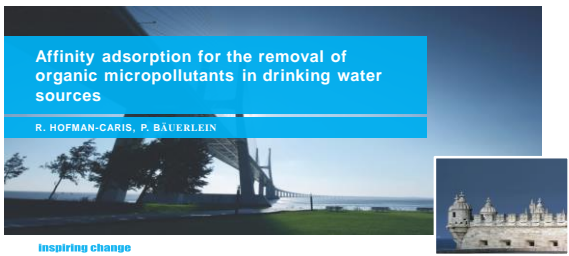


Affinity adsorption for the removal of organic micropollutants in drinking water sources

R. HOFMAN-CARIS, P. BAUERLEIN




Inspiring change

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Outline of presentation

- Introduction
- Principle of affinity adsorption
- Results: proof of principle
- Conclusions



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Introduction

Pharmaceuticals in the watercycle

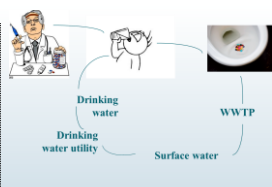
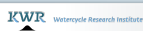
Many organic micropollutants in water cycle

Pharmaceuticals are found in sources of drinking water:

- Groundwater
- Surface water
- Bank filtrate

Origin:

- Human
- Veterinarian

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Introduction


Pharmaceuticals in the watercycle

Concern:

- Designed to affect organisms
- Metabolites may be at least as reactive

Problems:


- "small" molecules
- Hydrophilic/charged
- Difficult to remove by common treatment methods



Adsorption: too small break through

Filtration: too small charge formation of concentrate Large energy demand

(Advanced) oxidation: not always sensitive formation of byproducts large energy demand




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Introduction

Pharmaceuticals in the watercycle


Two possible strategies:

1. Polishing step in drinking water production process
2. Removal at the source



Advantages:

- Limited amount of different pharmaceuticals
- "high" concentrations



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Principle of affinity adsorption

Adsorption depends on:

- Properties adsorbate
- Surface properties adsorbent
- Presence of compounds/groups on surface
- Presence of competitors (other compounds, NOM, salts, etc.)
- pH

Affinity adsorption depends on:

Specific interactions between adsorbent surface groups and functional groups within molecule.

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Principle of affinity adsorption

Interaction	example
Van der Waals	(Induced) dipole interactions
Dative bond	
Coulomb forces	NaCl
Hydrogen bonding	
Base pairing (special case of hydrogen bonding)	
Acid - base reaction	
π - stacking	

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Results

Polymer adsorbents

Oasis materials:

Polymer backbone

Different functional groups

R = SO₃⁻ (MCK), COOH (WCX), H (HLB)

—N(Me)₂Bu (MAX)

—N (WAX)

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Results

Polymer adsorbents: effect of competition

Material	Removal MAX (%)	Removal PAC (%)
Unmodified	100	100
MAA	100	100
MAE	100	100
MAH	100	100
MAK	100	100
MAO	100	100
MAW	100	100
MAZ	100	100
MAAA	100	100
MAAAE	100	100
MAAAH	100	100
MAAAK	100	100
MAAAO	100	100
MAAAW	100	100
MAAAZ	100	100

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Results

Polymer adsorbents

Affinity adsorption: proof of principle

Disadvantages of adsorbents:

- Limited availability
- Expensive
- Difficult to remove in e.g. WTPP (density = 1)

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Results

Silica modified with silanes

TBA-Cl 1.56 μmol/m²

Fenyl 2.74 μmol/m²

Tosylic Acid 2.21 μmol/m²

Particle size ca. 50 μm

Specific surface area ca. 500 m²/g

Density ca. 2.65 g/cm³

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Results

Silica

Benzoic acid O=C(O)c1ccccc1

Carbamazepine CN1C=NC2=C1C(=O)N(C2)c3ccccc3

Diclofenac O=C(O)c1ccc(Cl)c(Cl)c1

Ibuprofen CC(=O)O[C@@H](C)C1=CC=C(C=C1)C

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Results

Silica

compound	Bmax (g/kg)	Mol/mol TBA or fenyl
Diclofenac	12	0,062
Benzoic acid	24	0,313
Ibuprofen	30	0,225
carbamazepine	12	0,042

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Results

Column experiments for removal of fullerene n-C60; break through curves

Activated Carbon

n-C60 UPW(AC)

Bare SiO₂

n-C60 in UPW(SiO2)

SiO₂/TBA

n-C60 in UPW(SiO2/TBA)

Effect of charge interactions: surface n-C60 is negatively charged.

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Conclusions

Proof of principle:

- Affinity adsorption effective method to deal with specific contaminants
- Extra filtration step in drinking water process
- Removal at source (high density → removal together with sludge)

Further research required:

- Optimization of adsorbents
- Adsorption kinetics: is adsorption fast enough for removal at source?
- Influence water matrix
- Economical aspects

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