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Environmental Engineering
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Effect of Co-existing Parameters on the Adsorption of Perfluorooctanoic Acid (PFOA) on Powder Activated charcoal

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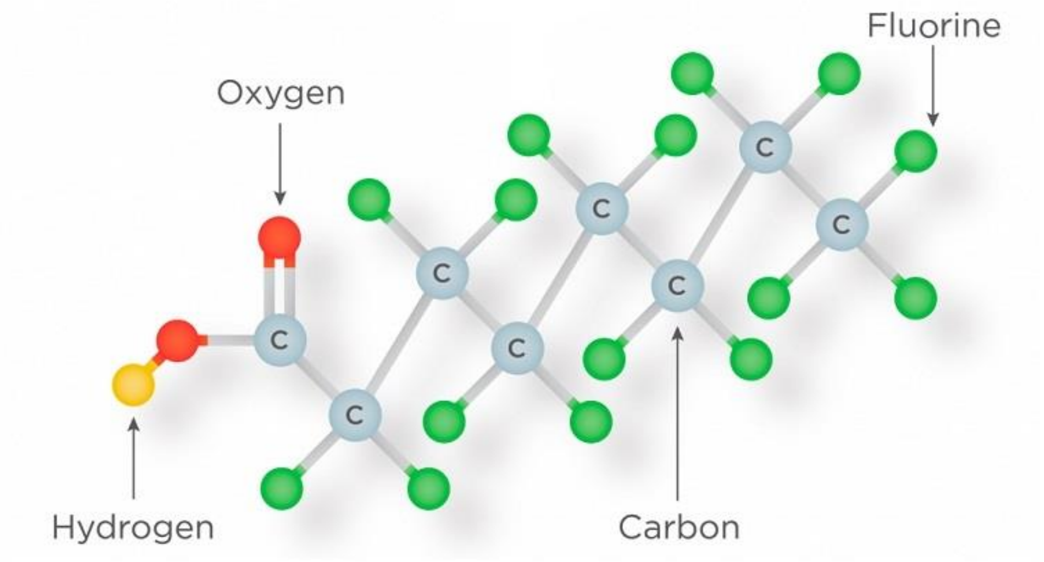
Thesis work by Mr. Aung Htit Htun

ภัยคุกคามจากสาร **PFAS** และการตรวจวิเคราะห์ล่าสุด

ศูนย์ความเป็นเลิศด้านวิศวกรรมสิ่งแวดล้อม ศาสตราจารย์ อรุณ สรเทศน์

29 November 2024

Background



PFOA

- ✓ PFOA half-live is1.2 to 14.9 years (Dourson and Gadagbui 2021)
- ✓ No significant odor and taste
- ✓ People can absorb significant dangerous dose
- ✓ Because of the highly stable c–f bond, it is difficult for PFOA to undergo microbial degradation, hydrolysis and other transformation reactions

Introduction

Where can PFOA be found in our daily life?

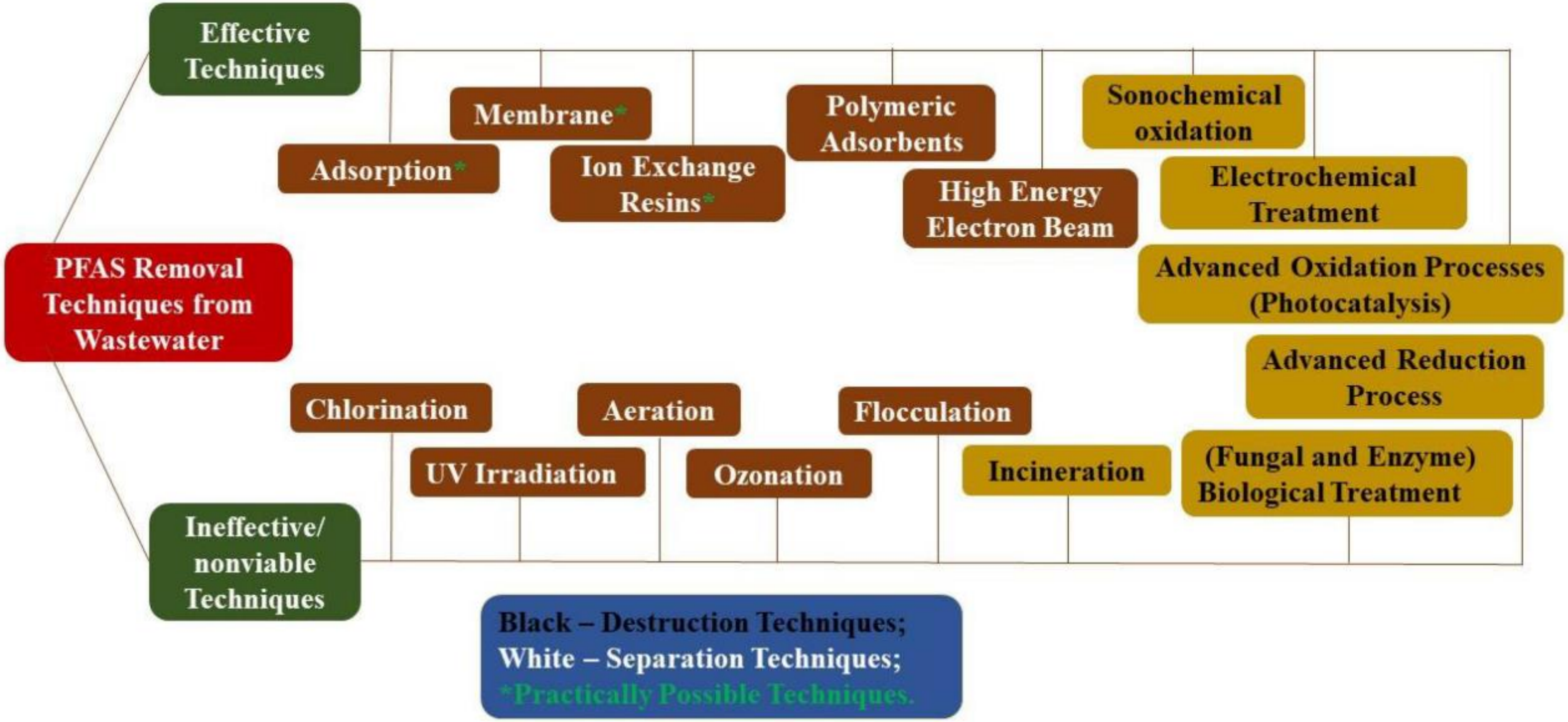
Effects of PFOA on human health

Standard values for PFOA in drinking water for different authorities

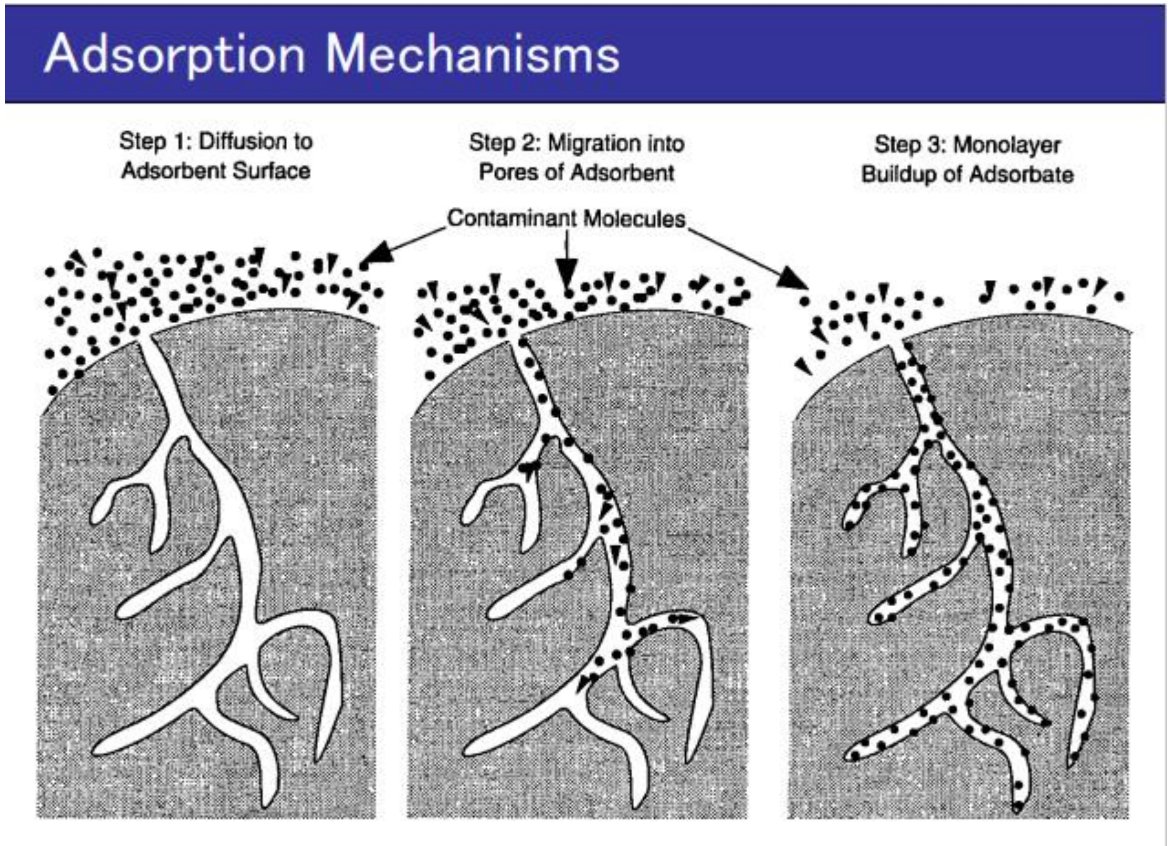
State	Guideline Level	Critical Effect Study
U.S. EPA, 2016, Health Advisory Level	70 ppt	(Lau et al.)
Australia	560 ppt	(USEPA 2022)
Canada	200 ppt	(Environment Canada Health Canada, 2010)
ATSDR	100 ppt	(ATSDR 2020)
New Jersey DEP, 2017, Maximum contaminant level (recommended)	14 ppt	(Loveless et al.)
North Carolina DENR, 2012, Interim maximum allowable concentration (proposed)	1000 ppt	(Macon et al.)
Texas CEQ 2017, Protective concentration level	290 ppt	(Macon et al.)
EFSA	70 ppt	(EFSA 2020)
WHO	100 ppt	(WHO, 2022)

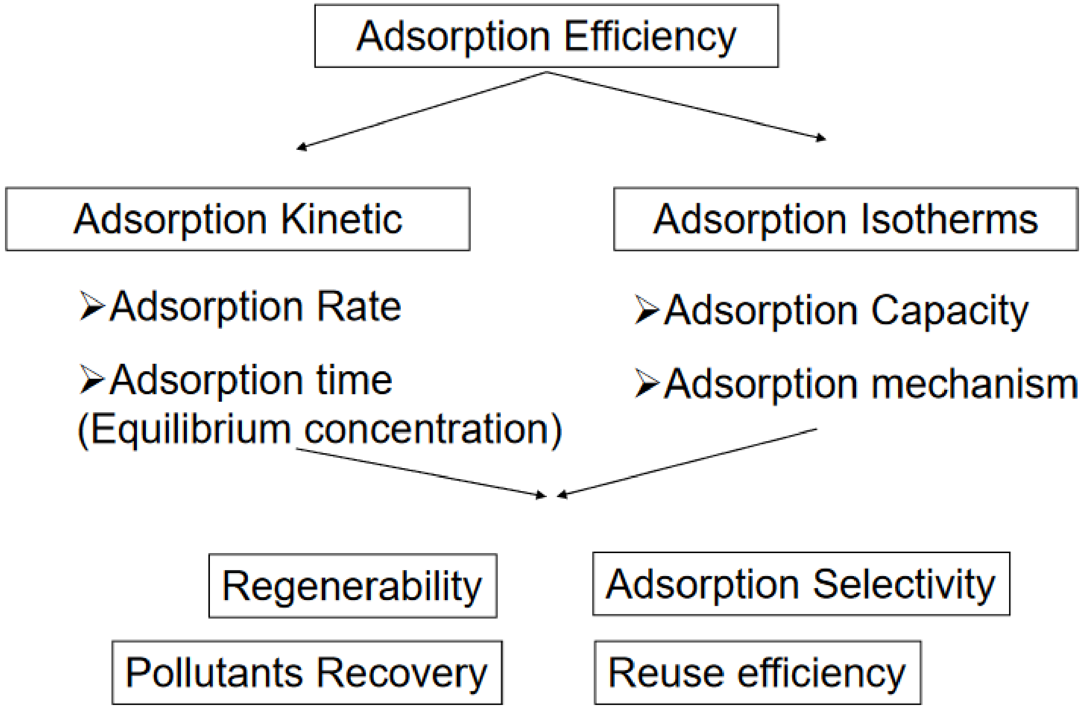
3M, C. 1999. Current Summary of Human Sera, Health and Toxicology Data. *3M Company*.

Pros and Cons of PFOA Removal Methods (Das and Ronen, 2022)

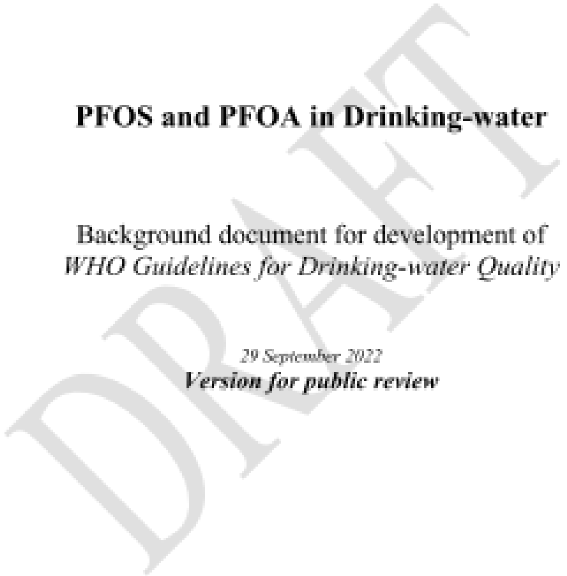


ADSORPTION


Adsorption Mechanisms
Step 1: Diffusion to Adsorbent Surface
Step 2: Migration into Pores of Adsorbent
Step 3: Monolayer Buildup of Adsorbate
Contaminant Molecules


Adsorption Efficiency
Adsorption Kinetic
Adsorption Isotherms
➢Adsorption Rate
➢Adsorption time (Equilibrium concentration)
➢Adsorption Capacity
➢Adsorption mechanism
Regenerability
Adsorption Selectivity
Pollutants Recovery
Reuse efficiency

Actual contamination


PFOS and PFOA in Drinking-water

Background document for development of
WHO Guidelines for Drinking-water Quality

29 September 2022
Version for public review

DRAFT

	Europe	US	China	Japan	Thailand
surface water samples	0.21 ng/L to 3640 ng/L	<1 ng/L to 1090 ng/L & 598 µg/L (near perfluorochemical industrial facilities)	<0.7 to 668 ng/L	0.2 to 1812 ng/L	10.7 ng/L
Ground-water samples	< 100ng/L				

Objectives

- ✓ The general research of this study aims to understand factors affecting the adsorption of PFOA on powder activated charcoal under different physical and chemical properties in water.
- ✓ To accomplish the general objective, the three main objectives that should focus on are as follows.

i. to investigate the effectiveness of powder activated charcoal adsorbent on PFOA removal,

ii. to investigate the effect of pH, temperature and hardness on adsorption capacity and

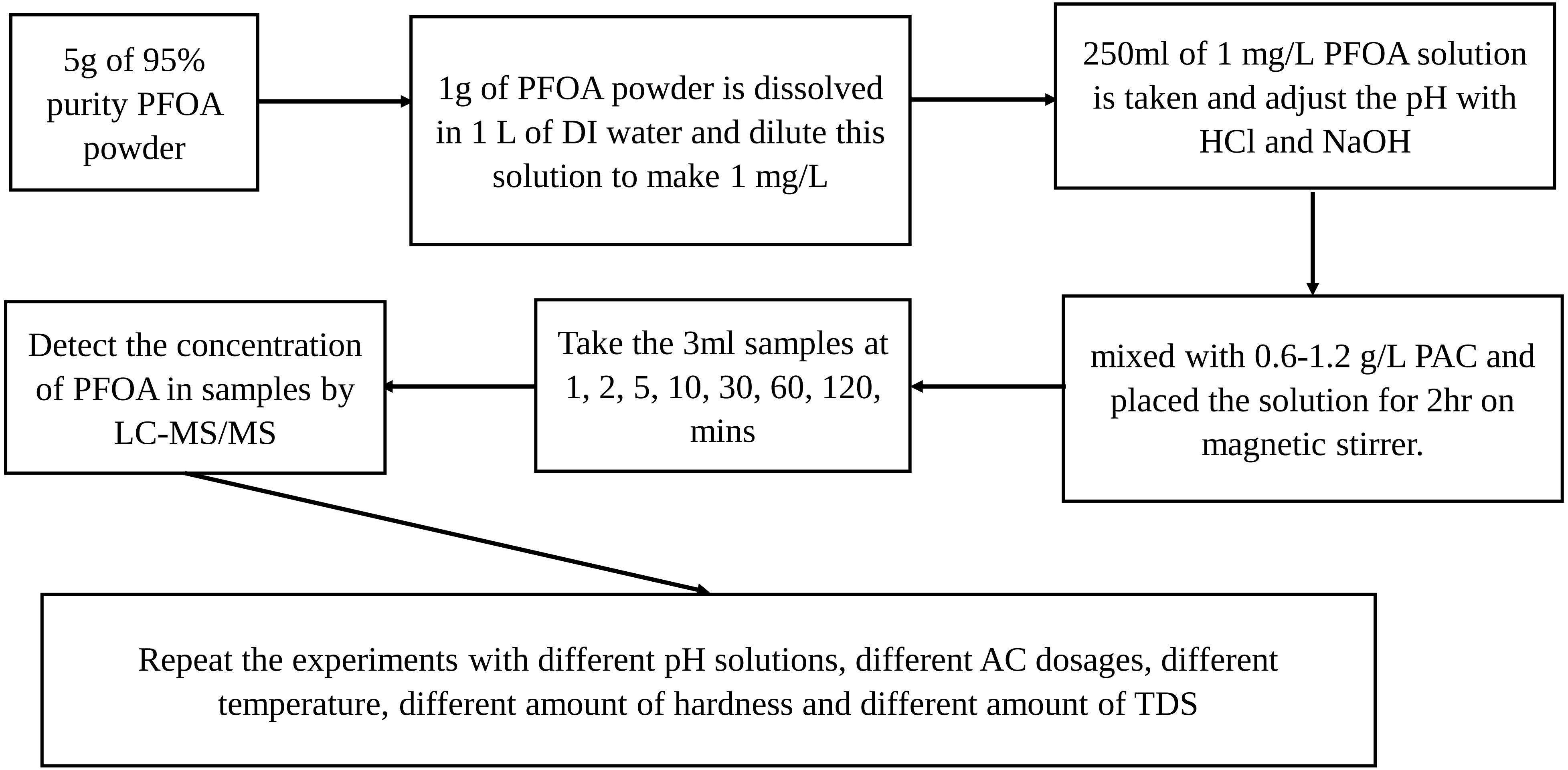
iii. to study adsorption mechanism (kinetic and isotherm) of PFOA on powder activated charcoal.

Scopes of Study

- Powder activated charcoal is utilized to remove PFOA
- 95% purity PFOA purchased from sigma Aldrich
- Initial concentration of 1-2 mg/L PFOA solution
- four main physiochemical parameters
  - ✓ pH (3-9),
  - ✓ temperature (20-40 °C),
  - ✓ hardness (200 mg/l), and

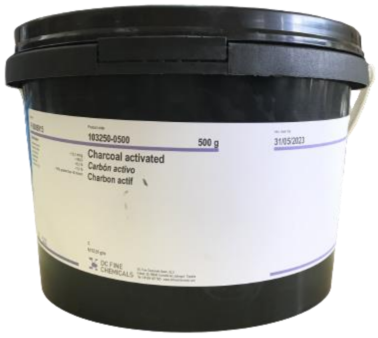
- Adsorption kinetic ⇒ pseudo-first-order equation and second-order equation
- Adsorption isotherm ⇒ Langmuir and Freundlich isotherm

Methodology



Flow Chart for Sample Preparation and PFOA Adsorption Experiments

Materials



Adsorbent Type	⟹	**Wood-based PAC**	**Bamboo-based PAC**	**Coconut-shell-based PAC**
Mesh size	⟹	-	300 U.S Mesh	325 U.S Mesh
Surface Characteristics	⟹	Hydrophobic	Hydrophobic	Hydrophobic

Adsorption Kinetic Study

Pseudo-First Order Equation

$$log\,(q_e - q_t) = log\,q_e - \frac{k_1}{2.303}t$$

Pseudo- Second Order Equation

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

q_t = adsorption capacity at time t,
q_e = adsorption capacity at equilibrium,
k_1 = first order rate constant,
k_2 = second order constant

** For all conditions, adsorption kinetic model will be studied by utilizing both equations.

ADSORPTION **ISOTHERM** STUDY

Langmuir Isotherm Model

$$q = \frac{q_m b C_e}{1 + b C_e}$$

Freundlich Isotherm Model

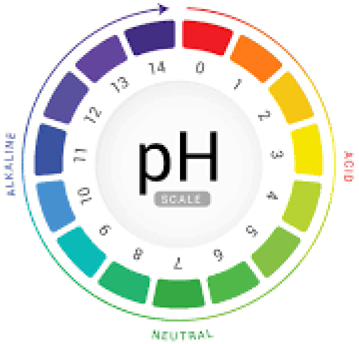
$$q_e = \frac{X}{M} = K_f C_e^{1/n}$$

C_e - equilibrium concentration of adsorbate (mg/L),
q_e - the amount of metal adsorbed per gram of the adsorbent at the adsorbent at equilibrium (mg/g),
q_m - maximum adsorption capacity (mg/mg)
K_f - Freundlich isotherm constant (mg/g)

Initial Concentration Range	5, 10, 50, 100, 500, 1000 ppb
pH	3, 7 & 9
Contact Time	60 mins
Temperature	Room Temperature
Adsorbent Dosage	Optimum
Model	Langmuir and Freundlich Isotherm Models

BATCH ADSORPTION EXPERIMENT

Effect of pH



Parameter	Value
Reactor	Batch
Initial Concentration	1 mg/L
Speed of magnetic stirrer	200 rpm
Adsorbent	Activated Charcoal
Temperature	Room temperature
Contact Time	120 mins
Adsorbent Dosage	Optimum
pH	3, 4.5, 6, 7, 9 (adjust by HCl & NaoH)
Sample Volume	250 mL

BATCH ADSORPTION EXPERIMENT

Temperature effect

Parameter	**Value**
Reactor	Batch
Initial Concentration	1 mg/L
Speed of magnetic stirrer	200 rpm
Adsorbent	Activated Charcoal
Temperature	20, 25, 30, 35, 40°C
Contact Time	120 mins
Adsorbent Dosage	Optimum
pH	Optimum
Sample Volume	250 mL

Adsorption Thermodynamics

To analyze the Gibbs free energy (ΔG^{0}), enthalpy (ΔH^{0}), and entropy (ΔS^{0})

$$\ln(K_d) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

$$\Delta G^{0} = -RT\ \ln(K_d)$$

$$K_d = \frac{q_e\left({}^{W}/_{V}\right)}{C_e}$$

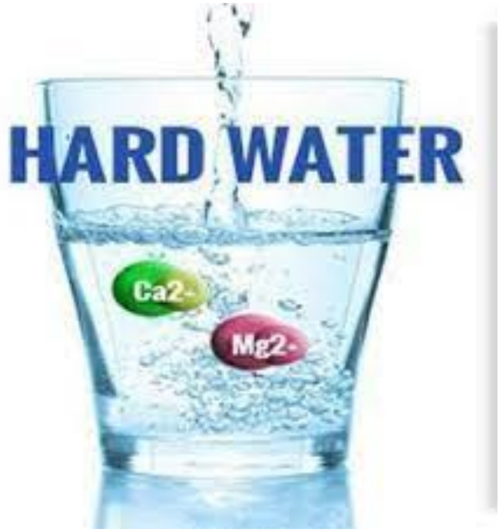
K_d is the adsorption distribution coefficient,

R is the universal gas constant (8.314 J/mol K) and

T is the temperature (K)

BATCH ADSORPTION EXPERIMENT

Effect of hardness ions (Mg^{2+} , Ca^{2+})



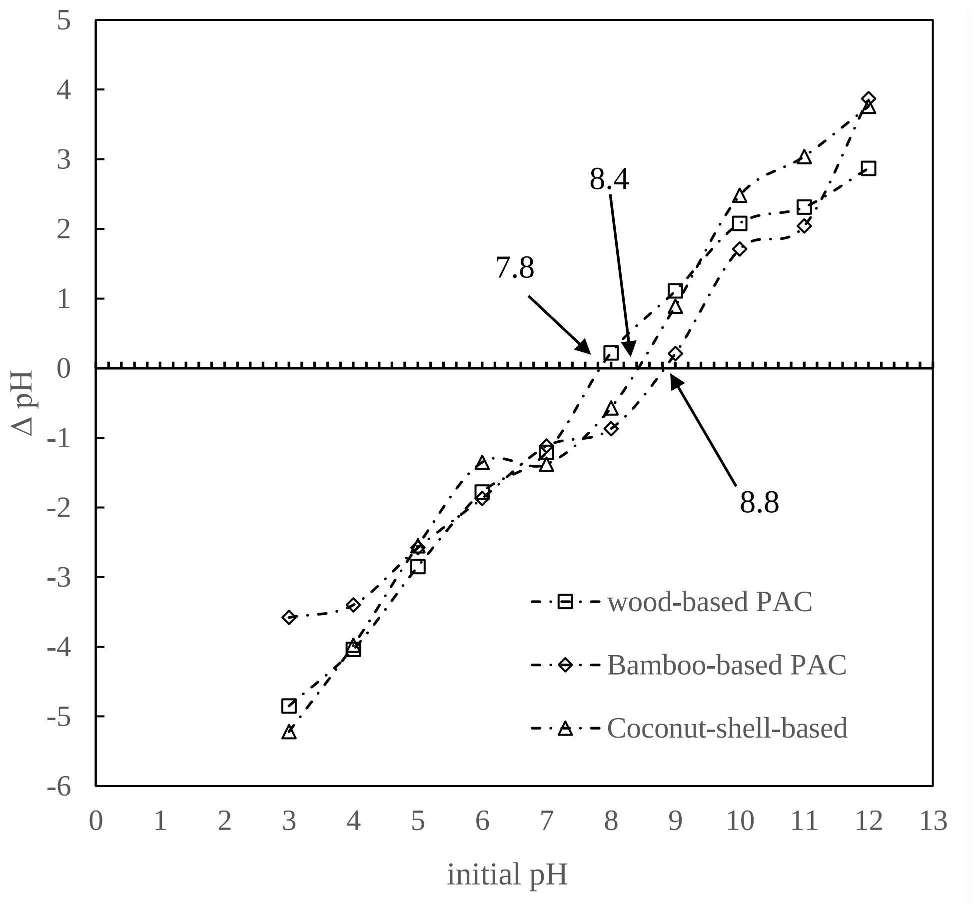
Parameter	**Value**
Reactor	Batch
Initial Concentration	1 mg/L
Speed of magnetic stirrer	200 rpm
Adsorbent	Activated Charcoal
Temperature	Room Temperature
Contact Time	180 mins
Adsorbent Dosage	Optimum
pH	Optimum
Sample Volume	250 mL
Total amount of Hardness	10 mM $MgCl_2$ & $CaCl_2$

RESULT & DISCUSSION

Characterization of Adsorbents

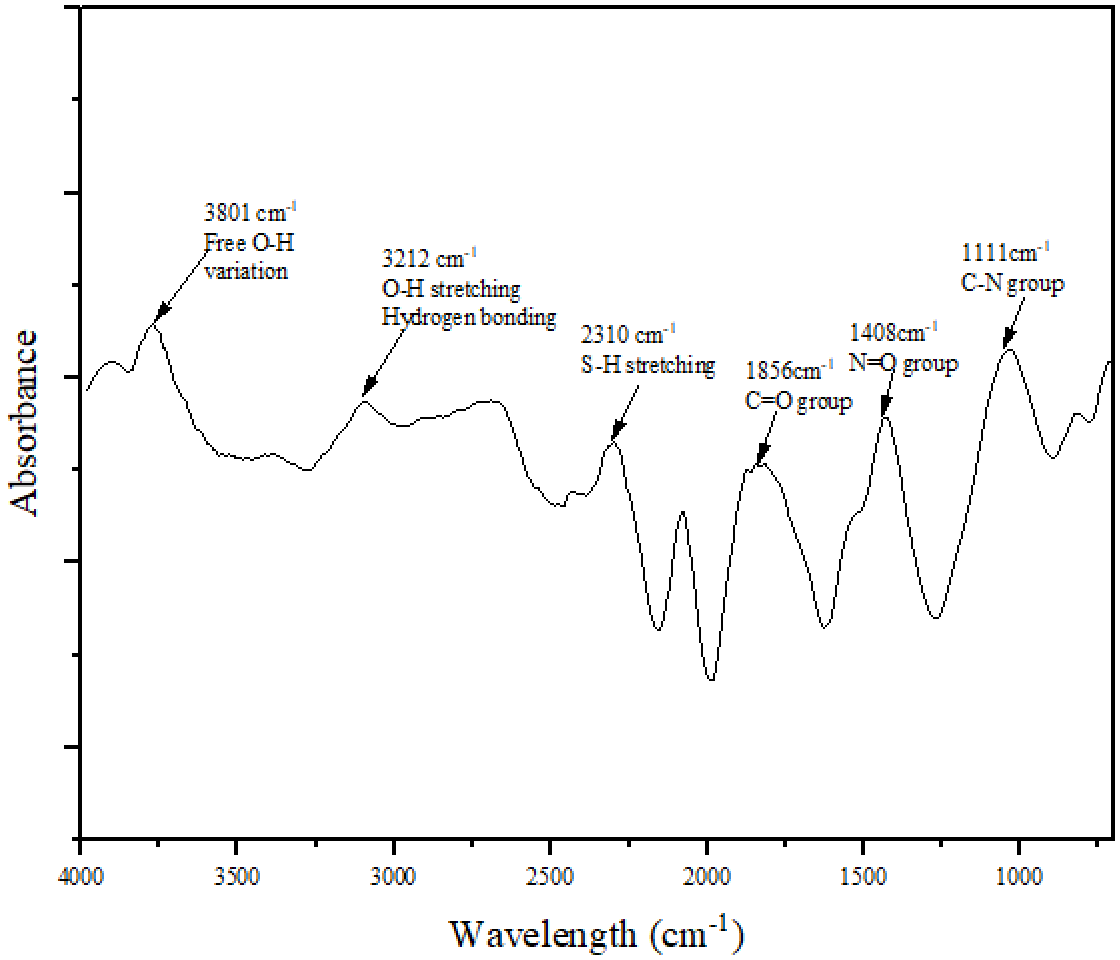
Adsorbents	Pore Diameter (nm)	BET surface area (m^2/g)	Pore Volume (mm^2 /g)	pH_{pzc}	Surface Functional Group
Wood-based PAC	5.19	833.75	706.023	7.8	-OH, C-H, C-N
Bamboo-based PAC	2.93	852.73	461.89	8.8	-OH, C-H, C-N
Coconut-shell-based PAC	2.48	1118.26	616.18	8.4	-OH, C-H, C-N

BET results

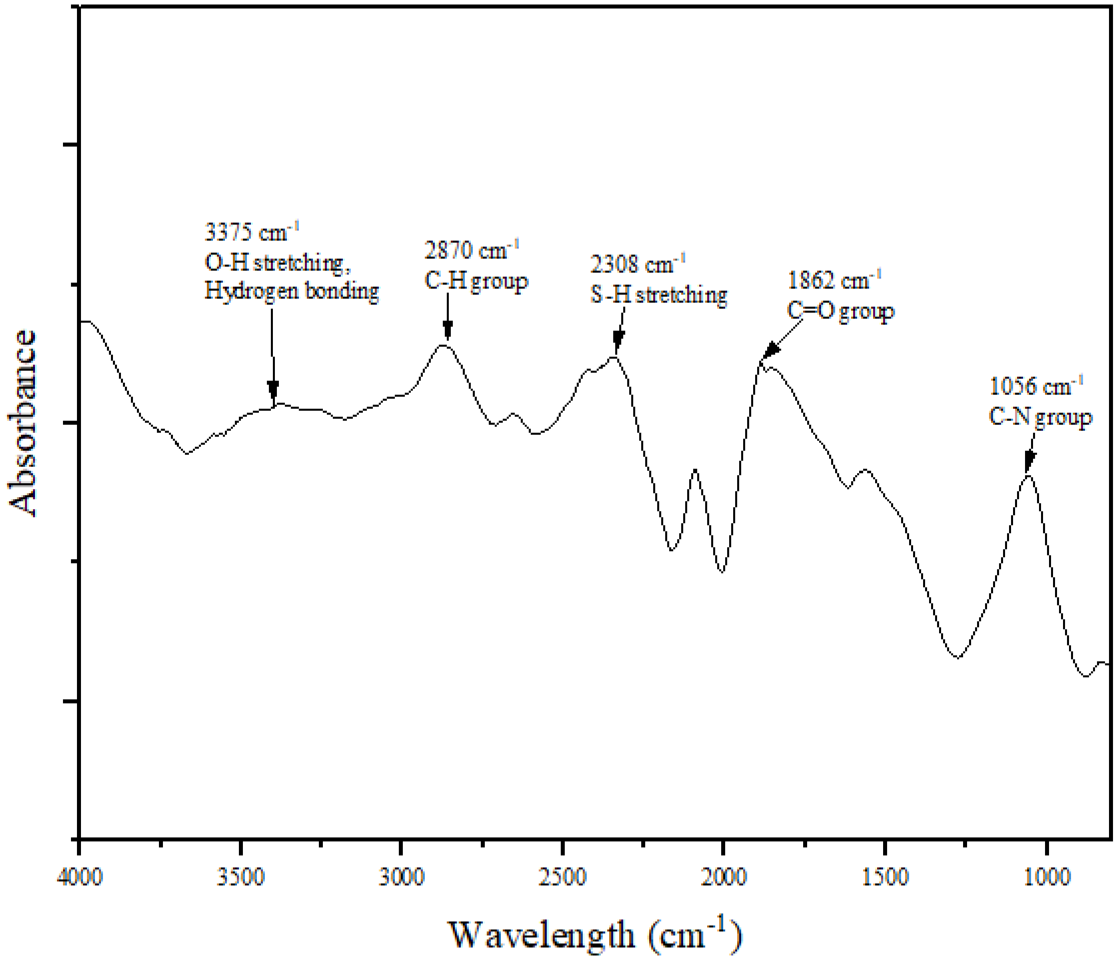


Point of Zero Charge

Characterization of Adsorbents (FT-IR Results)

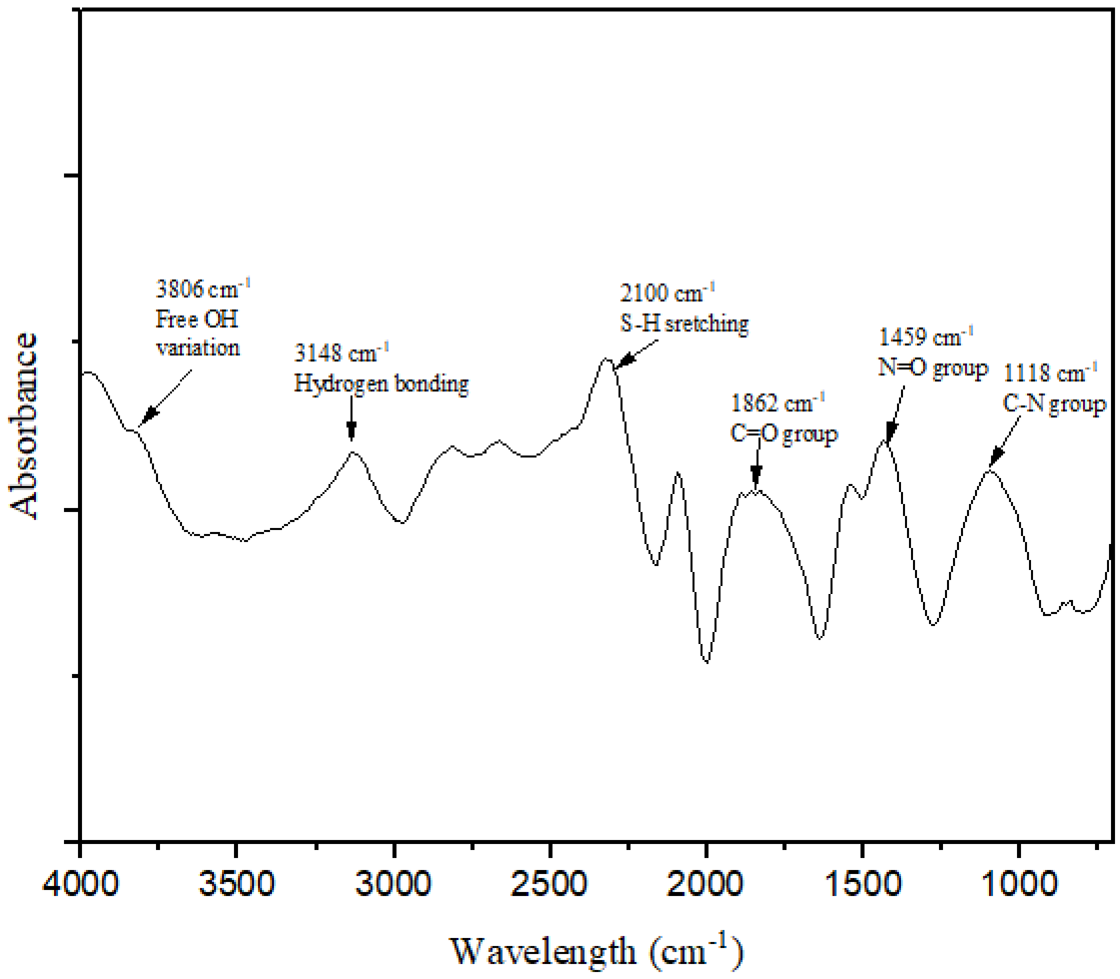


FT-IR Spectrum of Wood-based PAC



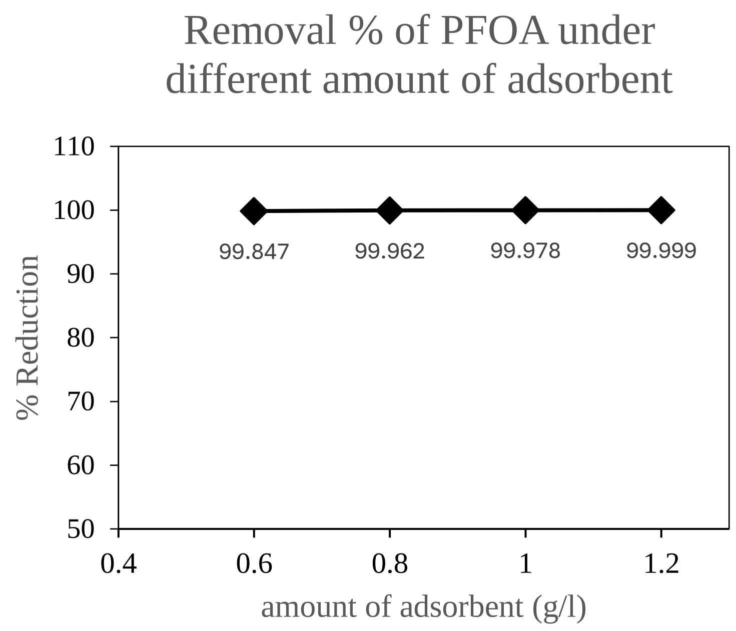
FT-IR Spectrum of Bamboo-based PAC

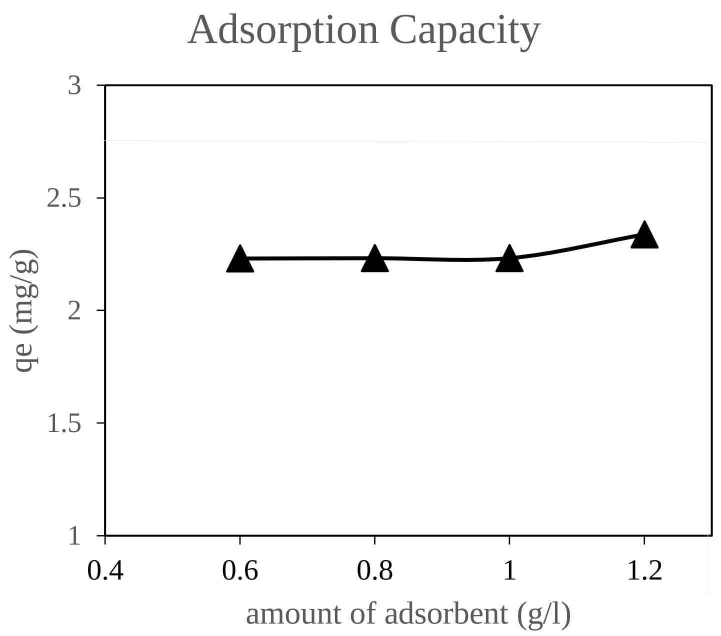
Characterization of Adsorbents (FT-IR Results)



FT-IR Spectrum of Coconut-shell-based PAC

Adsorbent Dosage

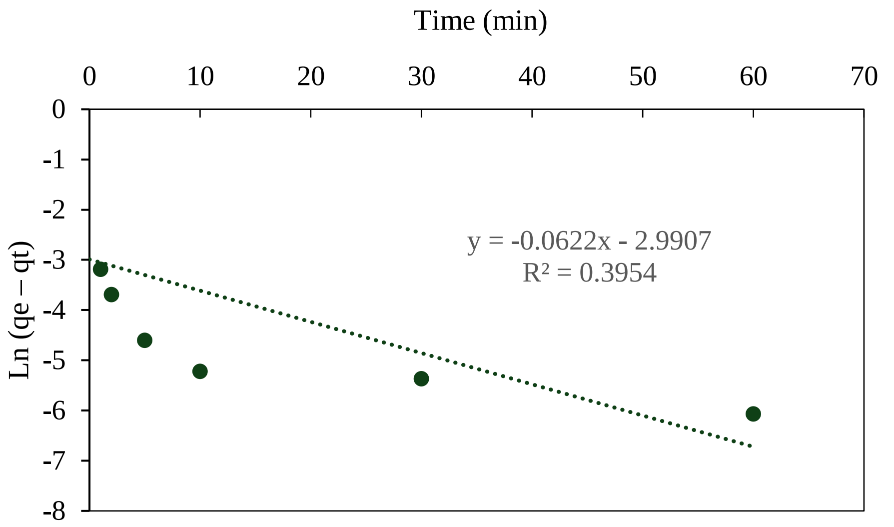




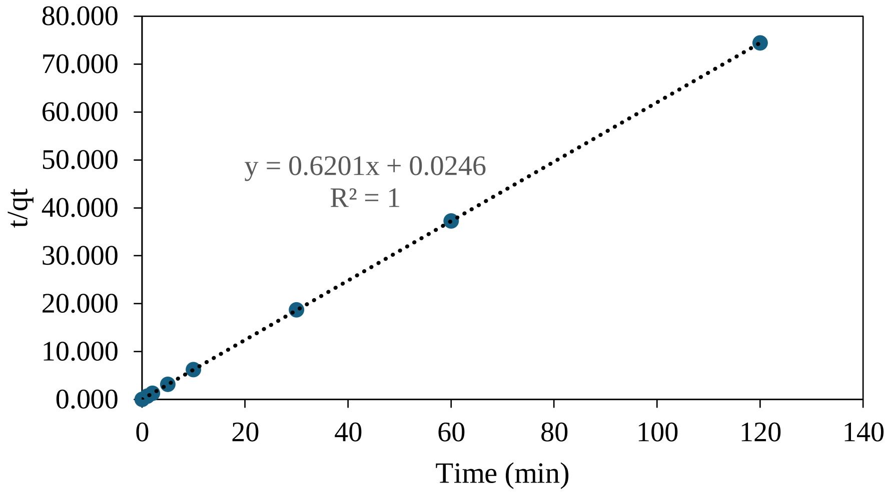
amount of adsorbent (g/l)	Remaining Conc (ug/l)
0.6	1.06
0.8	0.676
1	0.39
1.2	0.001

* For all adsorbent dosage conditions, the initial concentration of PFOA is 1000 µg/L, the solution initial pH is 7 and the saturation time is 120 minutes.

Adsorption Kinetic (Wood-based PAC)



Pseudo First-order model

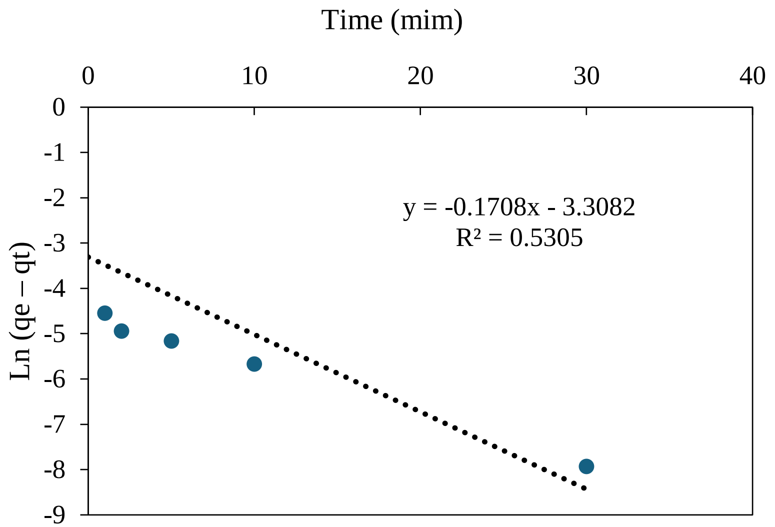


Pseudo Second-order model

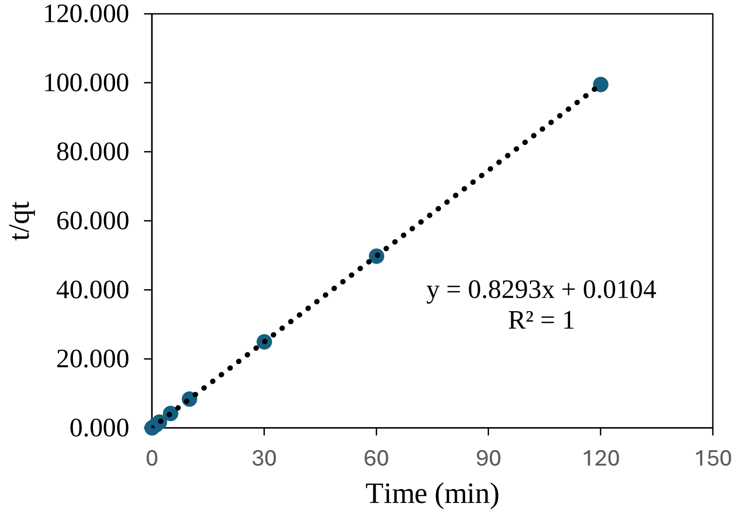
pH	Adsorbent	Pseudo First-order				Pseudo Second-order				
		R^2	k_1 (h^{-1})	Calculated qe (mg/g)	Experimental qe (mg/g)	R^2	k_2 (g/µg.min)	Calculated qe (mg/g)	Experimental qe (mg/g)	h (µg/g. min)
7	Wood-based	0.3954	3.504	0.0517	1.648	1	0.0156	1.6483	1.648	42384

Experimental Condition - (T = 30 ºC, PAC dose = 0.3g, C_0 = 1 mg/L, V = 250 mL)

Adsorption Kinetic (Bamboo-based PAC)



Pseudo First-order model

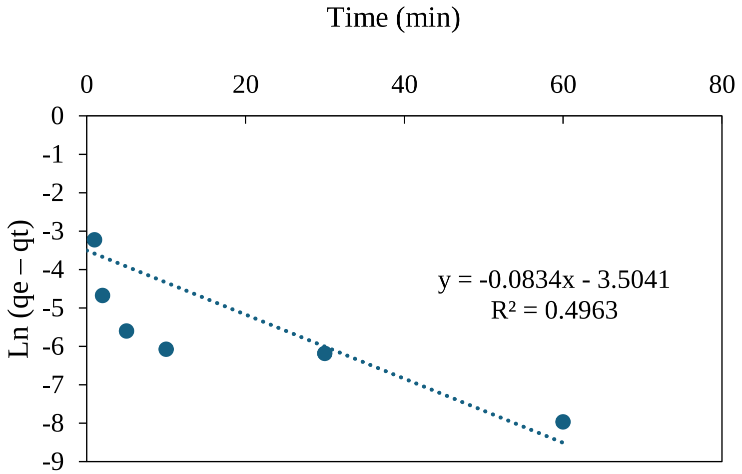


Pseudo Second-order model

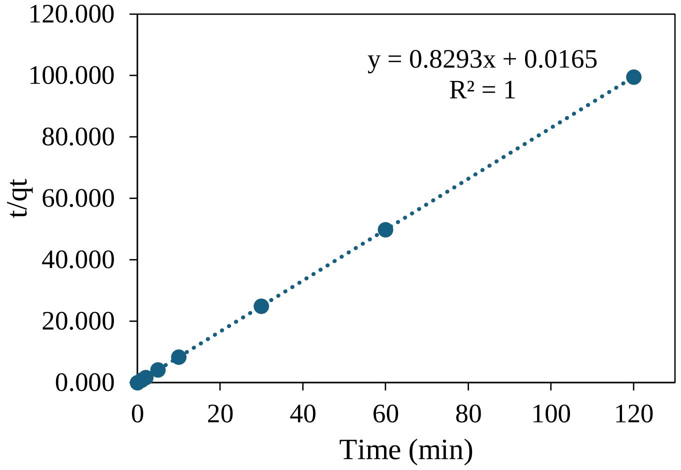
pH	Adsorbent	Pseudo First-order				Pseudo Second-order				
		R^2	k_1 (h^{-1})	Calculated qe (mg/g)	Experimental qe (mg/g)	R^2	k_2 (g/µg.min)	Calculated qe (mg/g)	Experimental qe (mg/g)	h (µg/g. min)
7	bamboo-based	0.5305	10.25	0.0366	1.206	1	0.0661	1.2058	1.206	96106

Experimental Condition - (T = 30 ºC, PAC dose = 0.3g, C_0 = 1 mg/L, V = 250 mL)

Adsorption Kinetic (Coconut-shell-based PAC)



Pseudo First-order model



Pseudo Second-order model

pH	Adsorbent	Pseudo First-order				Pseudo Second-order				
		R^2	k_1 (h^{-1})	Calculated qe (mg/g)	Experimental qe (mg/g)	R^2	k_2 (g/µg.min)	Calculated qe (mg/g)	Experimental qe (mg/g)	h (µg/g. min)
7	coconut-shell-based	0.4963	5.004	0.0301	1.206	1	0.0417	1.2058	1.206	60630

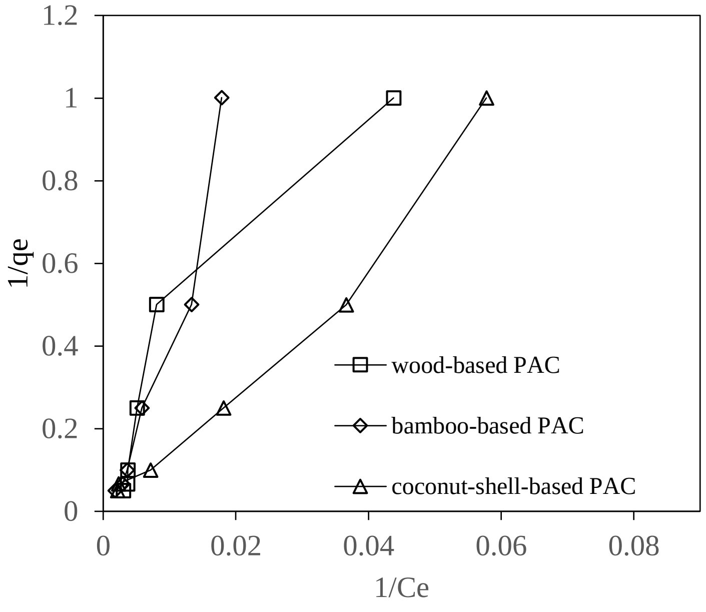
Experimental Condition - (T = 30 ºC, PAC dose = 0.3g, C_0 = 1 mg/L, V = 250 mL)

Adsorption Kinetic

Experimental Condition - (T = 30 ºC, PAC dose = 0.3g, C_0 = 1 mg/L, V = 250 mL)

pH	Adsorbent	Pseudo First-order				Pseudo Second-order				
		R^2	k_1 (h^{-1})	Calculated qe (mg/g)	Experimental qe (mg/g)	R^2	k_2 (g/µg.min)	Calculated qe (mg/g)	Experimental qe (mg/g)	h (µg/g. min)
7	Wood-based	0.3954	3.504	0.0517	1.648	1	0.0156	1.6483	1.648	42384
	bamboo-based	0.5305	10.25	0.0366	1.206	1	0.0661	1.2058	1.206	96106
	coconut-shell-based	0.4963	5.004	0.0301	1.206	1	0.0417	1.2058	1.206	60630

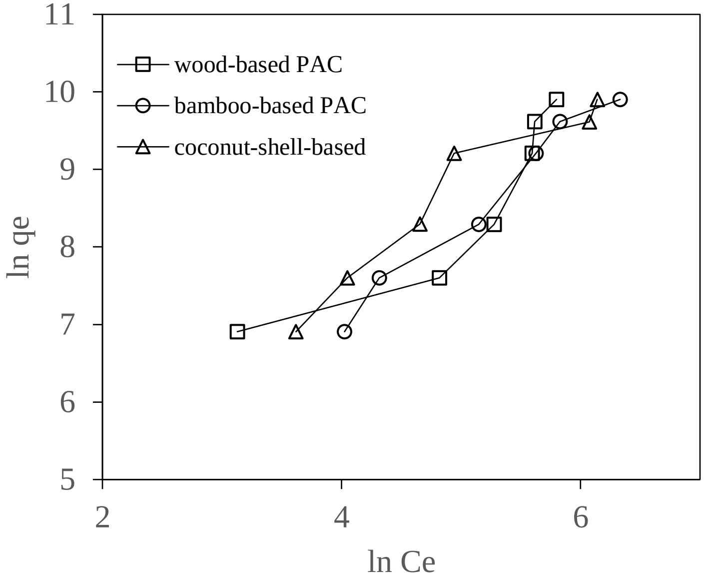
Adsorption Isotherm



Langmuir model at pH 7

Parameters of fitted adsorption isotherm, Langmuir and Freundlich models at initial pH solution 7

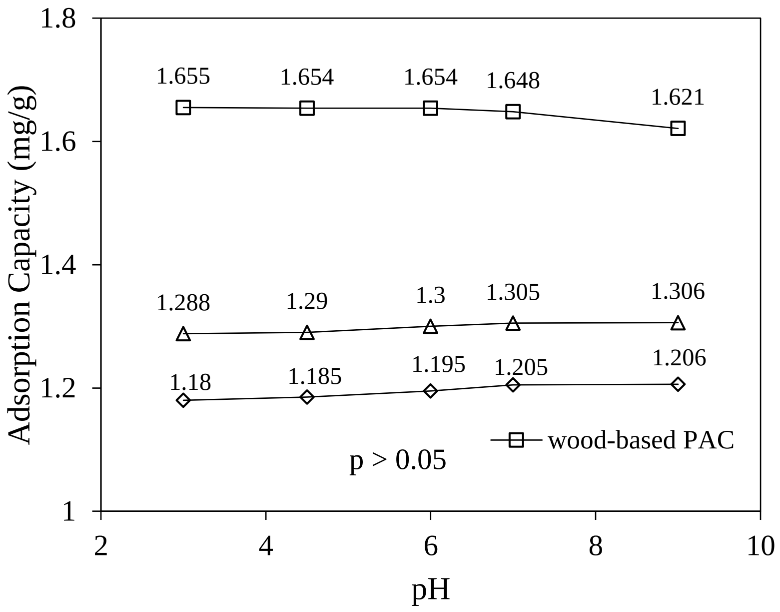
pH	Adsorbent	Langmuir			Freundlich		
		q_m	K_L	R^2	K_f	1/n	R^2
7	Wood-based	11111.111	0.0216	0.8746	25.138	1.0643	0.7984
	Bamboo-based	11111.111	0.0553	0.9497	5.828	1.3093	0.9758
	Coconut-shell-based	12500.000	0.0164	0.9625	118.831	0.8368	0.9654



Freundlich model at pH 7

Adsorption Mechanisms

1. Effect of pH

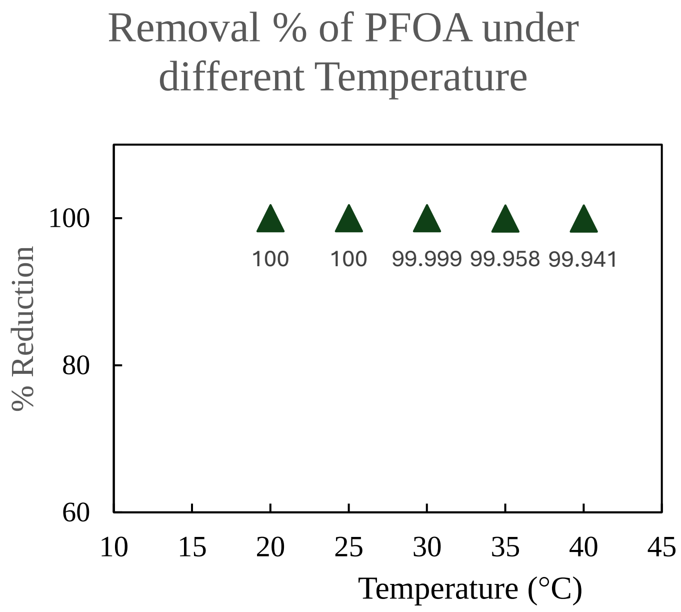


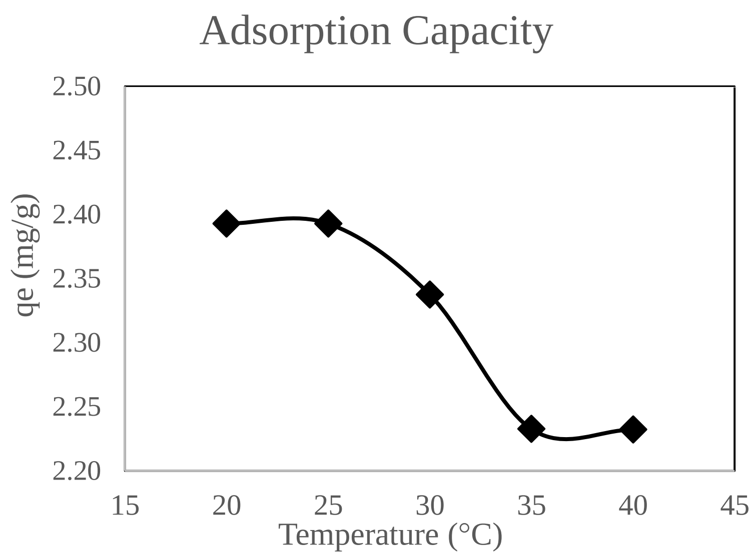
PFOA adsorption capacity

pH	Wood-based Remaining Conc; (µg/l)	Bamboo-based Remaining Conc; (µg/l)	coconut-shell-based Remaining Conc; (µg/l)
3	0.001	0.458	0.132
4.5	0.055	0.129	0.109
6	0.072	0.079	0.096
7	0.092	0.045	0.065
9	28.91	0.006	0.061

* For all pH conditions, the initial concentration of PFOA is 1000 µg/L and the saturation time is 120 minutes.

2. Effect of Temperature

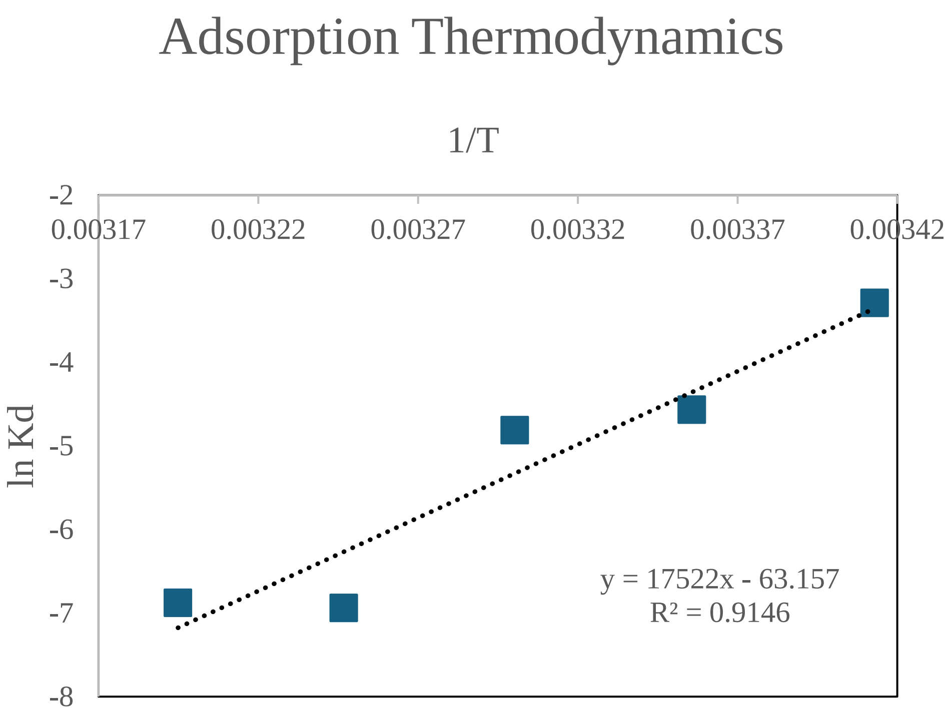




Temperature (°C)	Remaining Conc (ug/l)
20	0
25	0
30	0.01
35	0.75
40	1.06

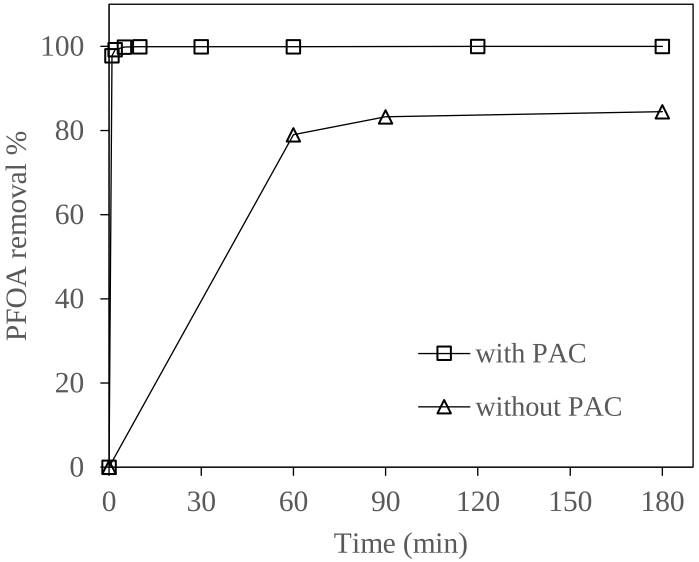
*For all temperature conditions, the initial concentration of PFOA is 1000 µg/L, the solution initial pH is 3, the adsorbent dosage 1.2 g/L and the saturation time is 120 minutes.

Adsorption Thermodynamics



Thermodynamic parameter	Value	Remark
Gibbs free energy (ΔG^{o}) kJ/mol.K	-9.354 to -0.661	Spontaneous
Enthalpy Change (ΔH^{0}) kJ/mol	-145.68	Exothermic
Entropy Change (ΔS^{0}) J/mol	-525.1	chemosorption

3. Effect of Hardness ions



PFOA removal percentage

Hardness	pH	Remaining Conc (ppb) at 120 mins	Remaining Conc (ppb) at 180 mins	Adsorption capacity (mg/g)
10mM of Ca^{2+} & Mg^{2+} ions	3	0.227	0.209	1.731
	7	0.425	0.2685	1.731
	9	0.623	0.328	1.731

*For all temperature conditions, the initial concentration of PFOA is 1000 µg/L, the solution initial pH is 3, the adsorbent dosage 1.2 g/L and the saturation time is 180 minutes.

Conclusions

PACs characteristics results

- The specific surface area of coconut-shell-based PAC was highest.
- The wood-based PAC has the largest pore size and pore volume.
- The FTIR characteristics results demonstrated that all adsorbents have the adsorption peak of the oxygen-containing functional groups. This result suggested that the PACs have the hydroxyl (O-H), and carbonyl (C=O).

Conclusions

Adsorption characteristics

- The kinetic model showed that different PACs have different adsorption characteristic depending on solution pH, wood-based > coconut-shell-based > bamboo-based in acidic condition and bamboo-based > coconut-shell-based > wood-based in basic condition.
- The kinetic adsorption of PFOA is found to be more consistent with chemical adsorption mechanism (fitted with pseudo-second-order).
- For the adsorption isotherms, the PFOA molecules adsorption onto all PACs have been proven to be monolayer adsorption (fitted to Langmuir isotherm).
- The main adsorption mechanism between PFOA molecules and PACs were electrostatic attraction force.

Conclusions

Effect of co-existing parameters

- The adsorption of PFOA on all PACs was found to have a pH-dependent where wood-based PAC perform the better at lower pH while the other two perform better at higher pH.
- The adsorption mechanisms were influenced by not only electrostatic interaction also hydrogen bonding.
- The effect of temperature tended to same influence to all PACs because the adsorption of PFOA on all PACs under this condition was shown as exothermic reaction.
- The presence of hardness ions in the solution was found to be associated with adsorption inhibition. This was because it could form the interaction between the positively charged hardness ions and negatively charge PFOA molecules that results precipitation of PFOA.

Recommendations

- ✓ Effect of other co-existing parameters in surface water like humid acid, turbidity and heavy metals.
- ✓ Effect of temperature variation and hardness ions on PFOA adsorption by bamboo-based and coconut-shell-based PACs.
- ✓ Effect of higher initial concentration PFOA on the adsorptions on all PACs in this study.
- ✓ To ensure the economically effectiveness of the commercial powder activated charcoal, cost analysis should be investigated comparing with other PAC that are expensive and synthesized adsorbents.
- ✓ Regeneration study should be done for recycling or reusing of PAC.
- ✓ Adsorption column test should be carried out to quantify the industrial scale parameters, e.g. flow rate, column height, etc.

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