Recent Progress on Advanced Adsorption Systems for Removal of Trace Contaminants in Water

James Economy and Zhongren Yue

Department of Materials Science & Engineering,

University of Illinois at Urbana-Champaign

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Center of Advanced Materials for Purification of Water with Systems

Examples Demonstrating Importance of Synthesis

- **High Surface Area Materials**
- **Ion Exchange and Chelating Systems**
- **Novel Systems for Disinfection**

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Evolution of High Surface Area Materials

Step 1	Commercialization of Activated Carbon Fibers	1970
Step 2	Control of Pore Surface Chemistry	1991-92
Step 3	Nature of Micropores and How They Form	1994-96
Step 4	Development of ACF on Glass Fiber Substrate	1995-97
Step 5	Contaminant Removal to Below 1 ppb	1998 -
Step 6	Low Temperature Chemical Activation	1999-
Step 7	Templating to Yield Activated Inorganic Fibers	2001-

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1970 , Development of Activated Carbon Fibers

Synthesis:

Using a commercial crosslinked phenolic precursor fiber (Kynol)

- Three grades:

  1500, 2000, 2500 m^2/g

Activated Carbon Fiber

Key Features:

- Greatly improved contact efficiency, much higher capacity and design flexibility.
- But expensive; brittle

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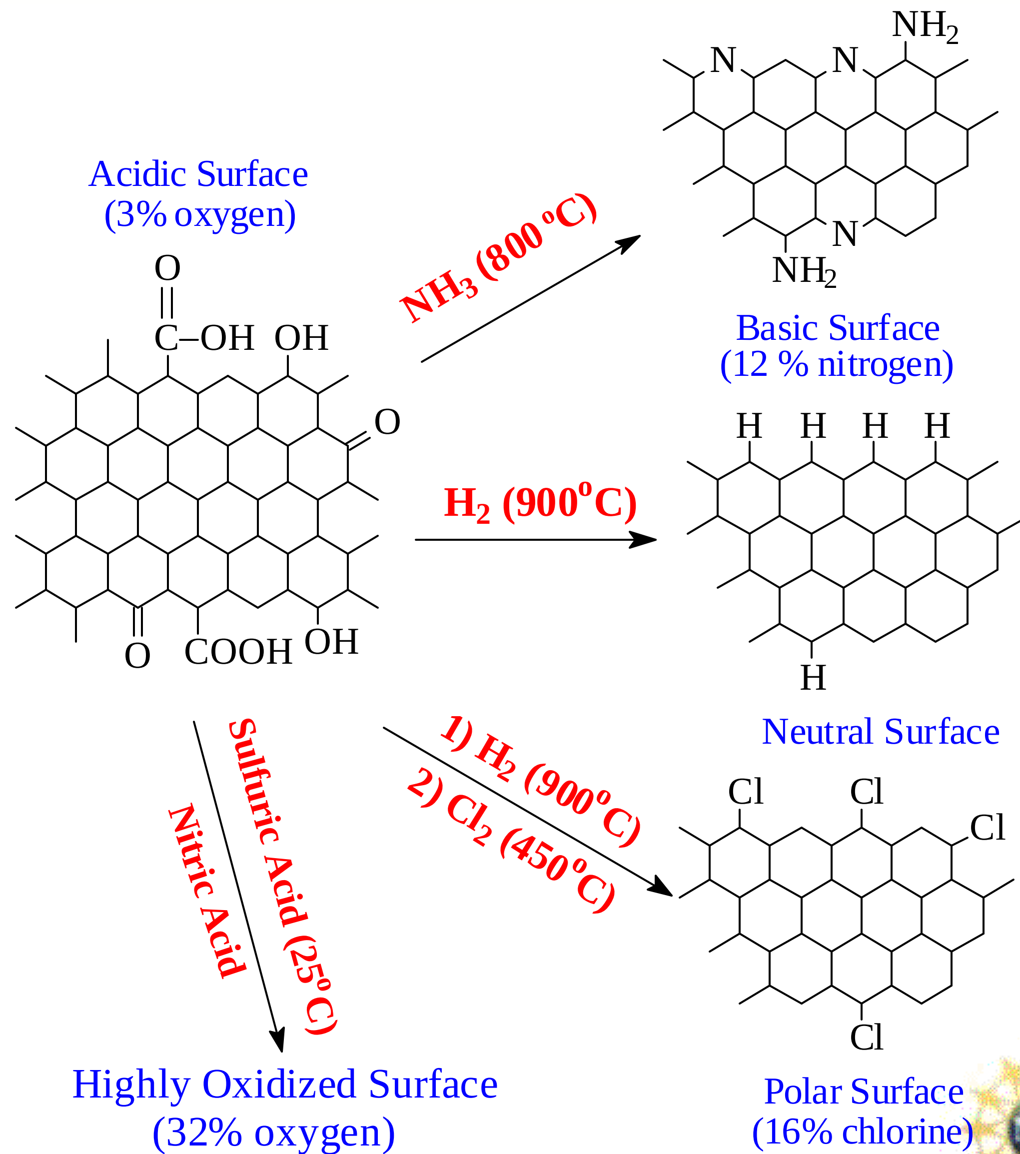
1991-92, Control of Pore Surface Chemistry---Acidic/Basic and Polar/Non-polar

Key Features:

- Can directly activate the phenolic fibers in presence of chemical reagent
- Greatly improved selectivity with even higher capacity, but still expensive; brittle



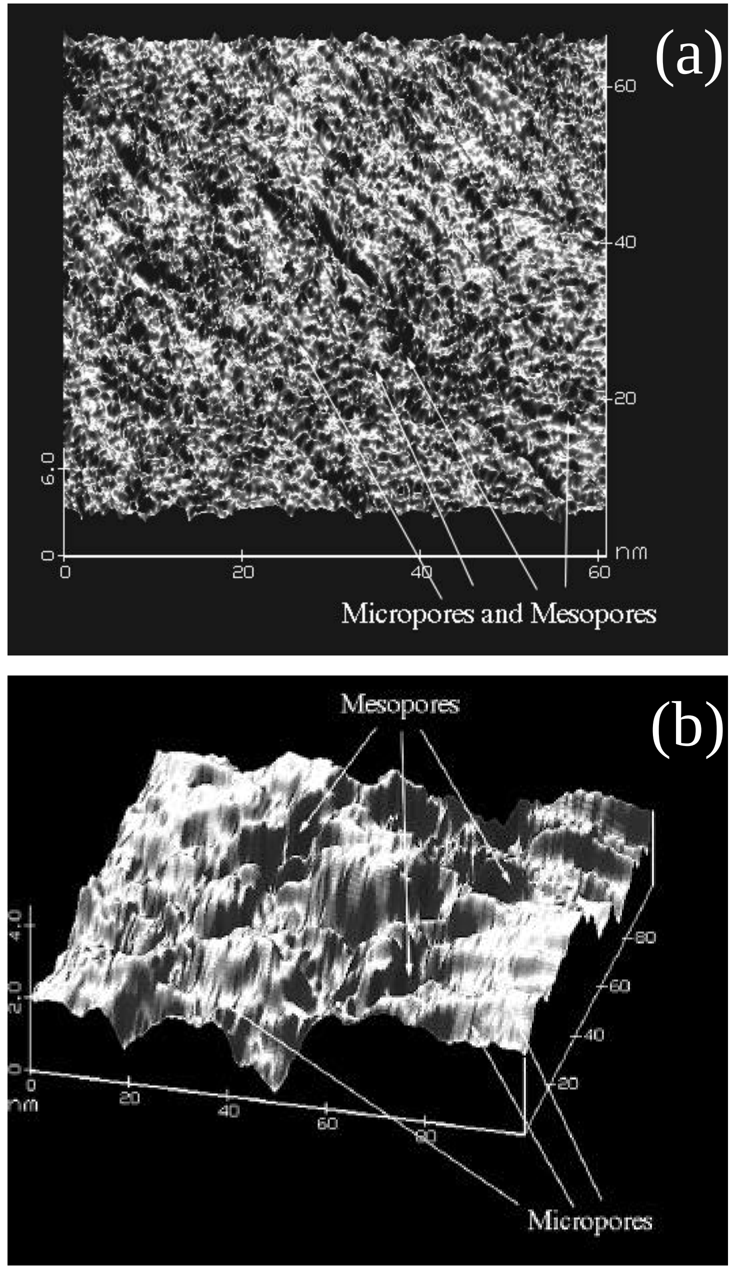
1994-96, Nature of Micropores and Their Origins

Key Features:

- **Micropores Accessed by using STM**
- **Can now control micropore dimension from 5-7 Å to 15-28 Å .**

Key Questions:

- **Slit sloped pores?**
- **Origins of porosity?**
- **Pore size distributions?**



Scanning Tunneling Microscopy (STM) of (a) a cross-section and (b) a highly etched surface of activated carbon fiber (ACF) *

* ***Carbon*** (1995), 33(3), 344-5.

1995-97, Development of ACF on Glass Fiber Substrate

Key Features:

- **Much lower cost, greatly simplified manufacture**
- **Excellent wear resistance (20 X over commercially available ACF's)**
- **Improved contact efficiency**
- **Ease of regeneration**

Synthesis of Activated Carbon Fibers

Glass Fiber

↓ Impregnate with Phenolic Resin and Cure

Phenolic Coated Glass Fiber

↓ Activate with steam, ammonia, air, CO_2 to create porous coating

Activated Carbon Coating on Glass Fiber

Cost of Precursor Materials:

Glass fiber: $0.4-0.5/lb

Phenolic: $0.7/lb

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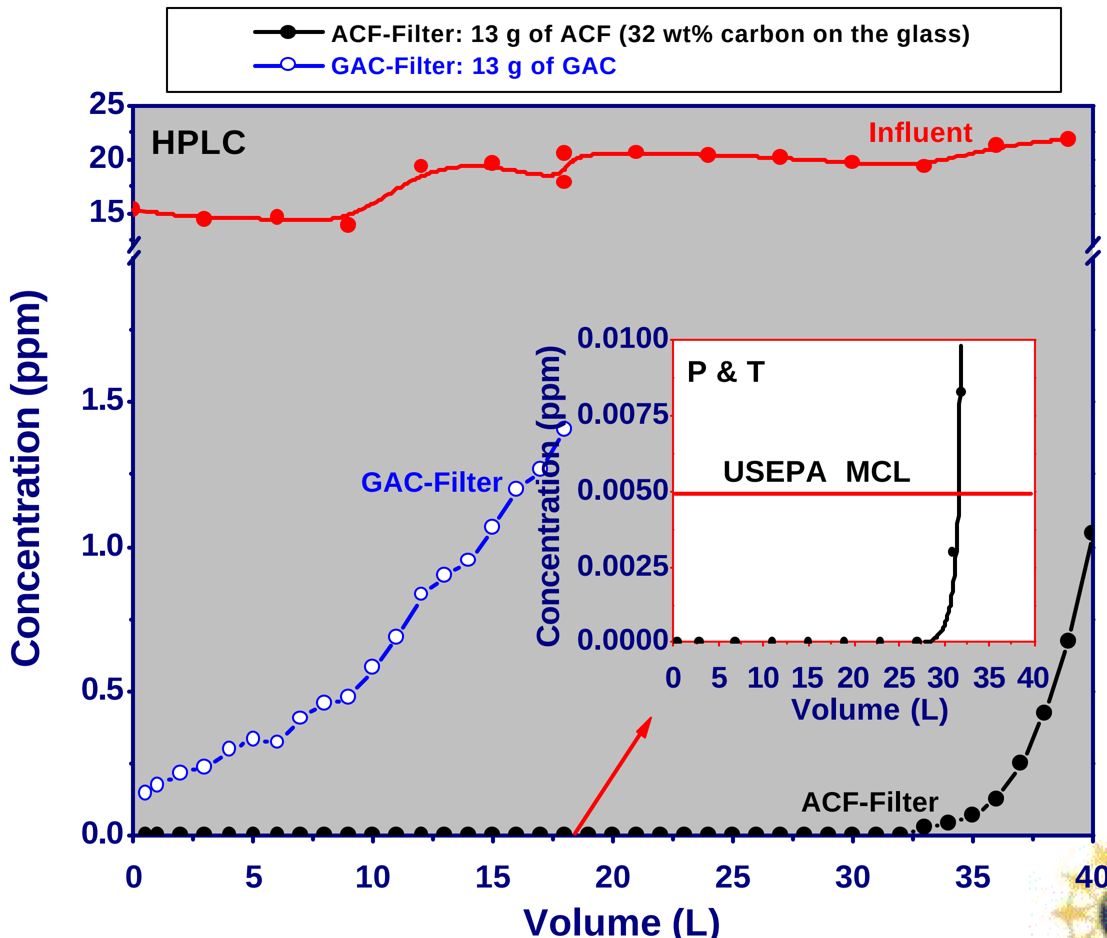
1998---, Design of Filters for Removing Contaminants to Below 1 ppb

Key Features:

- Much lower cost, greatly simplified manufacture
- Excellent wear resistance
- Improved contact efficiency
- Ease of regeneration
- Similar results observed with other organics

Breakthrough curves for benzene from both ACF and GAC filters

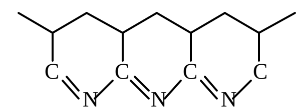
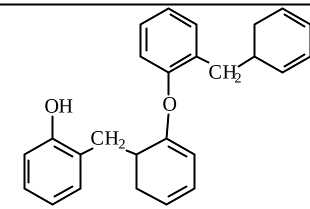
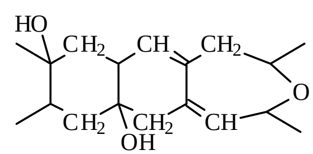
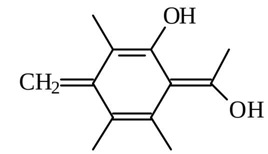


Enviro. Sci. Tech., 2001, 35, 2844-2848 .

1999---, Chemical Activation

Key Features:

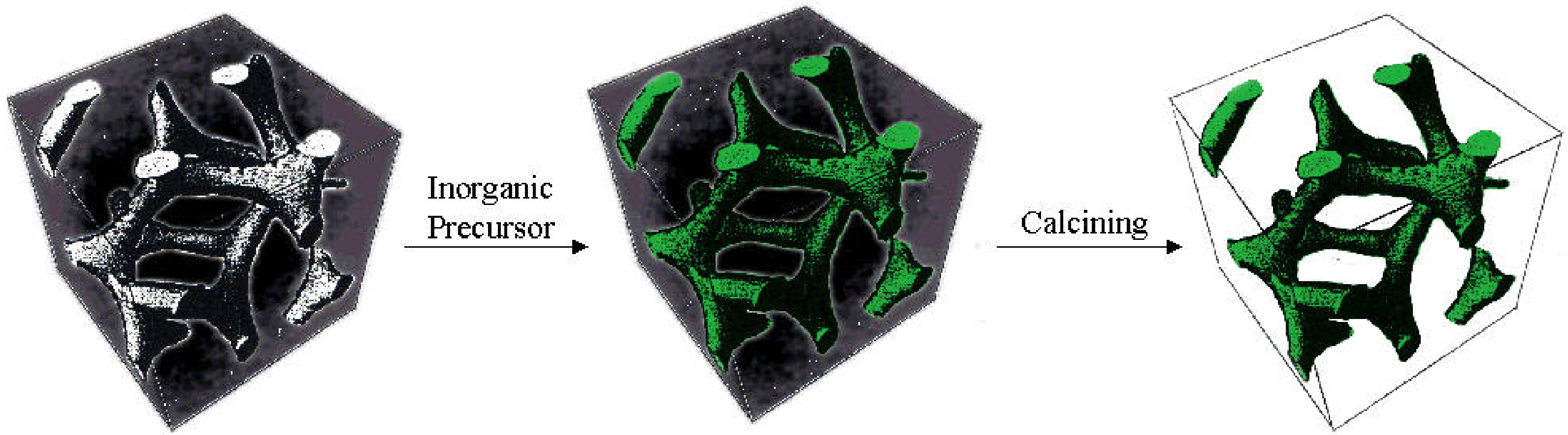
- Low activation temperature: 250-400°C
- Much higher yield (glass fiber substrate)
- Use of various phenolic, PAN, PVA and Cellulose etc.
- Controlled pore size distribution

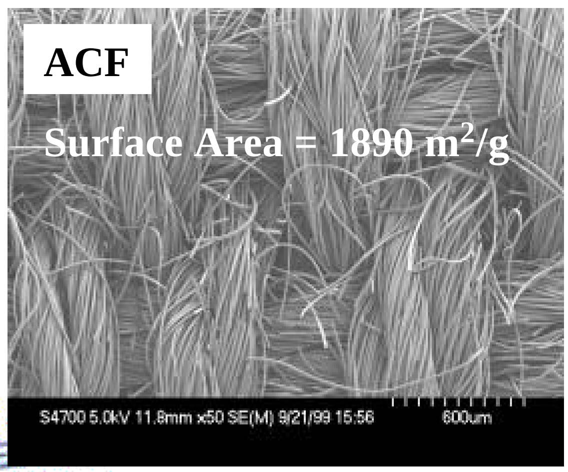
Resin	Activation Agent	Activation Temp. (°C)	Surface Area (m^2/g coating)	Yield (wt %)	Structure
PAN	$ZnCl_2$	400	1000	90	
Phenolic	$ZnCl_2$	400	1200	80	
PVA	H_3PO_4	250	1600	60	
Cellulose	$ZnCl_2$	400	2500	35	

Carbon, **2002, 40(8), 1181-1191** .

2001 ----, Activated Inorganic Fibers Templated from ACF

Key Features: A unique catalytic material and adsorption materials, higher thermal oxidative stability, ZrO_2, MgO, TiO_2, CaO, ZnO and Al_2O_3 fabrics





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Evolution of Ion Exchange and Chelating Systems

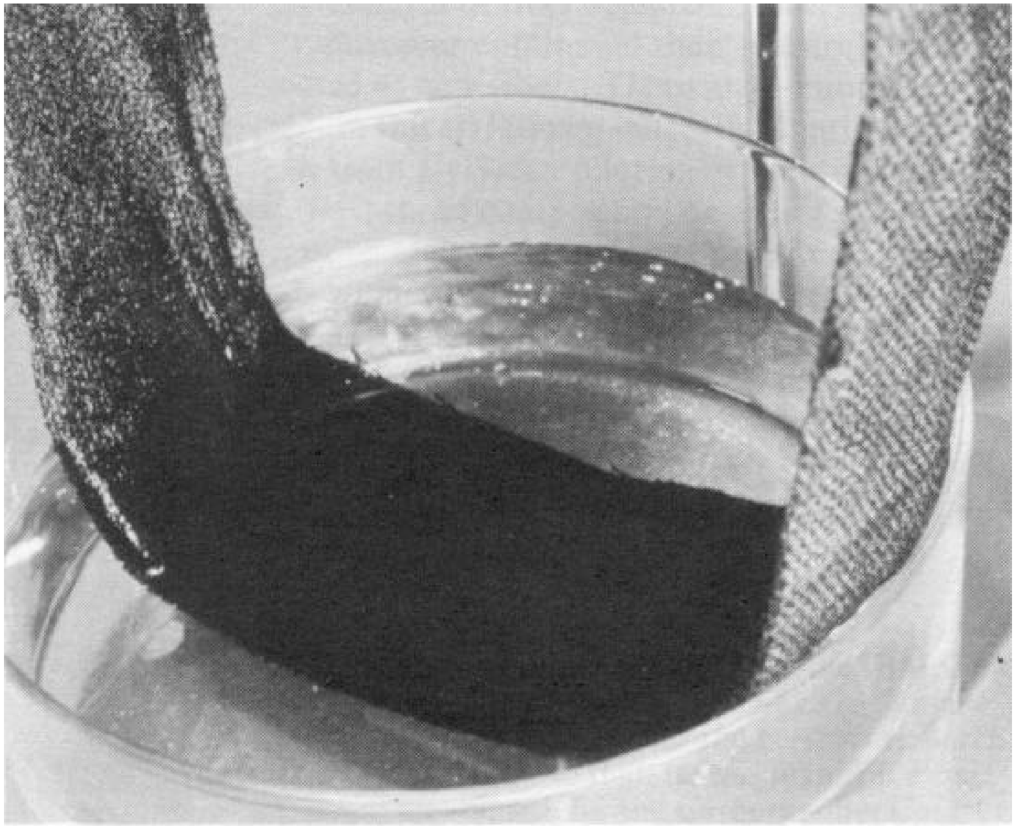
Step 1	**Discovery of Ion Exchange Fibers**	**1972**
Step 2	**Preparation of Cationic Fibers on Glass**	**2000**
Step 3	**Preparation of Anionic Fibers on Glass**	**2001**
Step 4	**Preparation of Sulfonated Carbon Fibers**	**2002**
Step 5	**Preparation of Chelating Fibers**	**2003**

1972, Development of Ion Exchange Fibers (Sulfonated Phenolic)

Key Features:

Several advantages over conventional ion exchange beads.

- Excellent ion exchange capacity,
- Design flexibility,
- But difficult to reproduce; expensive precursor.



Continuous reactivation of sulfonated phenolic fabric *

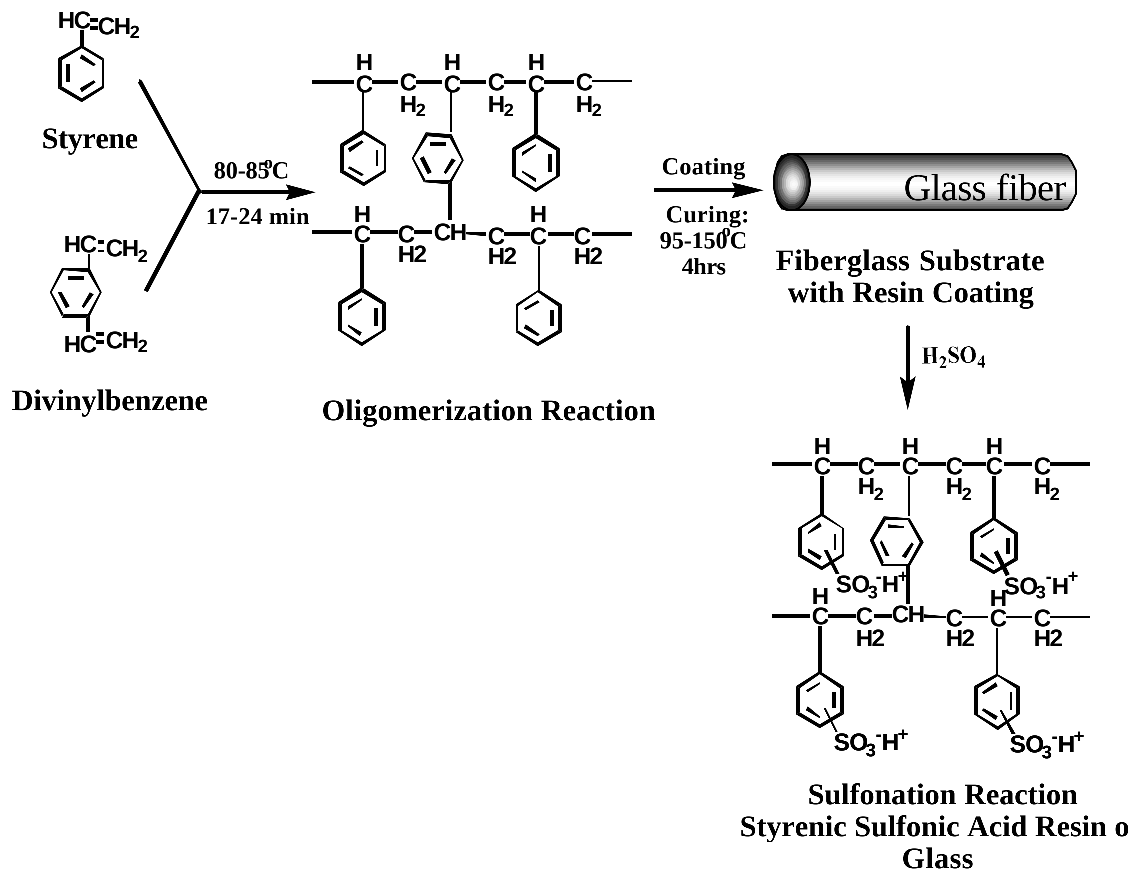
* CHEMTECH, Vol. 10, 1980

2000, Synthesis of Cationic Fibers on Glass Substrate

Key Features

Compared to Beads:

- Simplified synthesis (1/2 the steps)
- Resistance to osmotic shock
- Outstanding breakthrough data for Hg^{2+}, Pb^{2+} ion
- 10 × increase in rate of reaction / regeneration
- Remove most ionic contaminants to well below EPA standards



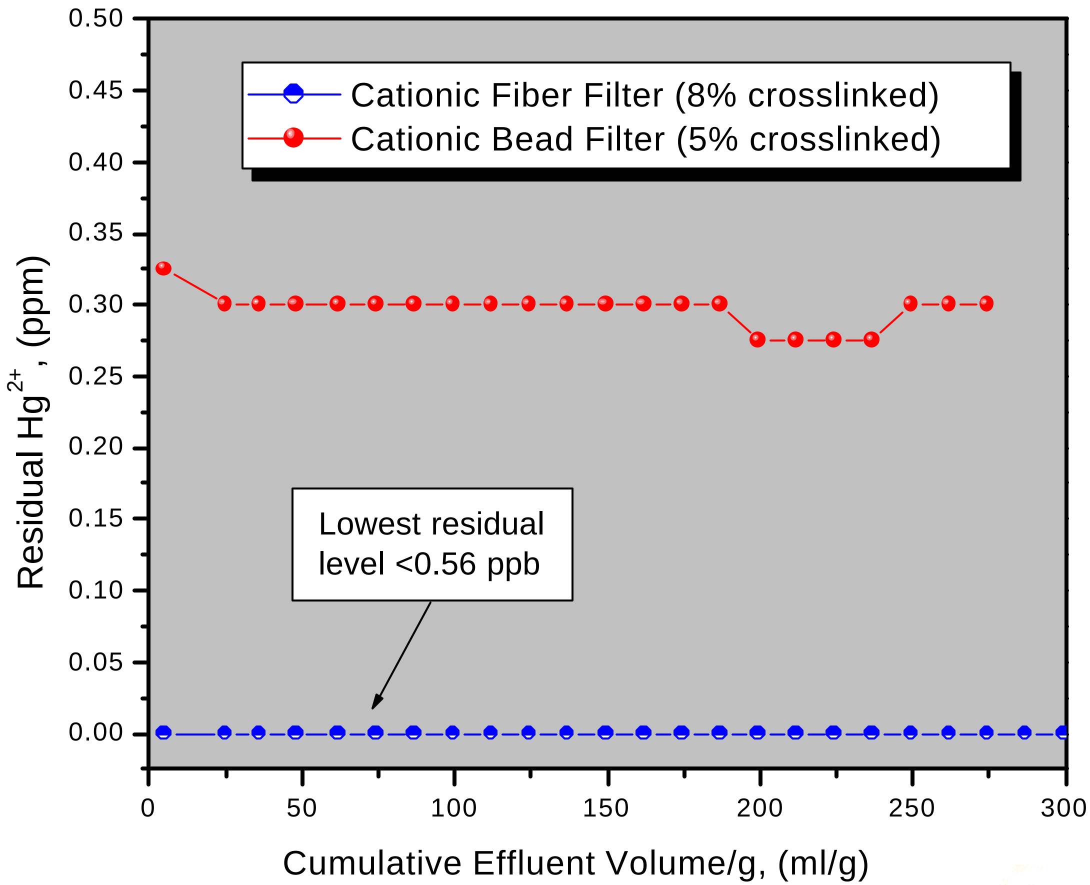
2000, Breakthrough Curves for Hg^{2+}

Key Features

Compared to Beads:

- Simplified synthesis (1/2 the steps)
- Resistance to osmotic shock
- Outstanding breakthrough data for Hg^{2+}, Pb^{2+} ion
- 10 × increase in rate of reaction / regeneration
- Remove most ionic contaminants to well below EPA standards

Breakthrough Curves for Hg^{2+} (0.75 ppm Influent) Comparing Cationic Fiber and Beads



Ind. Eng. Chem. Res., 2002, 41(25), 6436-42

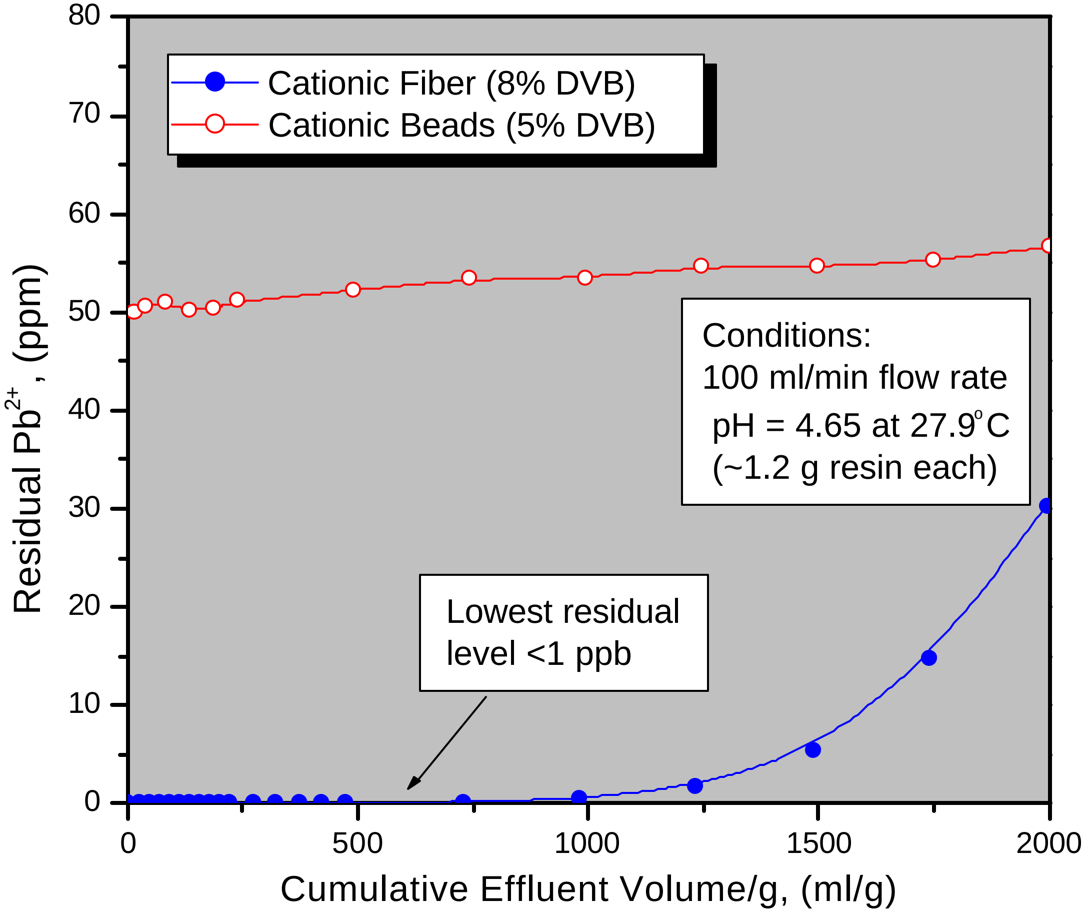
2000, Breakthrough Curves for Pb^{2+}

Key Features

Compared to Beads:

- Simplified synthesis (1/2 the steps)
- Resistance to osmotic shock
- Outstanding breakthrough data for Hg^{2+}, Pb^{2+} ion
- 10 × increase in rate of reaction / regeneration
- Remove most ionic contaminants to well below EPA standards

Breakthrough Curves for Pb^{2+} (150 ppm Influent) Comparing Cationic Fiber and Beads



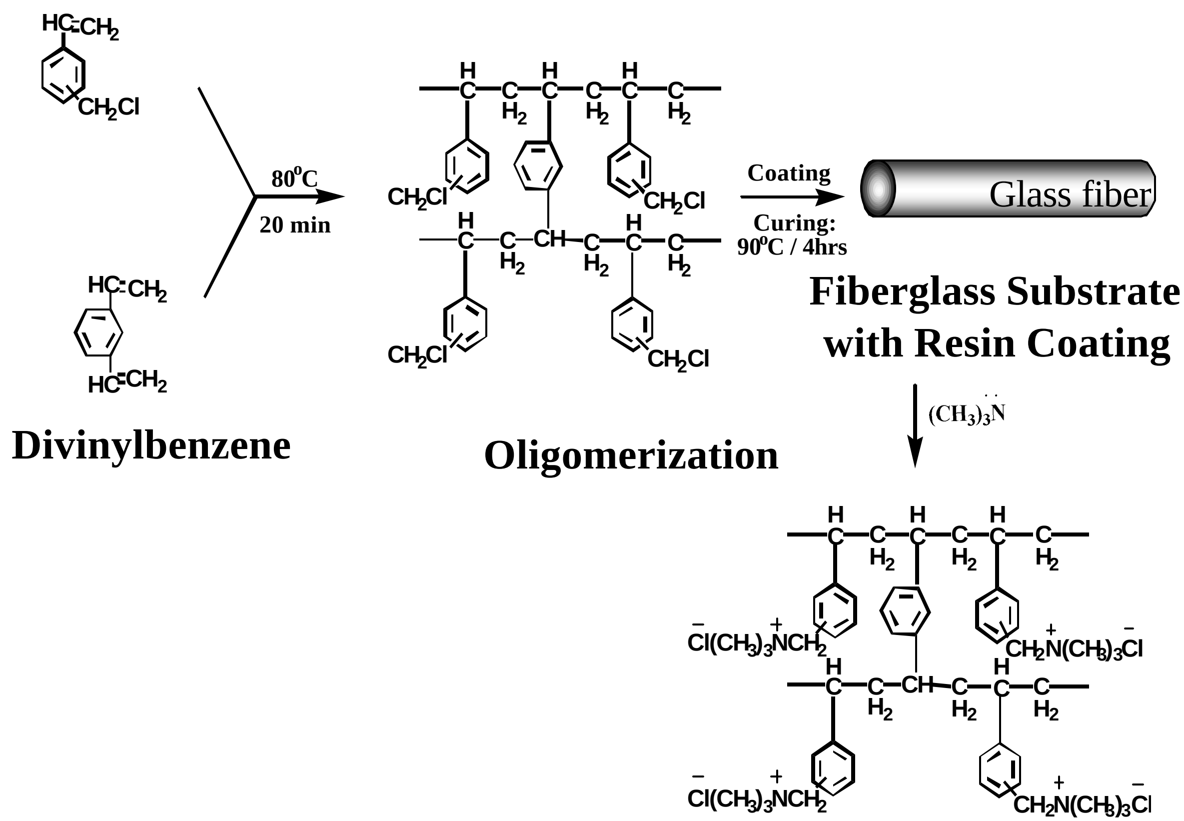
Ind. Eng. Chem. Res., 2002, 41(25), 6436-42

2001, Synthesis of Anionic Fibers on Glass Substrate

Key Features

Compared to Beads:

- Simplified synthesis (1/2 the steps)
- Resistance to osmotic shock
- Outstanding breakthrough data for arsenate ion
- 10 × increase in rate of reaction / regeneration
- Remove most ionic contaminants to well below EPA standards



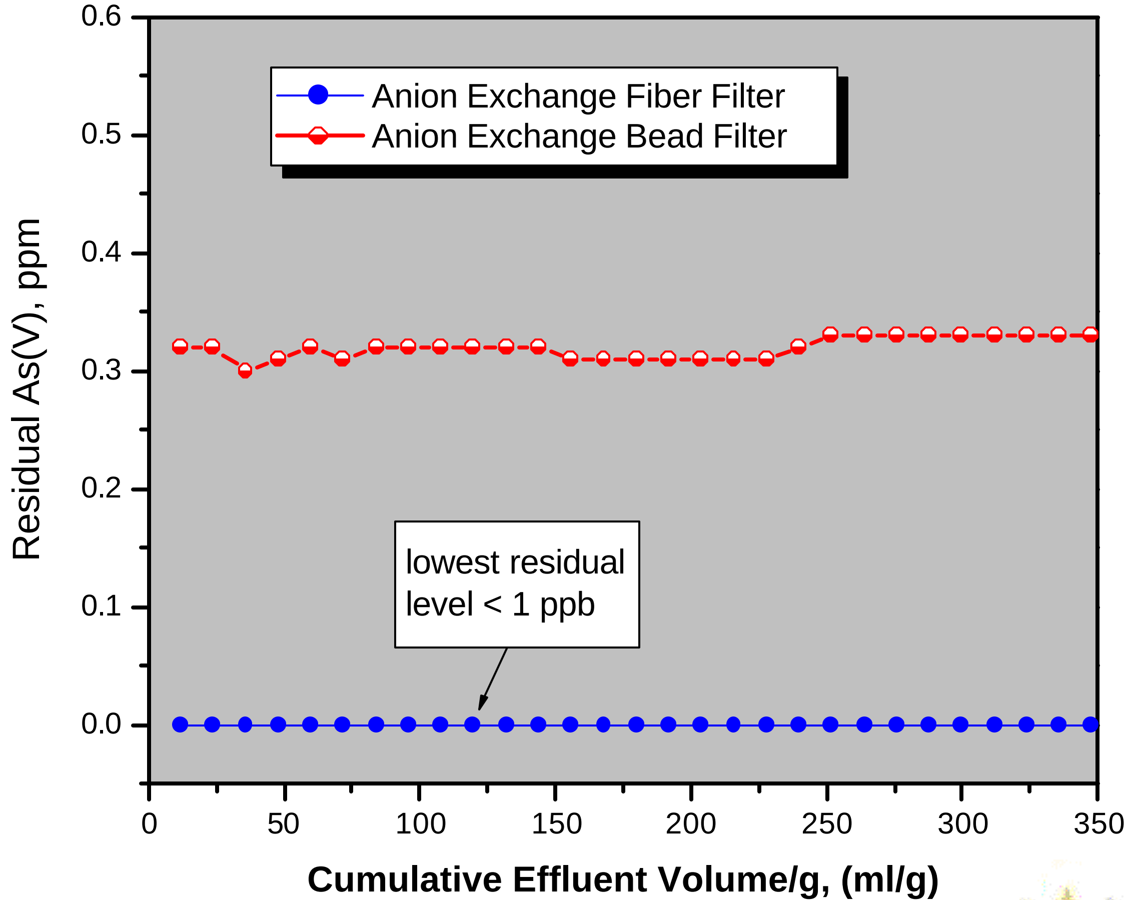
Ind. Eng. Chem. Res., 2002, 41(25), 6436-42

2001, Breakthrough Curves for Arsenate

Key Features
Compared to Beads:

- Simplified synthesis (1/2 the steps)
- Resistance to osmotic shock
- Outstanding breakthrough data for arsenate ion
- 10 × increase in rate of reaction / regeneration
- Remove most ionic contaminants to well below EPA standards

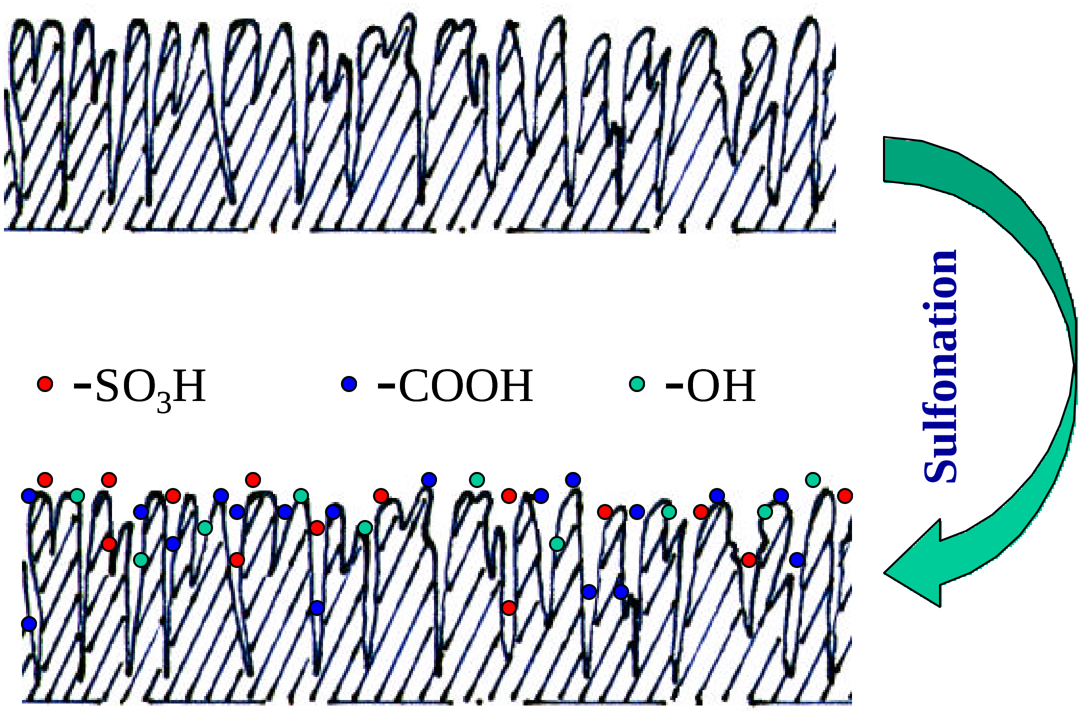
Breakthrough Curves for Arsenate (2.2 ppm Influent) Comparing Anionic Fiber and Beads



2002, Sulfonated Activated Carbon Fibers

Key Features: **Combines cationic exchange in a micropore structure; Higher thermal stability; High ion exchange capacities**

Activated Carbon Fiber Surface



Example:

Surface area:

1375 m^2/g coating

IE Capacity at pH=10:

2 meq/g coating

H_2SO_4 ↓ **250ºC**

Surface area:

1485 m^2/g coating

IE Capacity at pH=10:

17 meq/g coating

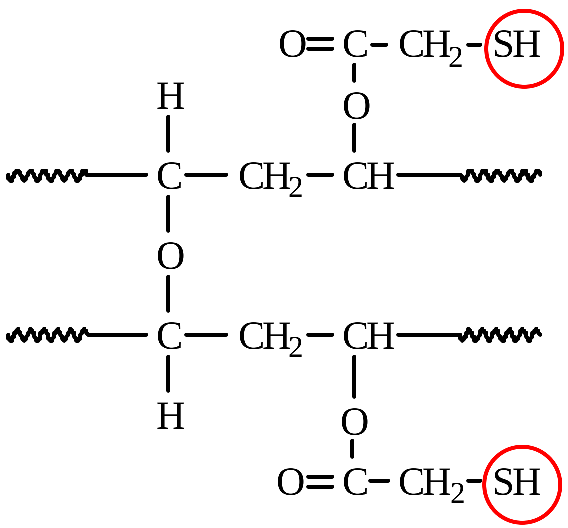
at pH=2:

2 meq/g coating

Carbon 2002, 40(13) 2323–32

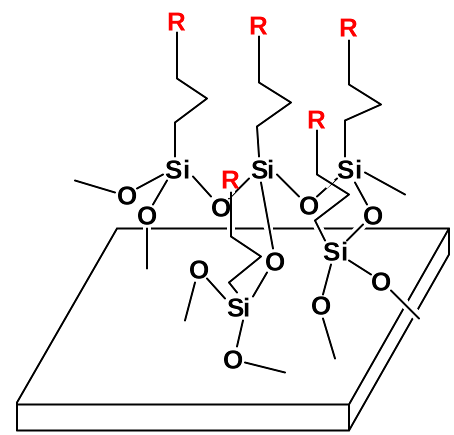
2003----, Chelating Fibers

Polyvinyl Alcohol Precursor



(A)

R = SH, $NH(CH_2)_2NH_2$



Polyorganosilsesquioxane coated fiber

(B)

Key Features:

- Permits removal of trace asenite to below 1 ppb.
- Mercaptyl group can also remove Hg^{2+}, Ag^{+} and Pb^{2+}
- Radioactive Cs^{+} can be removed to parts per billion in the presence of Na^{+}, K^{+}

Evolution of Novel Systems for Disinfection

Step 1 Ag on Glass Fiber or Carbon Fibers **2001**

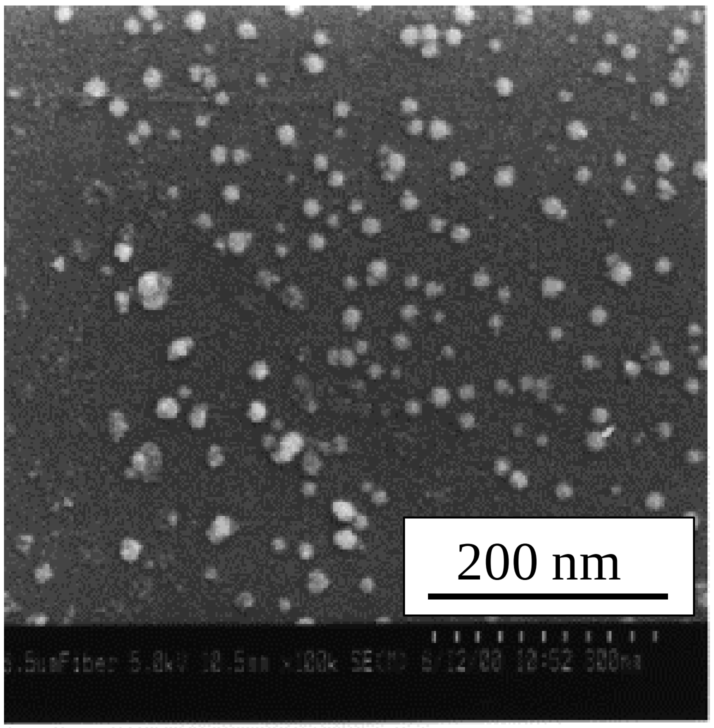
Step 2 Regeneration **2002**

Step 3 Ag on Metallic Foam **2003**

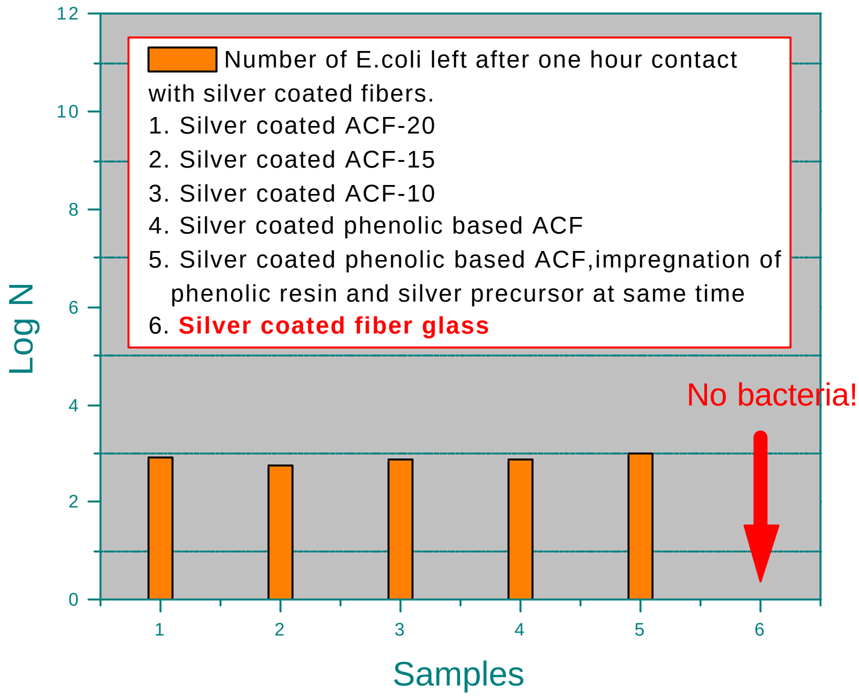
Step 4 $TiO_{2-x}N_x$ (also effective against NOM) **2003**

2001, Bactericide on Glass Fibers

Ag coated on glass fiber

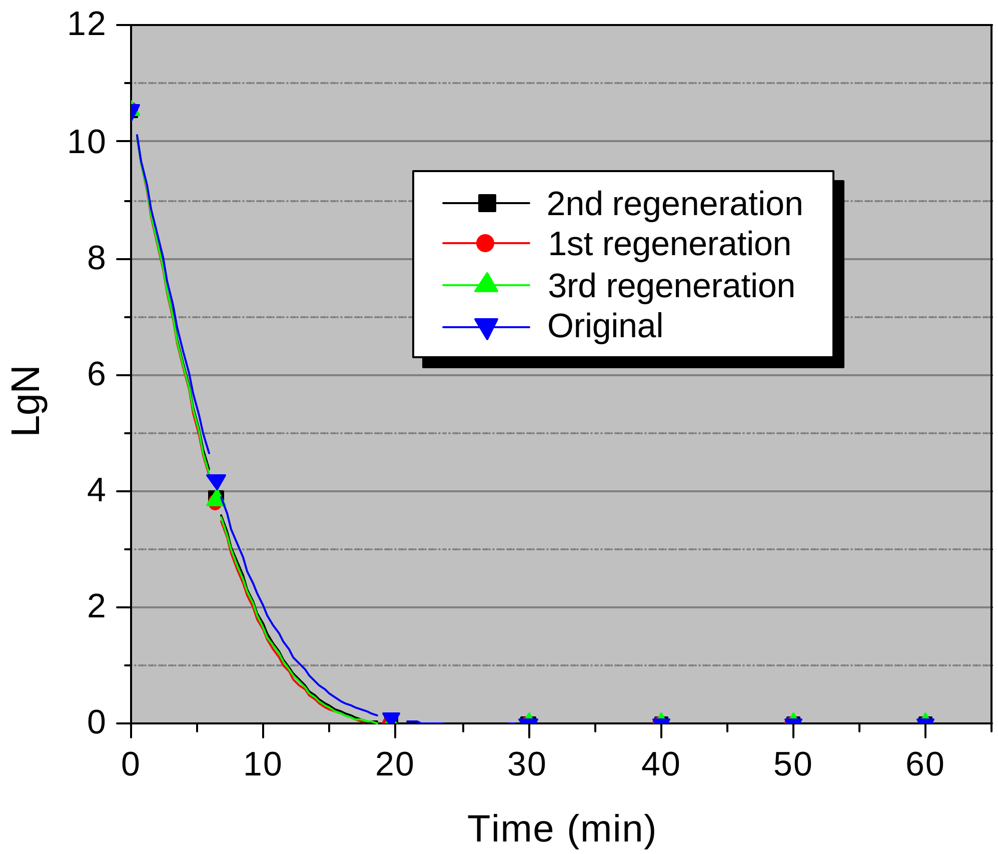


Colloidal Ag on glass fiber can effectively kill E.coli, as opposed to Ag on carbon fiber substrates.



2002, Regeneration of Ag-coated Glass Fiber Filter

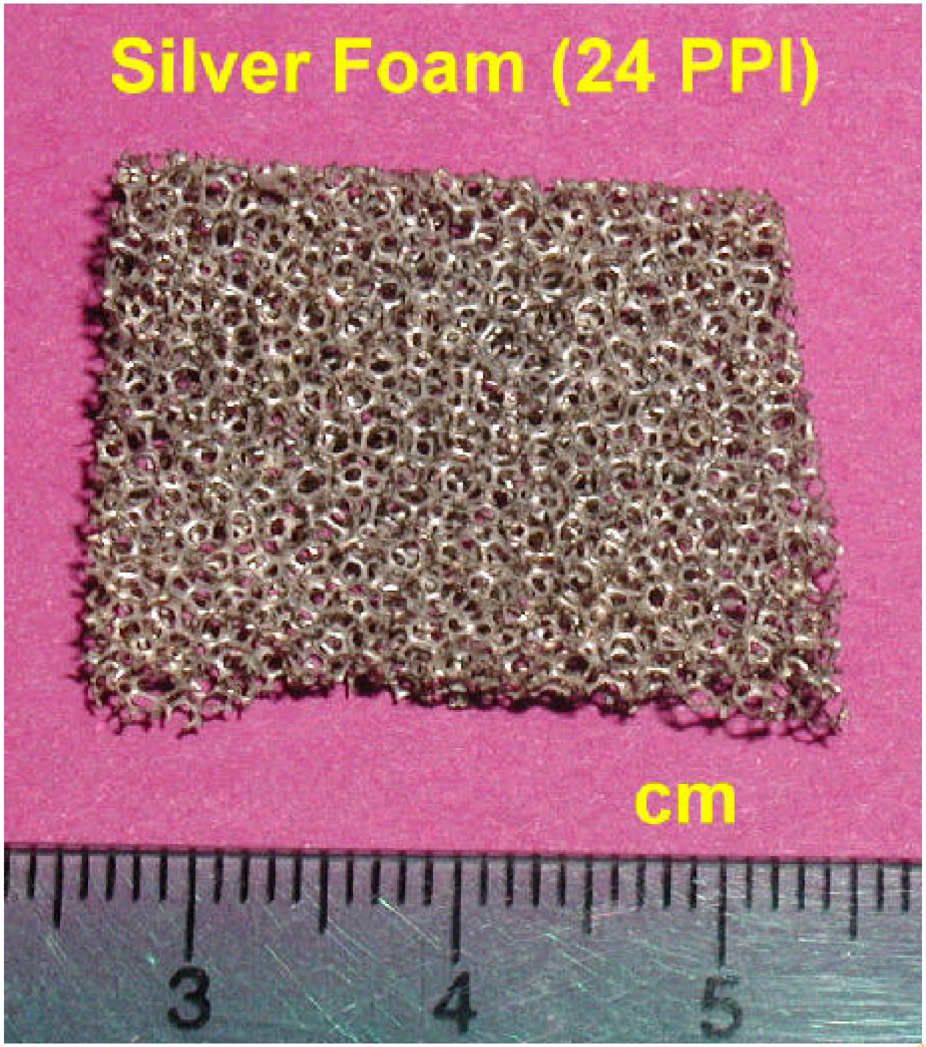
The filter can be readily regenerated to full activity.



2003 ---- , Design of Advanced Foams for Bactericidal Control

Key Features:

- Cu-Ag alloy foam, with large pores (3 mm), has been used to kill bacteria in water.
- To develop silver foams with fine cells by coating silver onto foams of metals and polymers.



Y.Q. Sun, T. Gao and A. Vincerns (CAMPWS members)

Conclusions

- Fiber form provides major advantages in greatly improving contact efficiency --- Impurities removal to below 1ppb in practically all cases.
- Use of glass fiber substrate simplifies and reduces cost of synthesis
- Glass substrate greatly improves wear resistance
- Possible applications

    Point of use for drinking water

    Treatment of effluent from chemical & related companies.

Acknowledgements of Work Done at UIUC

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