May 9, 2013

REMOVAL OF PHARMACEUTICALS BY PAC ADSORPTION

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PNWS-AWWA 2013

NC STATE UNIVERSITY

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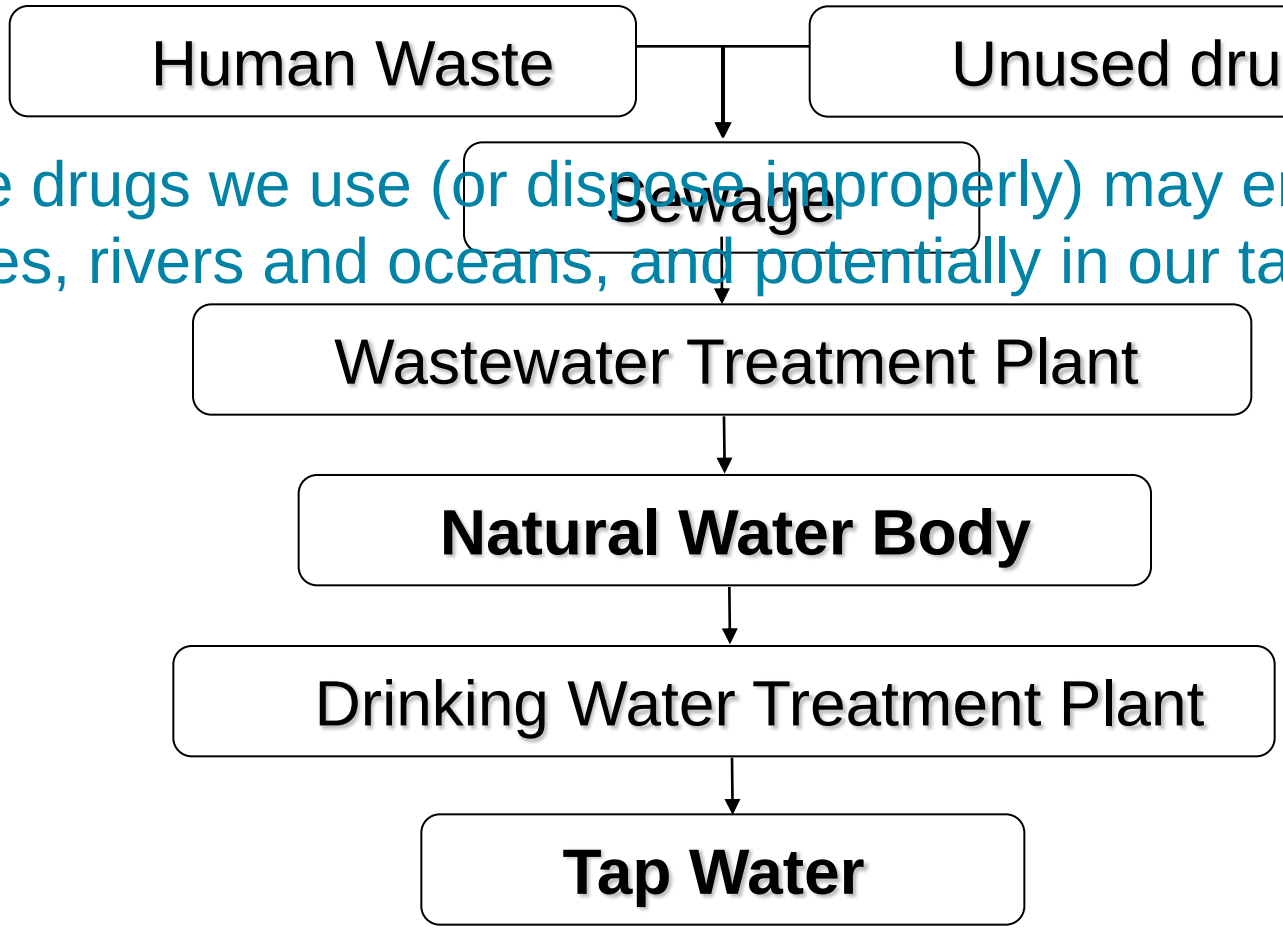
Acknowledgements

- North Carolina Urban Water Consortium for funding this research.
- Co-author: Koichi Ohno and Detlef Knappe

Pre-research Questions

- Why pharmaceuticals?
- Why PAC? What's new with PAC
- How well do PACs work for pharmaceutical removal?

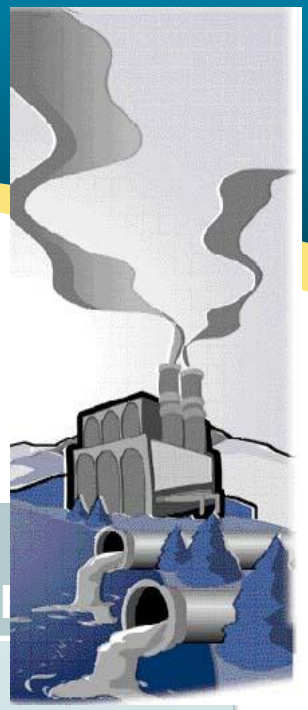
Concern of Pharmaceuticals



The drugs we use (or dispose improperly) may end up in our lakes, rivers and oceans, and potentially in our tap water.

Concern of Pharmaceuticals

Concentrations: ng/L to µg/L rang



From On Tap Magazine – Winter 2003

	Eco-toxicological Effects	Pot… Health Risk	El…
EDCs - Example: estrogenic hormones	X	X	X
PhACs - Example: antibiotics	X	X	X

Removal of Pharmaceuticals from Drinking Water

Process	Effectiveness
Sedimentation	**Very low**
Oxidation:	**Medium - High**
- Chlorine	High/Selective
- Ozone	High/Selective
- AOP	High
UV Light	**Low**
Adsorption:	**Medium - High**
- GAC	Medium - High
- PAC	Medium - High

Powdered Activated Carbon (PAC) Adsorption

- A new type of PAC: sub-micrometer PAC, or S-PAC

- Performance of PAC in coagulation/flocculation/ sedimentation process

Research Objectives

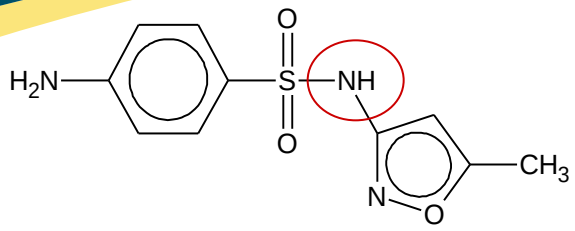
- Assess the effectiveness of PAC adsorption process for pharmaceutical removal

- Identify factors that affect the removal
  - pH
  - Background NOM
  - PAC particle size

- Evaluate the application of PAC in conjunction with coagulants

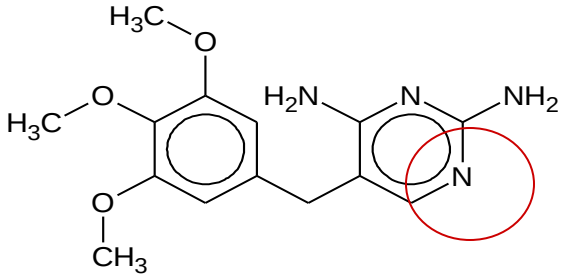
Materials and Methods

Pharmaceuticals



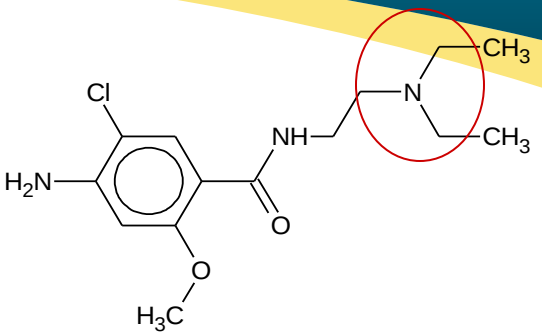
Sulfamethoxazole (SMX)

pK_a=5.8 (0/-)



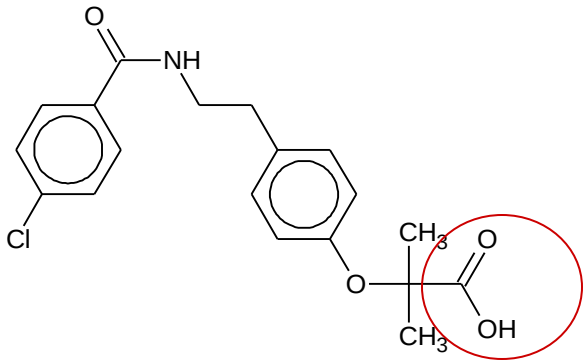
Trimethoprim (TMP)

pK_a=7.2 (+/0)



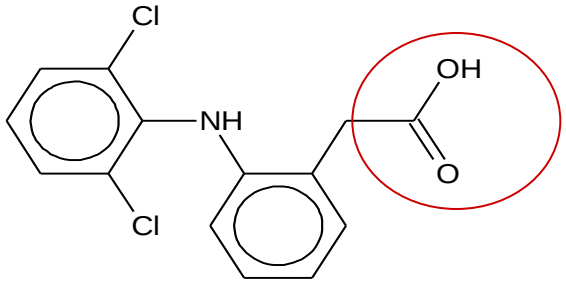
Metoclopramide (MCP)

pK_a=9.7 (+/0)



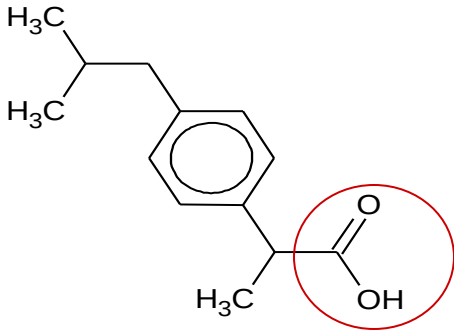
Bezafibrate (BZF)

pK_a=3.3 (0/-)



Diclofenac (DCF)

pK_a=4.2 (0/-)



Ibuprofen (IBP)

pK_a=4.4 (0/-)

Powdered Activated Carbons (PACs)

PAC Name	Material	Activation Method	d_{50} (µm)
NuChar	Wood	Chemical	22-26
Hydrodarco B	Lignite Coal	Thermal	18
WPH	Anthracite Coal	Thermal	**17.2**
S-WPH	Anthracite Coal	Thermal	**0.311**

- S-WPH was developed by wet-milling WPH

Experimental and Analytical Methods

Water

- OWASA (University Lake/Cane Creek Reservoir blend, Carrboro, NC)
  pH: ~7.2 TOC: ~5.0 mg/L
- Cary Wastewater Treatment Plant Effluent (WWTPE) (Cary, NC)
  pH: ~7.9 TOC: ~7.3 mg/L
- Spiked pharmaceutical concentration: ~100 µg/L

Experiments

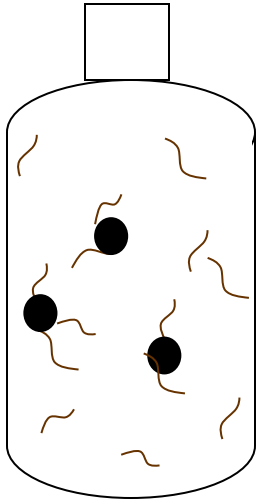
- Batch kinetic tests
- Batch isotherm tests
- Jar tests

Analytical Methods

- High-performance liquid chromatography (HPLC) equipped with a dual-wavelength UV detector and a C18 column

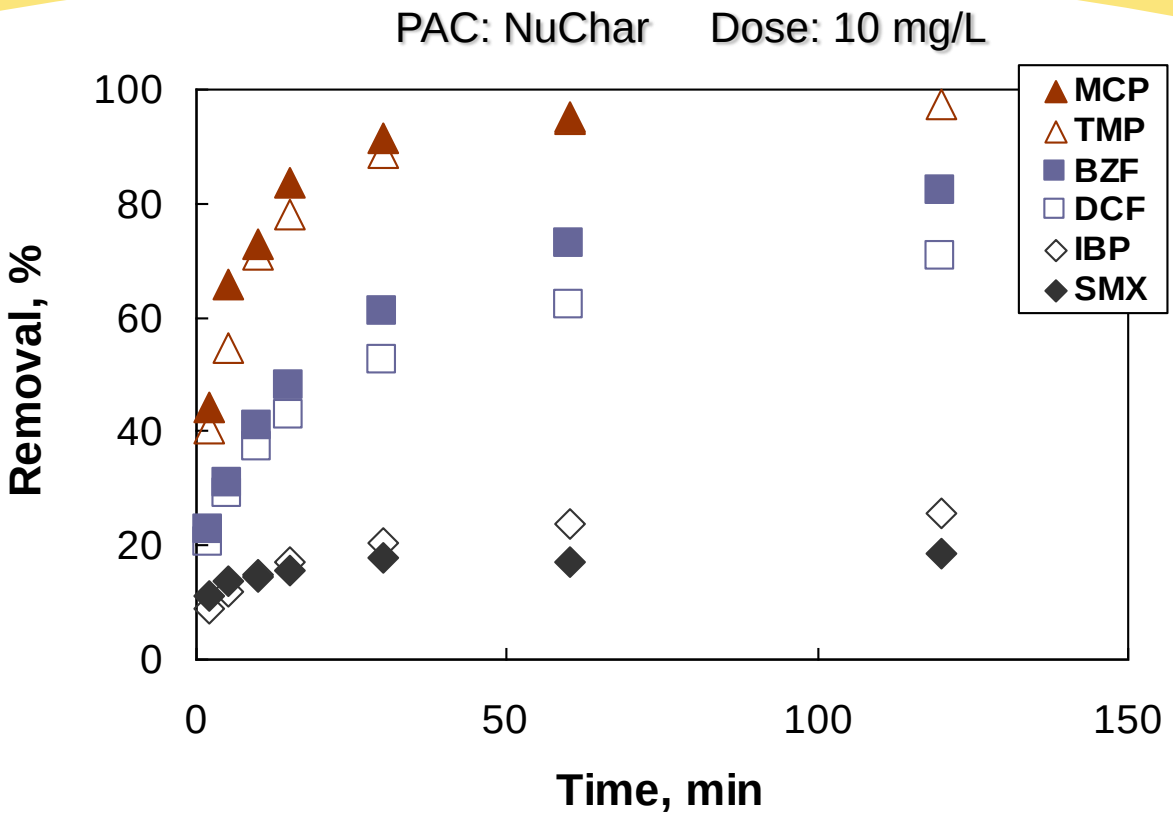
Results and Discussions

1. Batch Tests



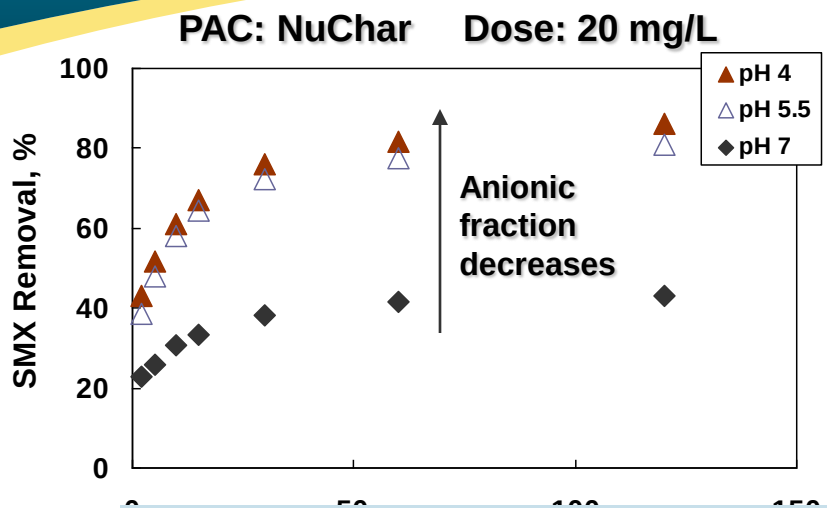
- Sample residual pharmaceutical concentration as a function of time
- Kinetics tests: 0-2 hour contact time
- Isotherm tests: 2 week contact time

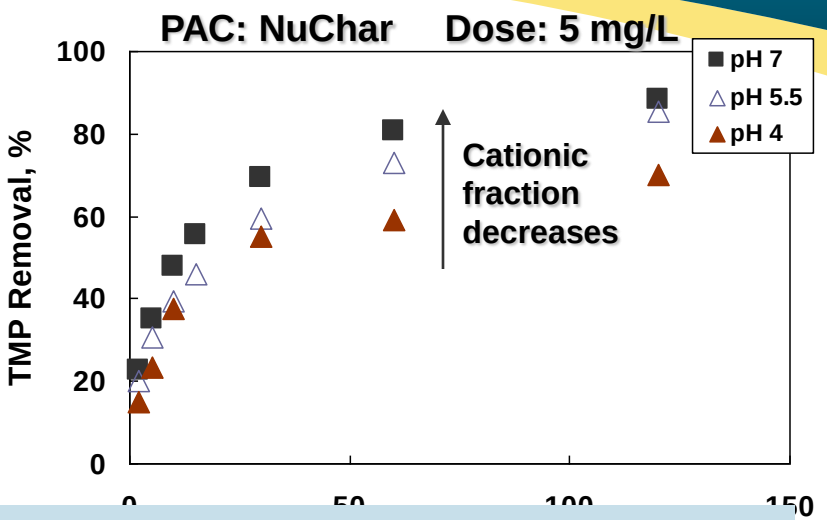
1. Adsorbability of Pharmaceuticals



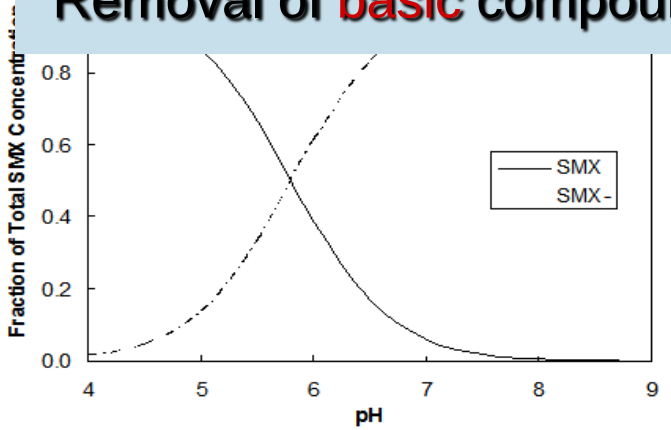
- Most adsorbable: Trimethoprim (TMP) and Metoclopramide (MCP)
- Least adsorbable: Sulfamethoxazole (SMX) and Ibuprofen (IBP)

2. Effect of pH

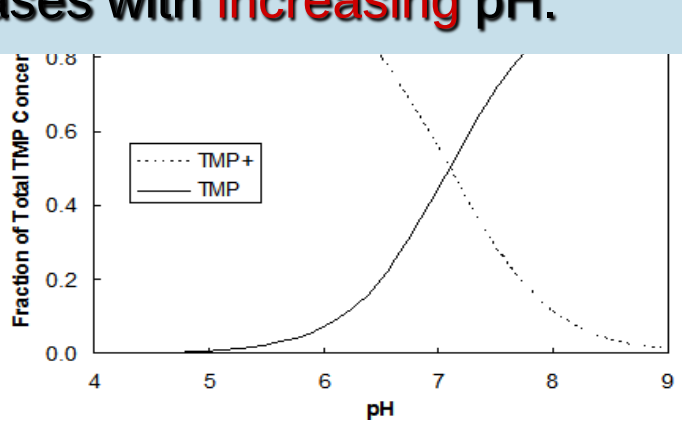




Removal of acidic compounds increases with decreasing pH.
Removal of basic compounds increases with increasing pH.

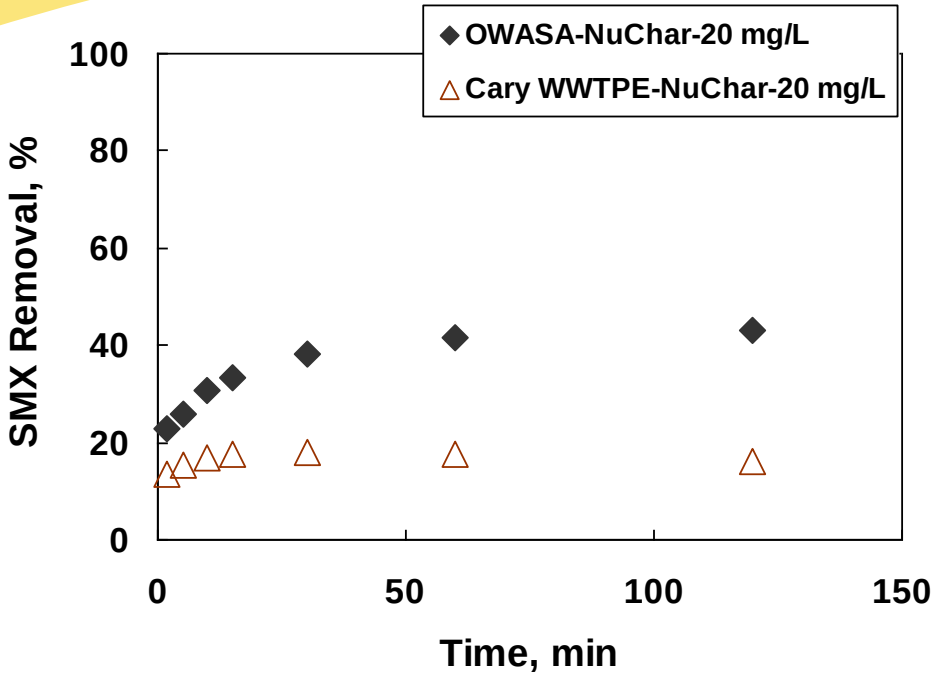


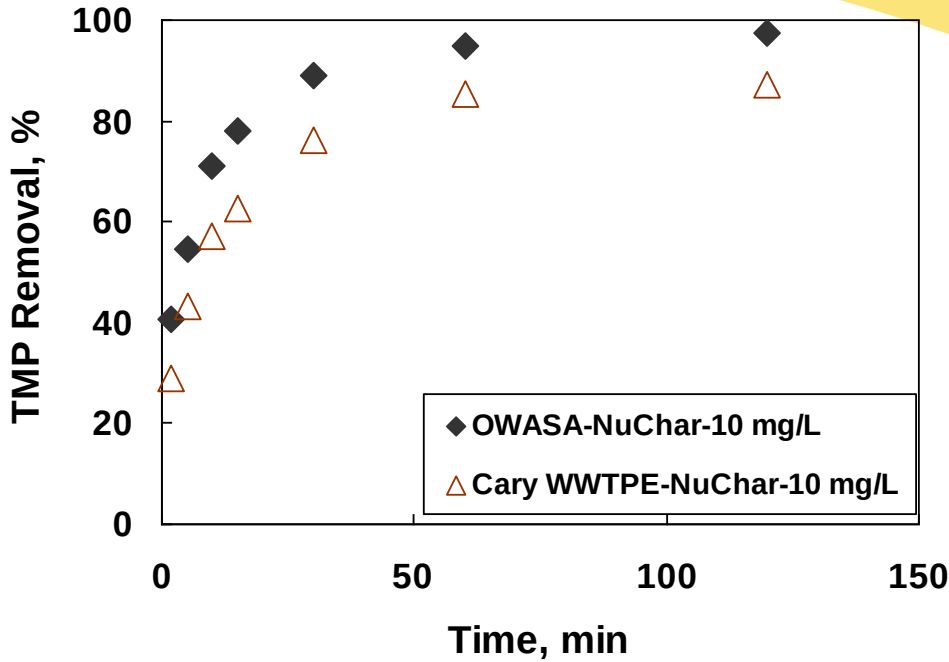
pKa of SMX: 5.8



pKa of TMP: 7.2

3. Effect of natural organic matter (NOM) in background water



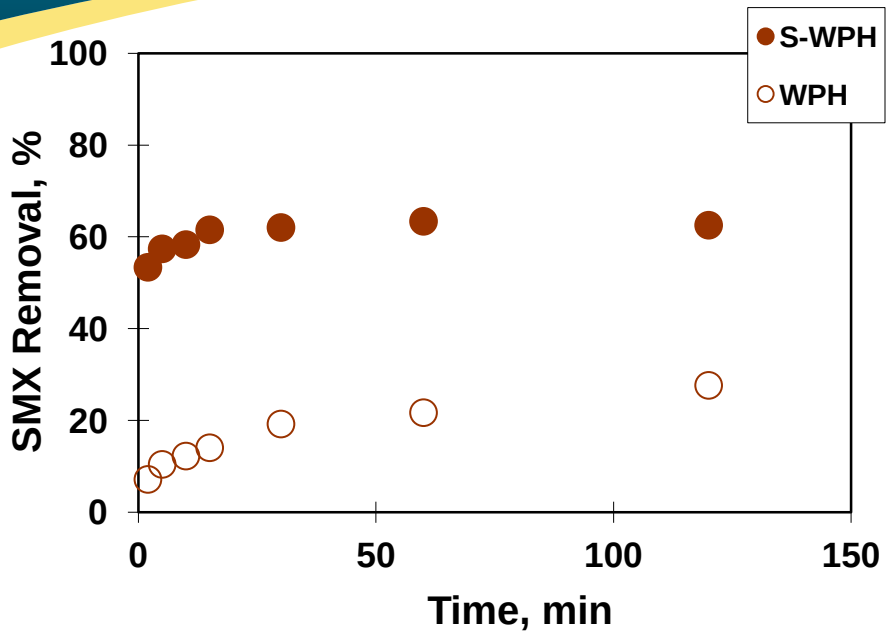


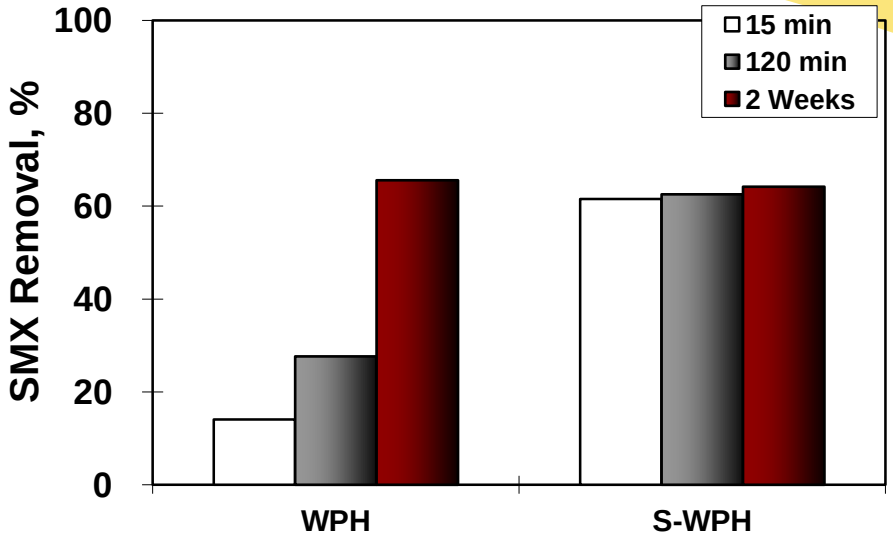
- OWASA: pH ~7.2 TOC ~ 5.0 mg/L
- Cary WWTPE: pH ~7.9 TOC ~ 7.3 mg/L

- **Background NOM adversely affected pharmaceutical adsorption.**

4. Effect of PAC particle size

PAC Dose: 10 mg/L

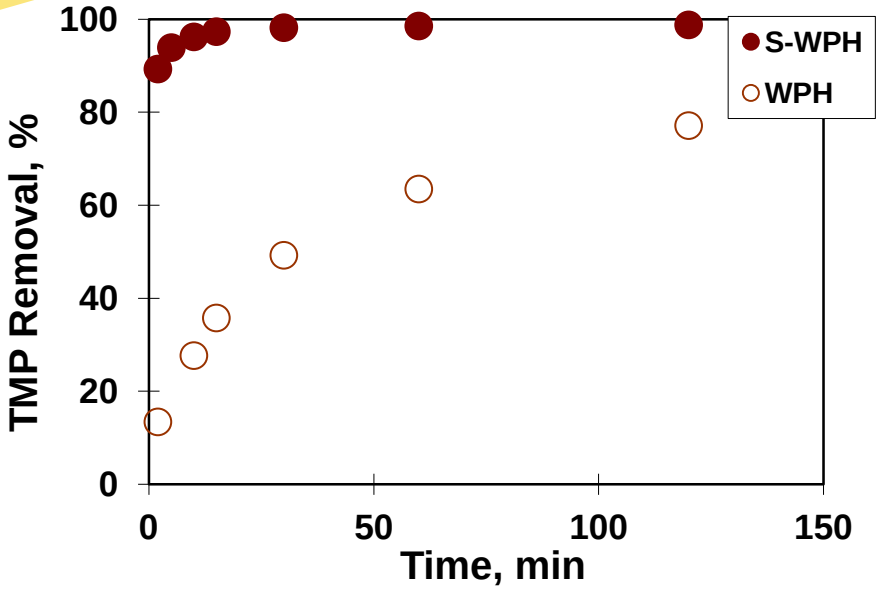


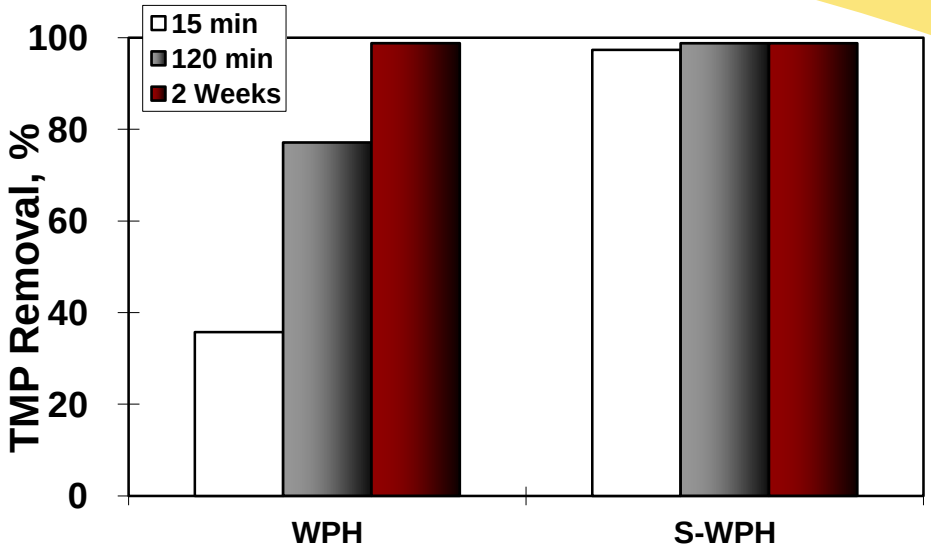


- SMX kinetics: S-WPH>>WPH
- SMX capacity: S-WPH≈WPH
- **S-WPH almost reached adsorption equilibrium at ~15 min!**

4. Effect of PAC particle size

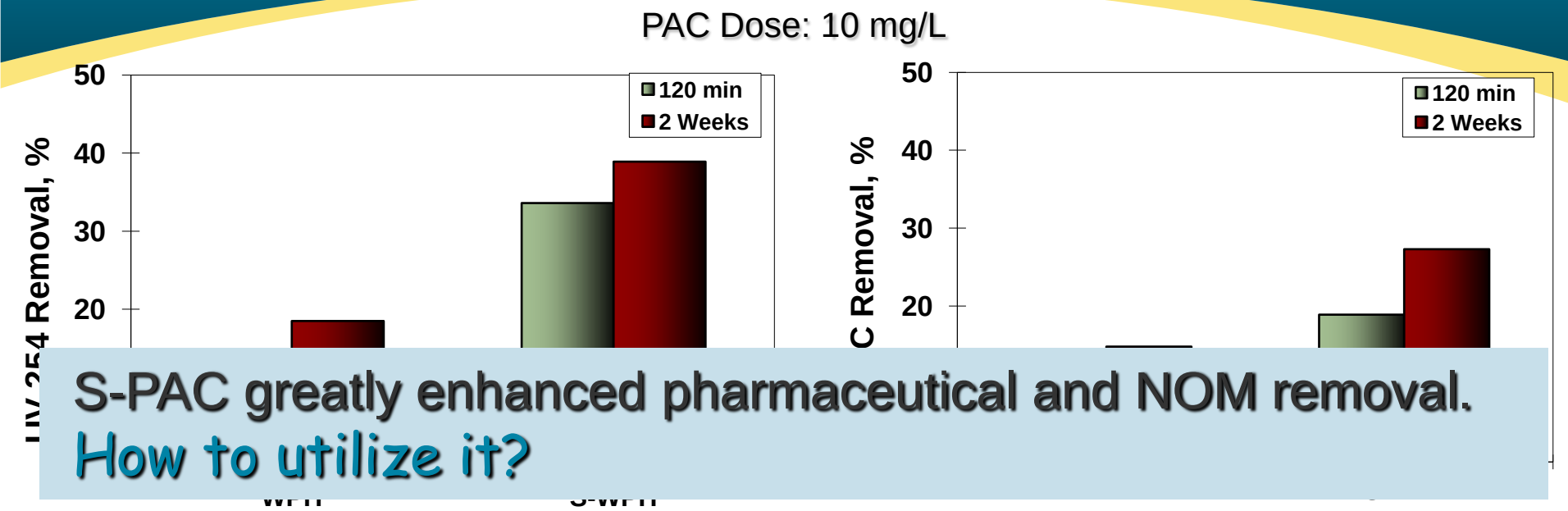
PAC Dose: 5 mg/L





- TMP kinetics: S-WPH>>WPH
- TMP capacity: S-WPH≈WPH
- **S-WPH almost reaches adsorption equilibrium at ~15 min!**

4. Effect of PAC particle size



S-PAC greatly enhanced pharmaceutical and NOM removal.

How to utilize it?

- NOM capacity: S-WPH>>WPH
- S-WPH provides better NOM removal (S-WPH≈2×WPH)!

Control DBP Formation?

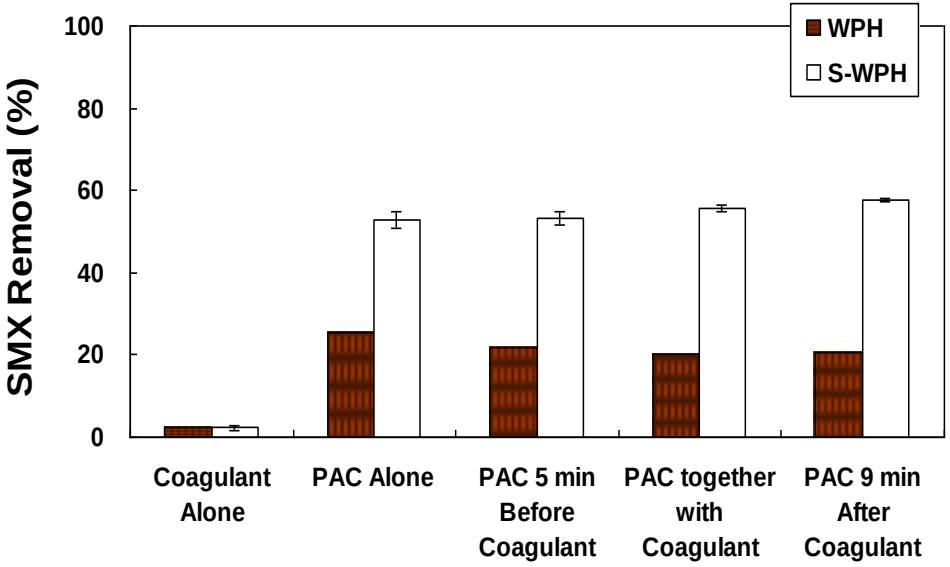
Control Membrane Fouling?

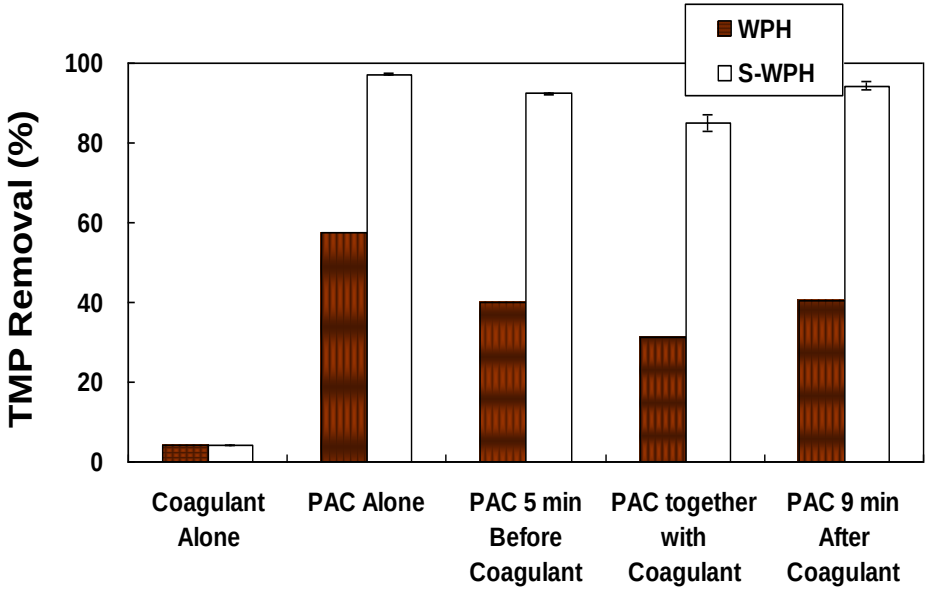
2. Jar Tests

- Rapid mixing: 100 rpm for 30 seconds (Coagulation)
- Slow mixing: 25 rpm for 36 minutes (Flocculation)
- Settling: 3.5 minutes (Sedimentation)

5. Effect of PAC particle size and timing of PAC addition

Coagulant: Alum Dose: 55 mg/L pH: 6.2 PAC Dose: 5 mg/L PAC Contact time: ~40 min





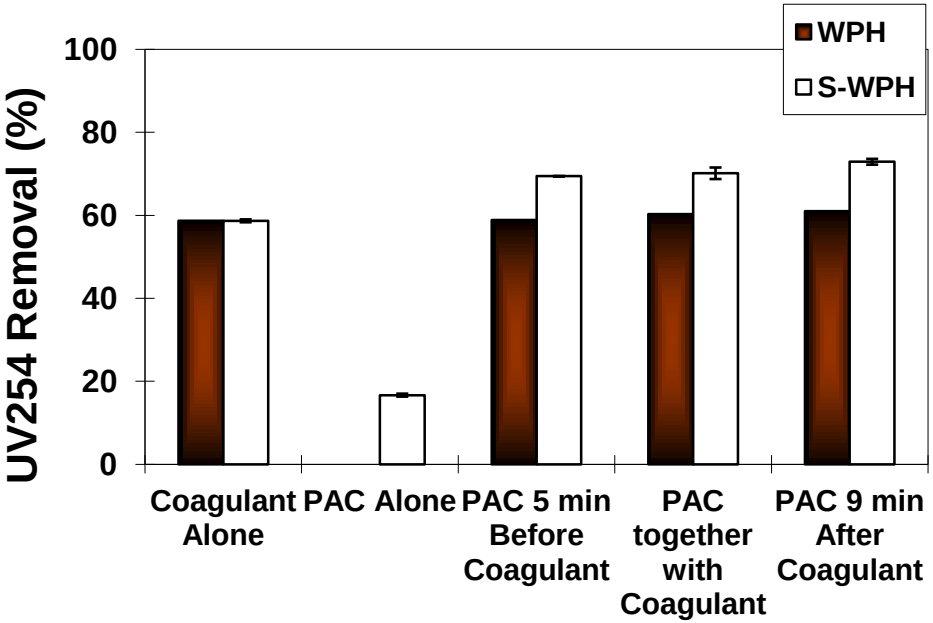
- SMX removal: S-WPH≈2-3×WPH
- TMP removal: S-WPH≈1.5-3×WPH

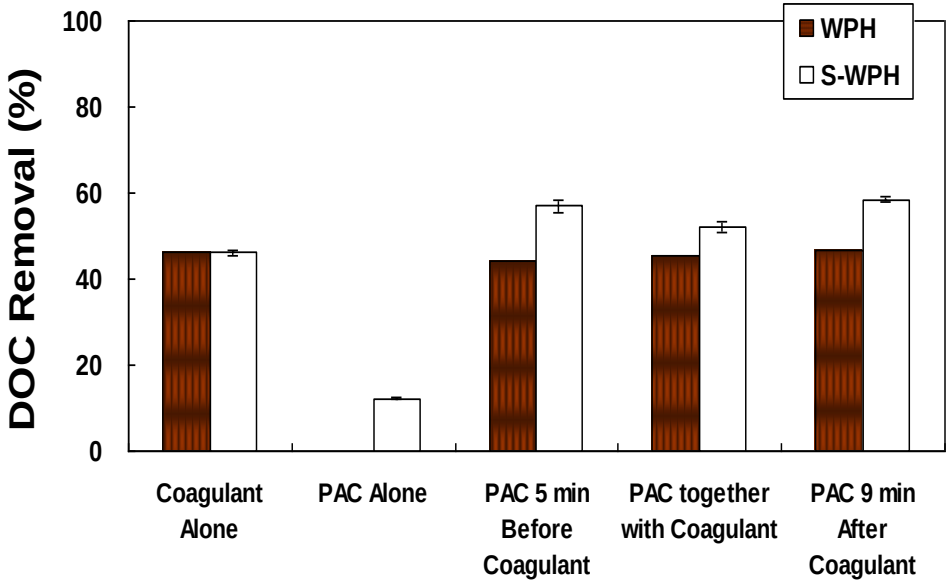
- Aluminum hydroxide floc adversely affected TMP removal.

The interference was largest when PAC was added together with alum.

5. Effect of PAC particle size and timing of PAC addition

Coagulant: Alum Dose: 55 mg/L pH: 6.2 PAC Dose: 5 mg/L PAC Contact time: ~40 min

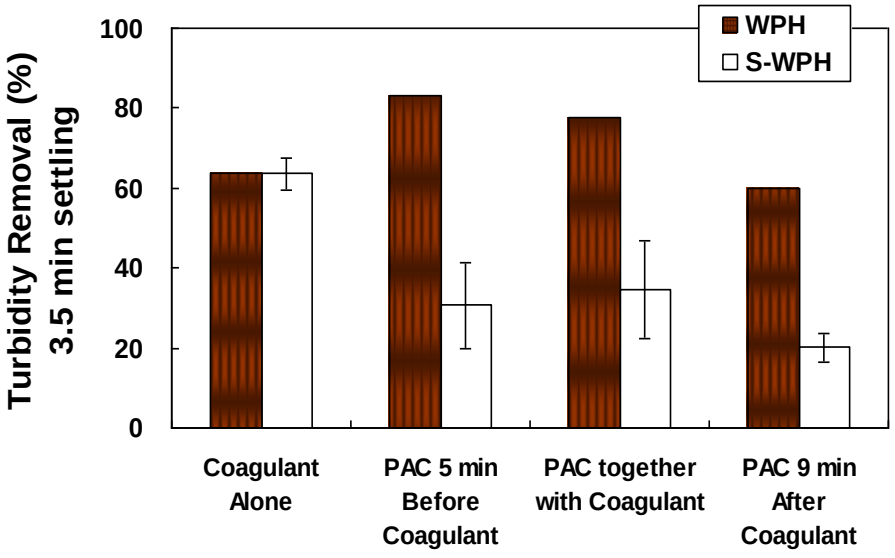


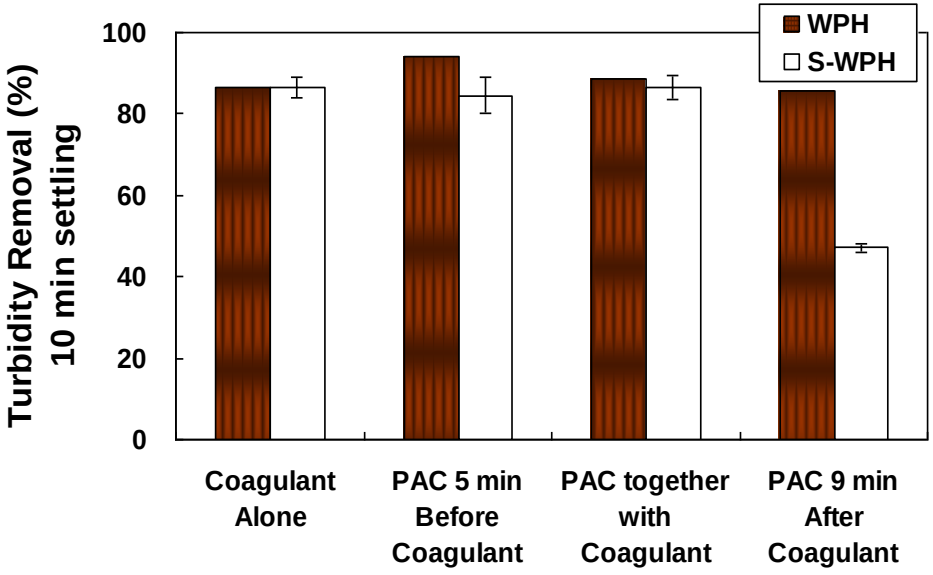


- Coagulant primarily contributed to NOM removal.
- Timing of PAC addition did not affect NOM removal.

5. Effect of PAC particle size and timing of PAC addition

Coagulant: Alum Dose: 55 mg/L pH: 6.2 PAC Dose: 5 mg/L PAC Contact time: ~40 min

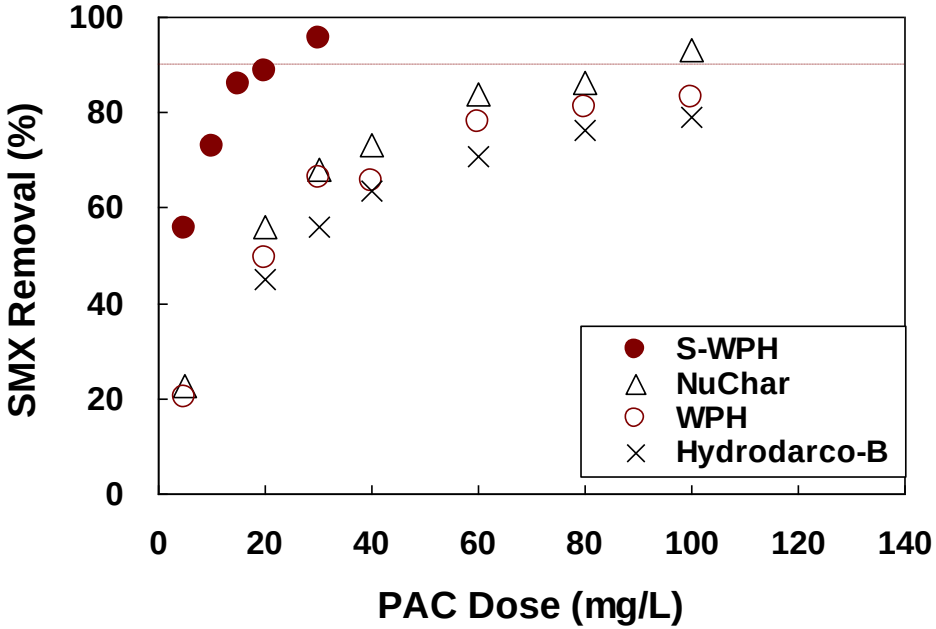


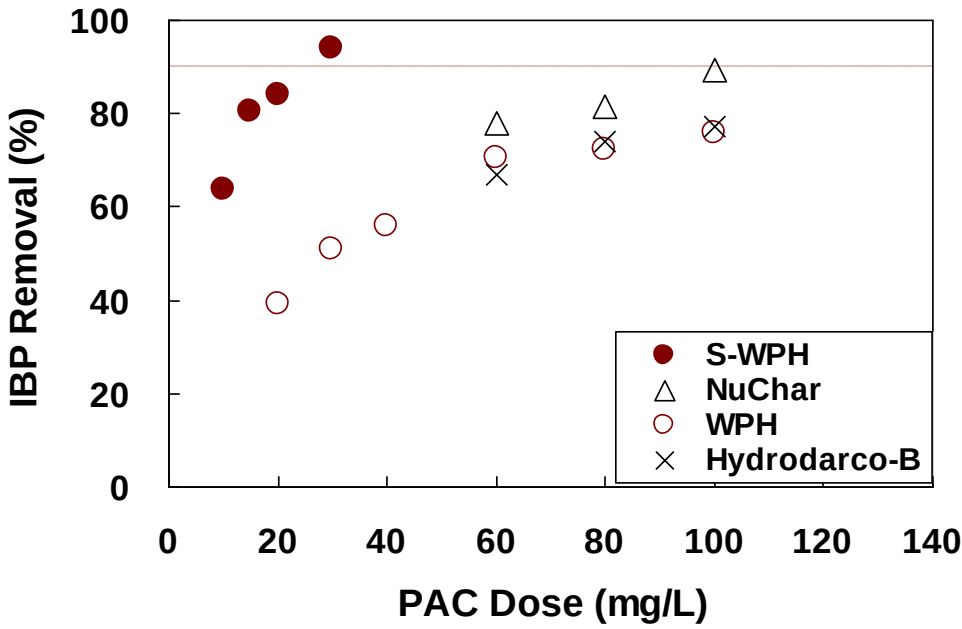


- S-WPH was incorporated into settleable floc, but floc settleability was adversely affected.
- PACs were better incorporated into floc when added before or together with coagulant.

6. Effect of PAC dosage

Coagulant: Alum Dose: 55 mg/L PAC contact time: ~40 min



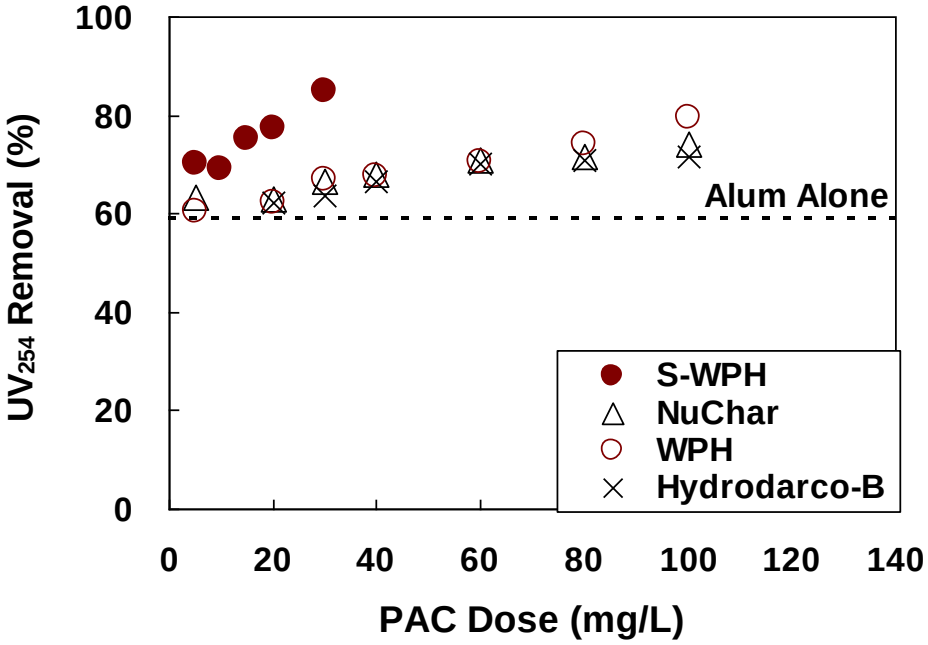


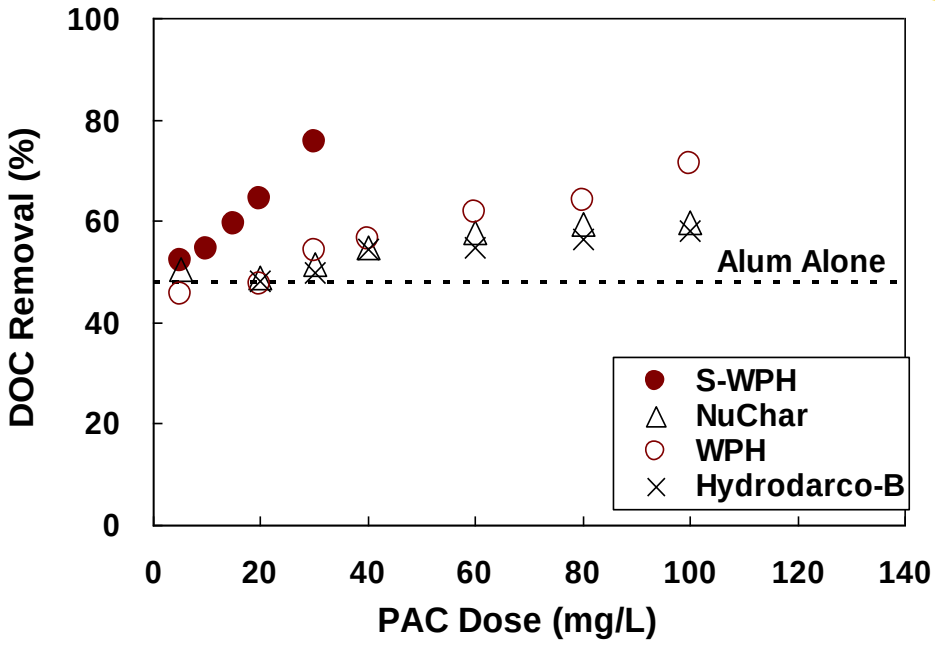
Required dosage for 90% SMX and IBP removal:

~ 25 mg/L for S-WPH ≥100 mg/L for normal PACs

6. Effect of PAC dosage

Coagulant: Alum Dose: 55 mg/L PAC contact time: ~40 min





Alum primarily contributed to NOM removal.

Required dosage for extra 10% NOM removal:

5 mg/L for S-WPH 40-60 mg/L for normal PACs

Conclusions

- **PACs effectively removed some pharmaceuticals.**

  - At 1-h contact time, 10 mg/L of PAC removed 95% TMP, but only 17% SMX
  - In jar tests, required dose of PAC for 90 % SMX and IBP removal was ≥100 mg/L

- **S-PAC greatly enhanced pharmaceutical removal.**

  - At 1-h contact time, 10mg/L of S-PAC removed 60% SMX
  - In jar tests, required dose of S-PAC for 90 % SMX and IBP removal was 25 mg/L

- **S-PAC can be incorporated into settleable floc, but with poorer settleability.**

- **PAC should be added before coagulant.**

  - Higher TMP removal
  - Lower settled water turbidity

Questions?

Removal of Pharmaceuticals by PAC Adsorption

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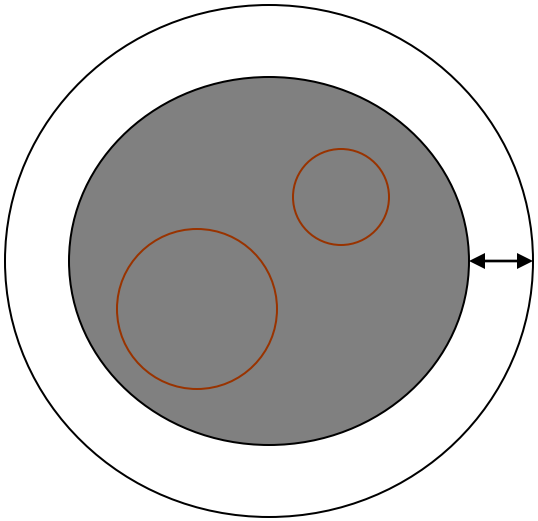
PNWS-AWWA 2013
Spokane, WA

NOM Adsorption Mechanism

- **NOM is able to penetrate only certain distance into PAC particles. (Matsui *et al*., 2009)**

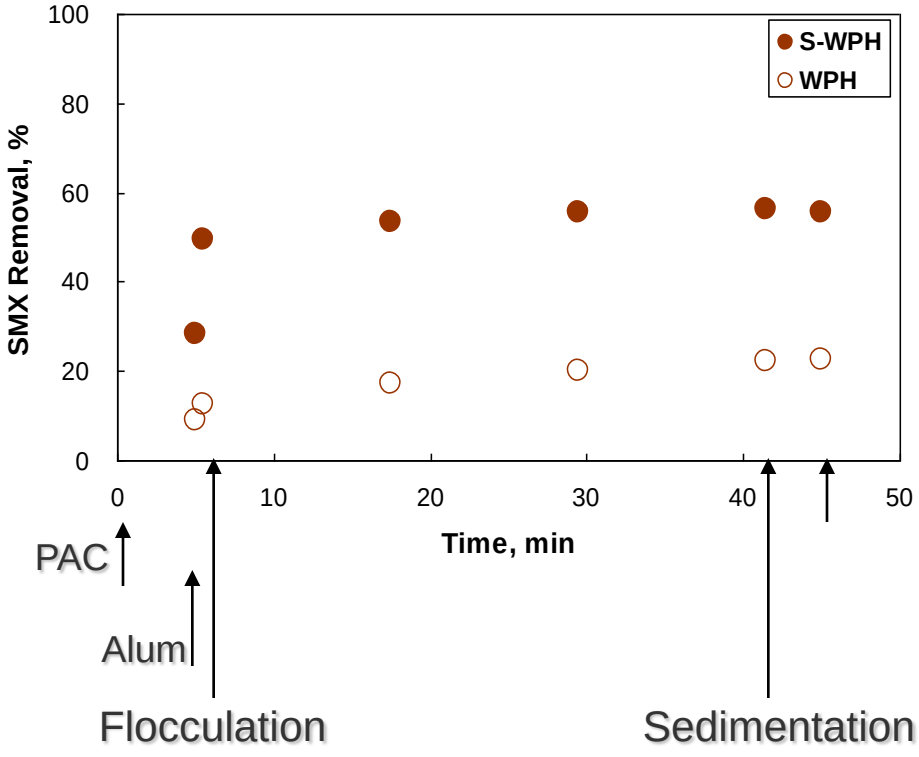


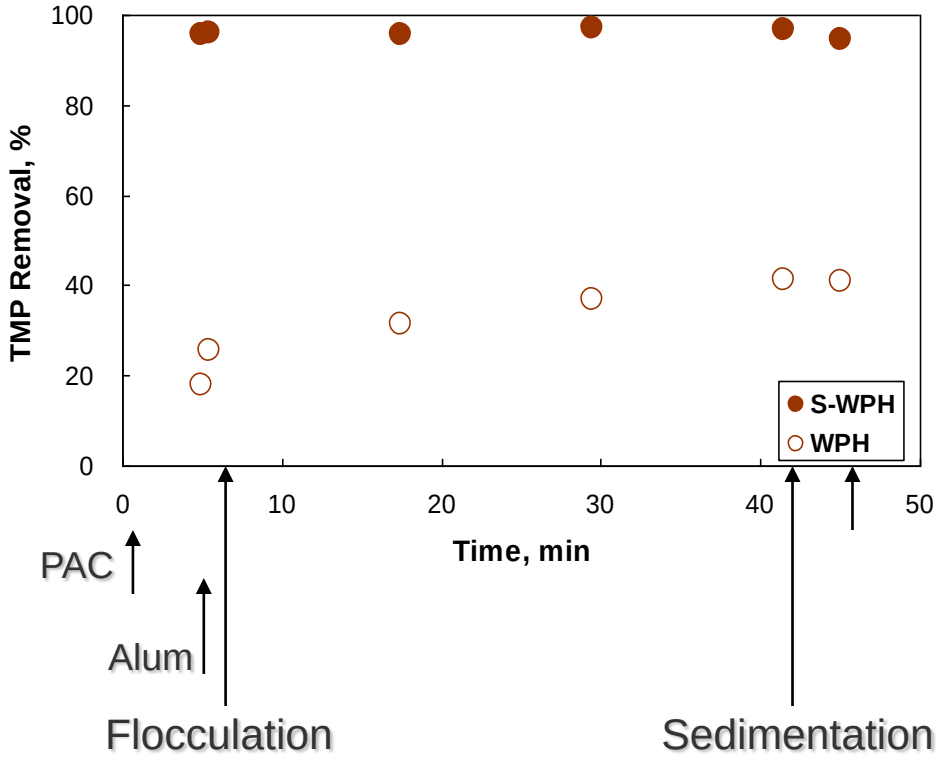
Normal PAC

Sub-micrometer PAC

Jar Test Kinetics

Coagulant: Alum Dose: 55 mg/L pH:6.2 PAC Dose: 5 mg/L





Pharmaceutical removal in jar tests occurred mostly in flocculation process.