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SANITATION DISTRICTS OF LOS ANGELES COUNTY

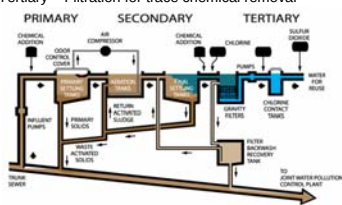
Abstract

This study aims to develop carbon aerogels capable of adsorbing halides, organics, trace metals, and other contaminants in wastewater. Carbon aerogels and silver-doped carbon aerogels were made using sodium carbonate and silver acetate catalysis of the resorcinol-formaldehyde polymerization, respectively. The surface area and pore data of these aerogels were determined through nitrogen gas sorption analysis. The sodium carbonate catalyzed aerogel was found to have a surface area of 813 m²/g and an average pore diameter of approximately 4 nm as determined by BET calculations. The BET surface area of the silver-doped gel was 586 m²/g, and its average pore diameter was slightly less than 2 nm. Further pore structure data was gathered through TEM. The effectiveness of adsorption by these aerogels and by anthracite coal, the commercially used material, was tested with solutions of bromide, hexavalent chromium, and toluene. The surface area and pore size of the sodium carbonate catalyzed aerogel would be conducive to the more effective physisorption of toxic chemicals, particularly organics like toluene. While the surface area and pore size are smaller for the silver-doped aerogel, the chemisorption provided by the silver (I) cations would likely allow it to adsorb more halides and other anions more effectively. Both of the aerogels should adsorb more than the anthracite coal because of the highly porous morphology and high surface area of carbon aerogels.

Background

Current Methods:

- ❖ Primary – Settling tanks for solid removal
- ❖ Secondary – Bacterial treatment for organic removal
- ❖ Tertiary – Filtration for trace chemical removal

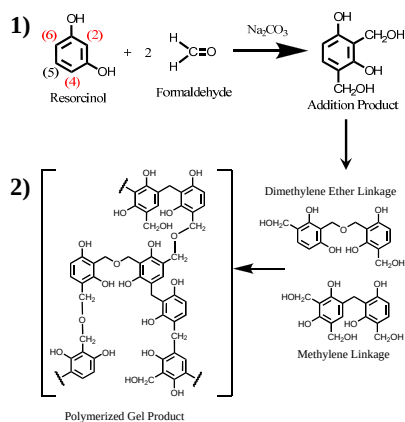


Our Objective:

- ❖ Replace activated carbon with carbon or silver-doped carbon aerogels for the tertiary phase
- ❖ Activated Carbon functions by adsorbing with its high surface area and porosity
- ❖ Carbon Aerogels will work in a similar fashion

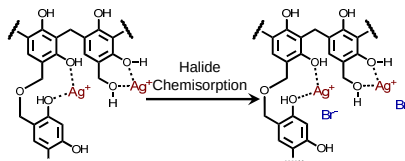
How to make a carbon aerogel

- ❖ Two-step resorcinol-formaldehyde polymerization in water

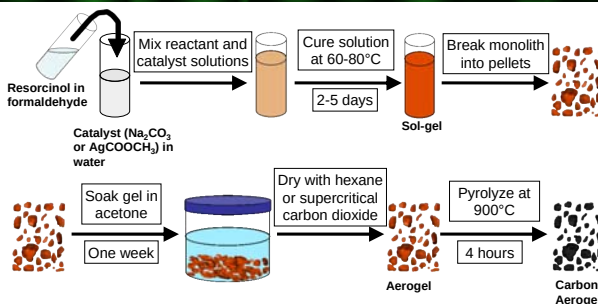


Making silver-doped carbon aerogels

- ❖ Same reaction, but using silver acetate as catalyst instead of sodium carbonate



Procedure



Formulations:

- ❖ Na₂CO₃ catalyzed aerogel (A-Na)
 - ❖ R:F – 1:2, R:W – 1:27, R:C – 48:1
 - ❖ Supercritically dried
- ❖ AgCOOCH₃ catalyzed aerogel (A-Ag)
 - ❖ Various ratios were tried
 - ❖ R:F – 1:2, R:W – 1:27, R:C – 225:1
 - ❖ Dried ambiently from hexane solution

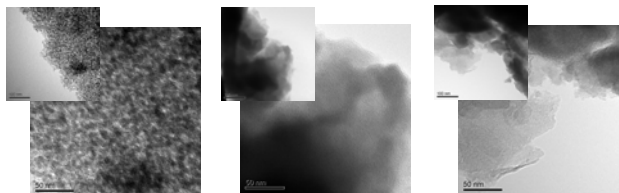


Above: A finished carbon aerogel

Results

Table 1: Surface area, pore diameter, pore volume and density measurements, and calculated porosity from gas sorption analysis and pycnometry

	A-AC	A-Na	A-Ag
BET Surface Area (m ² /g)	3.2*, 0.27*	813.7	586.0
Average Pore Diameter (nm)		4.1	1.8
Total Pore Volume (cm ³ /g)		0.852	0.276
Density (g/cm ³)	1.50	1.80	1.76
Porosity		60.6%	32.7%



Above: TEM pictures at magnifications of 300,000x and 600,000x. Samples are A-Na, A-Ag, and A-AC from left to right.

Table 2: A-Na equilibrium adsorption experiment results for chromium (VI) after 96 hours

C ₀ (ppm)	C _e (ppm)		% removal	
	A-AC	A-Na	A-AC	A-Na
0.72	0.6	< 1	16.5	
1.44	1.2	< 1	16.5	
2.875	2.3	0.147	20	94.9
5.75	5.14	< 0.1	10.6	> 98.3
11.5	9.7	< 0.1	15.7	> 99.1
23	10	< 0.1	56.5	> 99.6

Table 3: A-Ag equilibrium adsorption experiment results for bromide after 72 hours

C ₀ (ppm)	C _e (ppm)		% removal	
	A-AC	A-Ag	A-AC	A-Ag
1.074	1.12	<0.20	-4.28	>81.38
10.74	12.6	1.77	-17.32	83.52
21.48	22.6	11.8	-5.21	45.07
53.7	61.3	26.8	-14.15	50.09

Table 4: A-Ag equilibrium adsorption experiment results for Chromium (VI) after 72 hours

C ₀ (ppm)	C _e (ppm)		% removal	
	A-AC	A-Ag	A-AC	A-Ag
2.0125	2.18	1.34	-8.32	33.42
4.025	4.04	3.84	-0.37	4.60
8.05	8.75	7.90	-8.70	1.86
16.1	16.8	16.3	-4.35	-1.24
32.2	33.0	32.0	-2.48	0.62
64.4	64.2	63.6	0.31	1.24

Characterization:

- ❖ Gas sorption analysis using nitrogen for surface area and pore data using BET and BJH Theory
- ❖ Micromeritics ASAP 2010 using nitrogen at 77K
- ❖ Density measurements made with the helium pycnometer
- ❖ Micromeritics AccuPyc 1330
- ❖ Transmission electron microscopy (TEM) with 80 kV electron beam
- ❖ JEOL-JEM120EX
- ❖ Aerogels were tested against anthracite coal (A-AC)

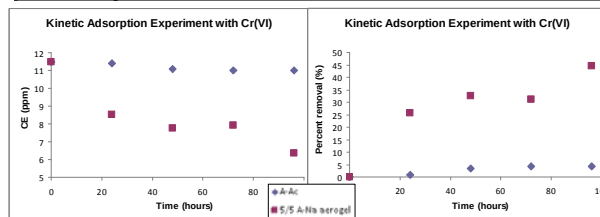
*Beyond detection limit

Adsorption experiments:

- ❖ Halides (Bromide), trace metals (chromium (VI)), and organic compounds were used as contaminants
- ❖ Stock solutions were made of each of the contaminants
- ❖ 20 mL of solution and 0.1g of adsorbent were used
- ❖ Equilibrium and kinetic experiments were conducted
- ❖ Samples tested by LACSD
- ❖ Only chromium (VI) results were reported for A-Na because the others were beyond the detection limit

Table 5: A-Na kinetics adsorption experiment results for chromium (VI) after 96 hours

Time (hours)	C _e (ppm)		% removal		q (mg Cr ⁶⁺ / g Aerogel)	
	A-AC	A-Na	A-AC	A-Na	A-AC	A-Na
0	11.5	11.5	0	0	0	0
24	11.4	8.54	0.87	25.74	2.12	2.692
48	11.1	7.76	3.48	32.52	2.18	2.848
72	11.0	7.92	4.35	31.13	2.2	2.816
96	11.0	6.36	4.35	44.70	2.2	3.128



Above: Kinetic adsorption experiments of chromium (VI) using A-Na versus A-AC, showing concentration and percent removal from left to right.

Conclusions and the Future Work

Conclusions:

- ❖ Carbon aerogels were successfully synthesized
- ❖ Characterization showed a high surface area and microporosity
- ❖ Adsorption experiments showed a high percentage adsorption of chromium (VI)
- ❖ The adsorption kinetics of chromium (VI) was faster than using anthracite coal
- ❖ Silver-doped carbon aerogels were made
- ❖ There was some formulation optimization
- ❖ The surface area and pore size were both smaller
- ❖ Adsorption experiments showed better bromide adsorption than the anthracite coal
- ❖ Chromium (VI) adsorption experiments were only slightly effective

Future Work:

- ❖ More adsorption experiments, increasing concentrations beyond the detection limits
- ❖ Endocrine-disrupting compound adsorption experiments
- ❖ Further optimization of the silver-doped aerogels formulation
- ❖ Other gel formulation techniques to increase porosity

Acknowledgements

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References

- [1] Los Angeles County Sanitation Districts (LACSD). Wastewater Treatment and Water Reclamation. http://www.lacsd.org/about/wastewater_facilities/moresan/default.asp (accessed 02 July 2009).
- [2] Al-Muhtaseb, S.A.; Ritter, J.A. Preparation and Properties of Resorcinol-Formaldehyde Organic and Carbon Gels. *Adv. Mater.* 2003, 15, 102-114.
- [3] Sanchez-Polo, M.; Rivera-Utrilla, J.; Salhi, E.; von Gunten, U. Ag-doped carbon aerogels for removing halide ions in water treatment. *Water Research* 2007, 41, 1031-1037.
- [4] Pekala, R.W. Organic aerogels from the polycondensation of resorcinol with formaldehyde. *J. Mater. Sci.* 1989, 24, 3221-3227.

