneration was performed by Heating the porous polymer at 100°C under vacuum for 4 hours.

Adsorption of Iodine dissolved in cyclohexane

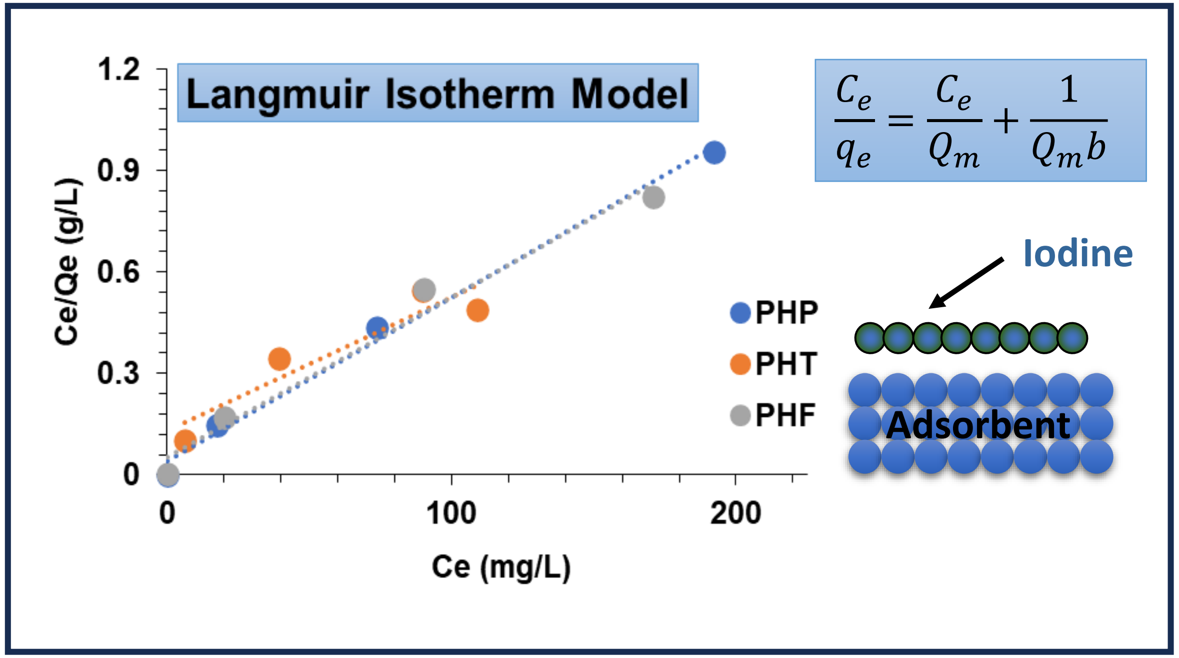
Adsorption of iodine from cyclohexane solution:

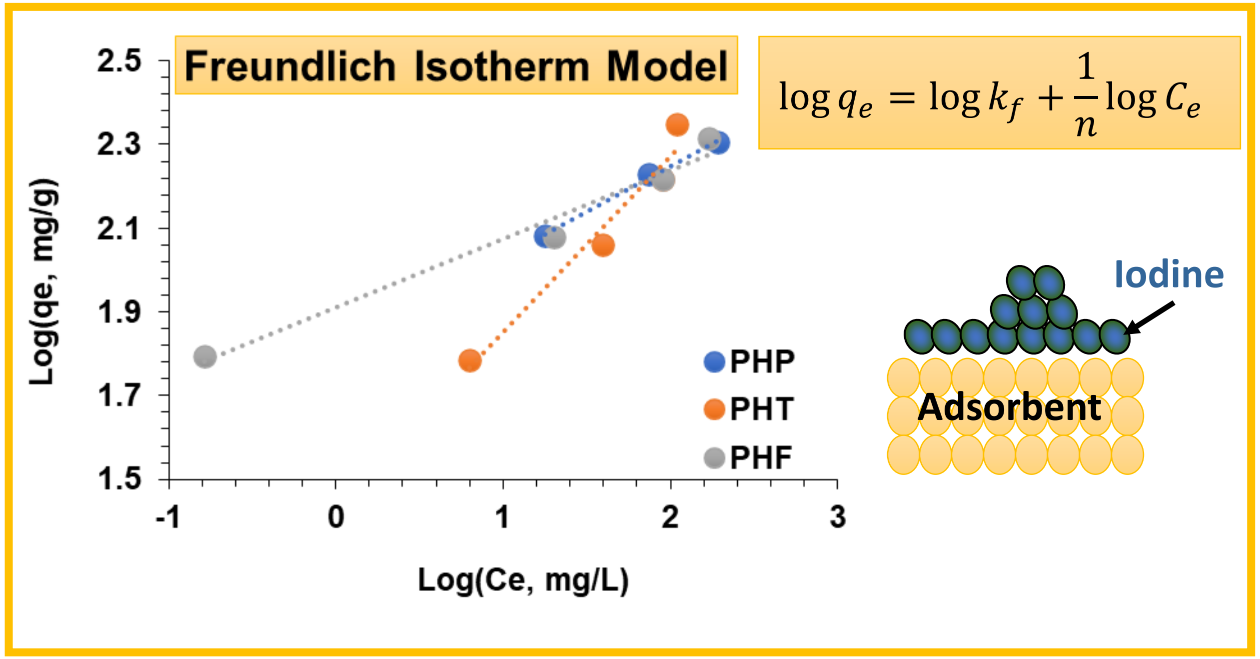






Adsorption Isotherm Models:





Langmuir isotherm model parameters for the adsorption of iodine in cyclohexane by PHP, PHT and PHF porous polymers.

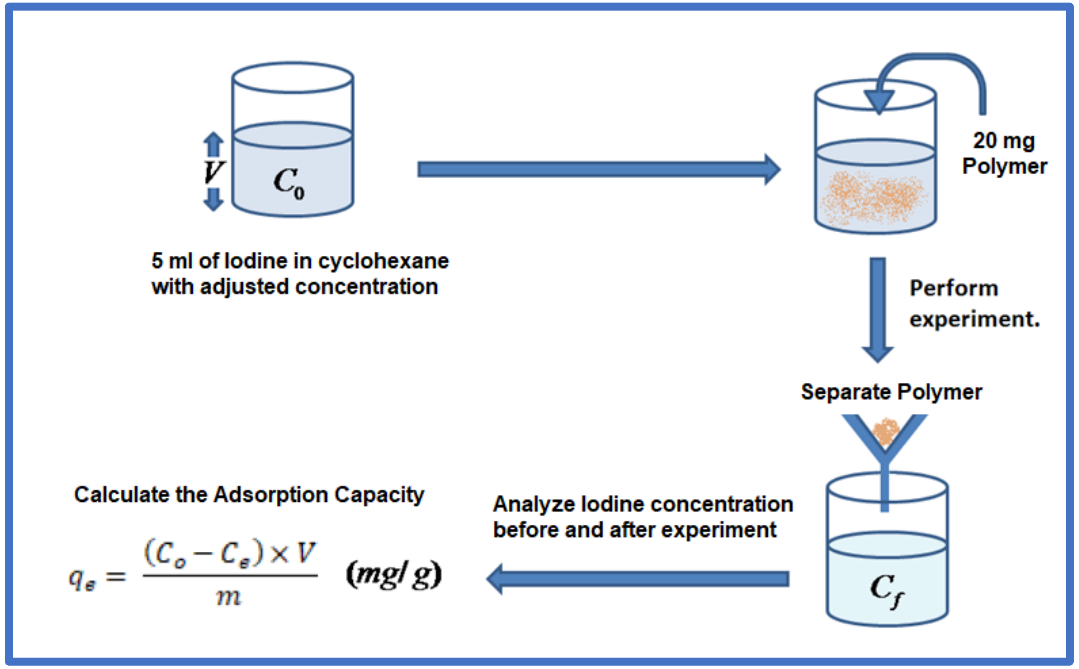
Model	Polymer	Constants			
		$q_{e(exp)}$	$q_{m(calc.)}$	b	R^2
Langmuir	PHP	202.0	208.3	0.0120	**0.9926**
	PHT	222.0	256.4	0.0300	**0.8755**
	PHF	207.0	208.3	0.0940	**0.9778**

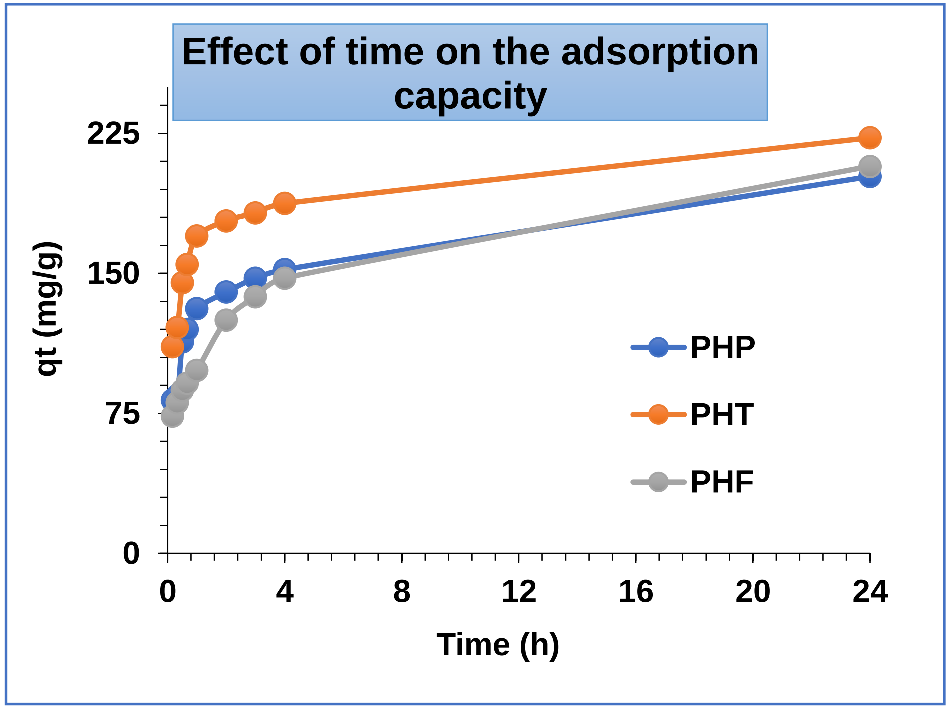
Freundlich isotherm model parameters for the adsorption of iodine in cyclohexane by PHP, PHT and PHF porous polymers.

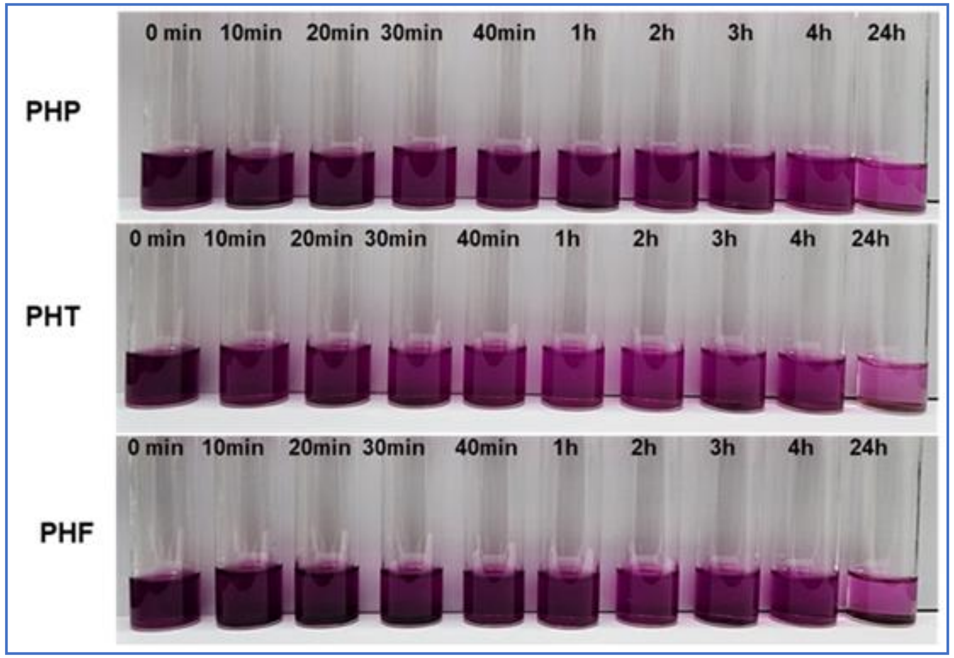
Model	Polymer	Constants			
		n	k_f		R^2
Freundlich	PHP	**4.595**	65.16		**0.9957**
	PHT	**2.379**	27.01		**0.9613**
	PHF	**4.024**	56.14		**0.9815**

Heterogeneous Adsorption

Adsorption Kinetics:



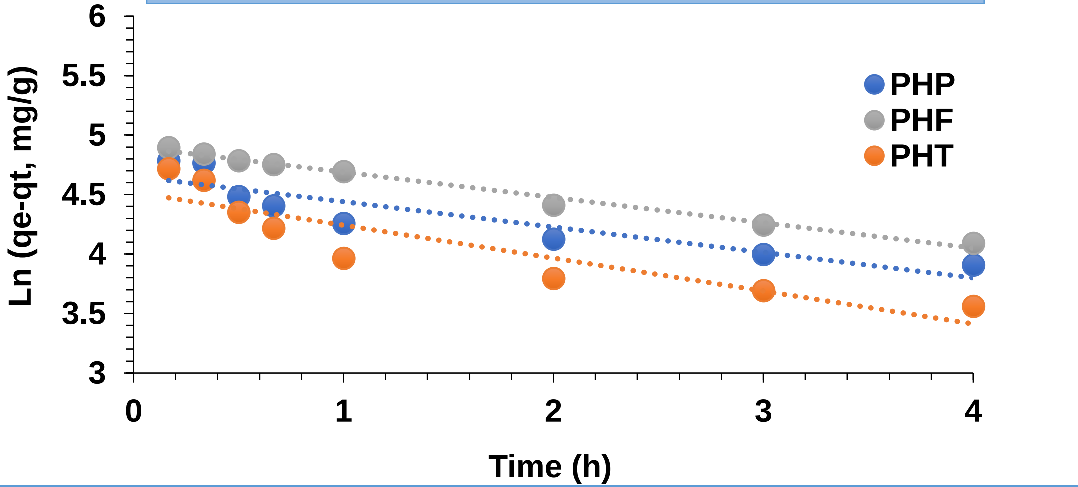




Kinetic Models:

Pseudo first-order kinetic model

$$\ln(q_e - q_t) = \ln q_e - kt$$

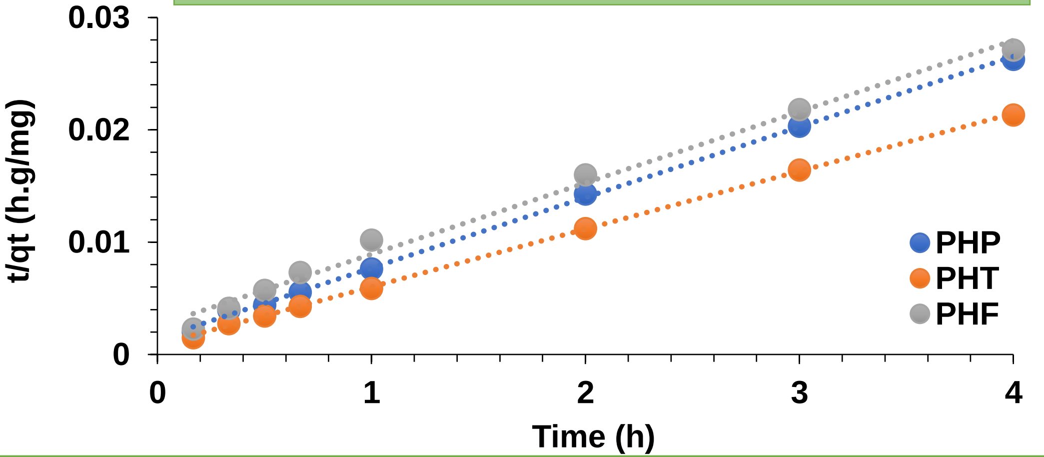


Pseudo first-order kinetic model parameters of the adsorption of iodine in cyclohexane by the porous polymers PHP, PHF and PHT.

Model	Polymer	Constants			
		$q_{e(exp)}$	$q_{e(calc.)}$	k	R^2
Pseudo first-order	PHP	201.9	104.9	0.2135	**0.8263**
	PHT	222.7	91.73	0.2765	**0.8143**
	PHF	207.3	134.3	0.2126	**0.9883**

Pseudo second-order kinetic model

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e}$$



Pseudo second-order kinetic model parameters of the adsorption of iodine in cyclohexane by the porous polymers PHP, PHF and PHT.

Model	Polymer	Constants			
		$q_{e(exp)}$	$q_{e(calc.)}$	k	R^2
Pseudo second-order	PHP	201.9	158.7	0.0284	**0.990**
	PHT	222.7	192.3	0.0338	**0.9996**
	PHF	207.3	158.7	0.0153	**0.9905**

CHEMISORPTION

Conclusions

1. Three novel porous polymers *PHP, PHT* and *PHF* were synthesized by microwave assisted Friedel crafts alkylation.

2. The structure of the synthesized polymers was confirmed by solid state 13C-NMR CP MAS, FT-IR and their thermal stability was investigated by TGA.

3. The polymers were amorphous in nature and permanently porous with surface areas 137-330 m^2/g.

4. The porous polymers showed their capability to adsorb iodine in gas phase and solution phase which shows their efficacy in the removal of iodine.

5. The efficacy of the polymers was investigated by pseudo first-order and second-order kinetic models and showed that the adsorption in the gas phase to be controlled by physisorption whereas, in the solution phase to be controlled by chemisorption.

6. These conclusions show that incorporating porosity and functionality enables the porous polymers to work efficiently under different environments. Also, it provides sufficient potential for the use of these porous polymers as an adsorbent for the removal of radioactive iodine release from nuclear reactors.