

US EPA ARCHIVE DOCUMENT

# Municipal sewage sludge and fish waste based composite adsorbents for removal of organic contaminants from water

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# Sludge

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- Municipal swage sludge: a mixture of exhausted biomass and inorganic materials such as sand and metal oxides
- Industrial sludge: wastes from industries such as shipyards, foundry, electroplating, tobacco, or paper mills
- About 10 million dry tons of sewage sludge produced in the US annually



Photo from wikipedia

# Fish waste

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- Over 70 million tons/yr of fish waste produced globally (FAO, 2006)
- Fish waste a source of carbonaceous materials and contains phosphorus, calcium, and magnesium that could form catalytic centers after pyrolysis
- Fatty acids contained in fish waste could be converted to bio-fuel during pyrolysis if so desired



FAO *The state of world fisheries and aquaculture*;  
Food and Agriculture Organization: Rome, 2006.

<http://www.bluepeacemaldives.org>

# Objectives

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- Conduct laboratory batch tests to evaluate the performance of sewage sludge based adsorbents for the removal of the following groups of compounds: (a) carcinogenic VOCs; (b) nitrosamine disinfection byproducts; and (c) pharmaceuticals and endocrine disrupting compounds (EDCs).
- Optimize processing conditions to produce the most efficient sludge based adsorbent for the removal of aforementioned contaminants from drinking water sources.
- Conduct field pilot scale column tests to evaluate the performance of the optimal adsorbent for the removal of VOCs at the Cadmus Place Groundwater Treatment Plant and pharmaceuticals and EDCs at the Little Falls Water Treatment Plant, both in New Jersey.

# Adsorbents

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- Raw materials:
  - Dewatered sewage sludge (SS) from Wards Island Water Pollution Control Plant , NYC, NY
  - Fish waste (F) from a seafood market in NJ
  - or their mixtures (SSF, 90:10, 75:25, and 50:50 ratio based on wet mass)
- Pyrolyzed at 950 °C in a nitrogen atmosphere in a fixed bed (horizontal furnace)
- 5 sludge-derived adsorbents:
  - SS
  - SS90F10, SS75F25, SS50F50
  - F
- Activated carbon (WVA900)



# Experimental procedures

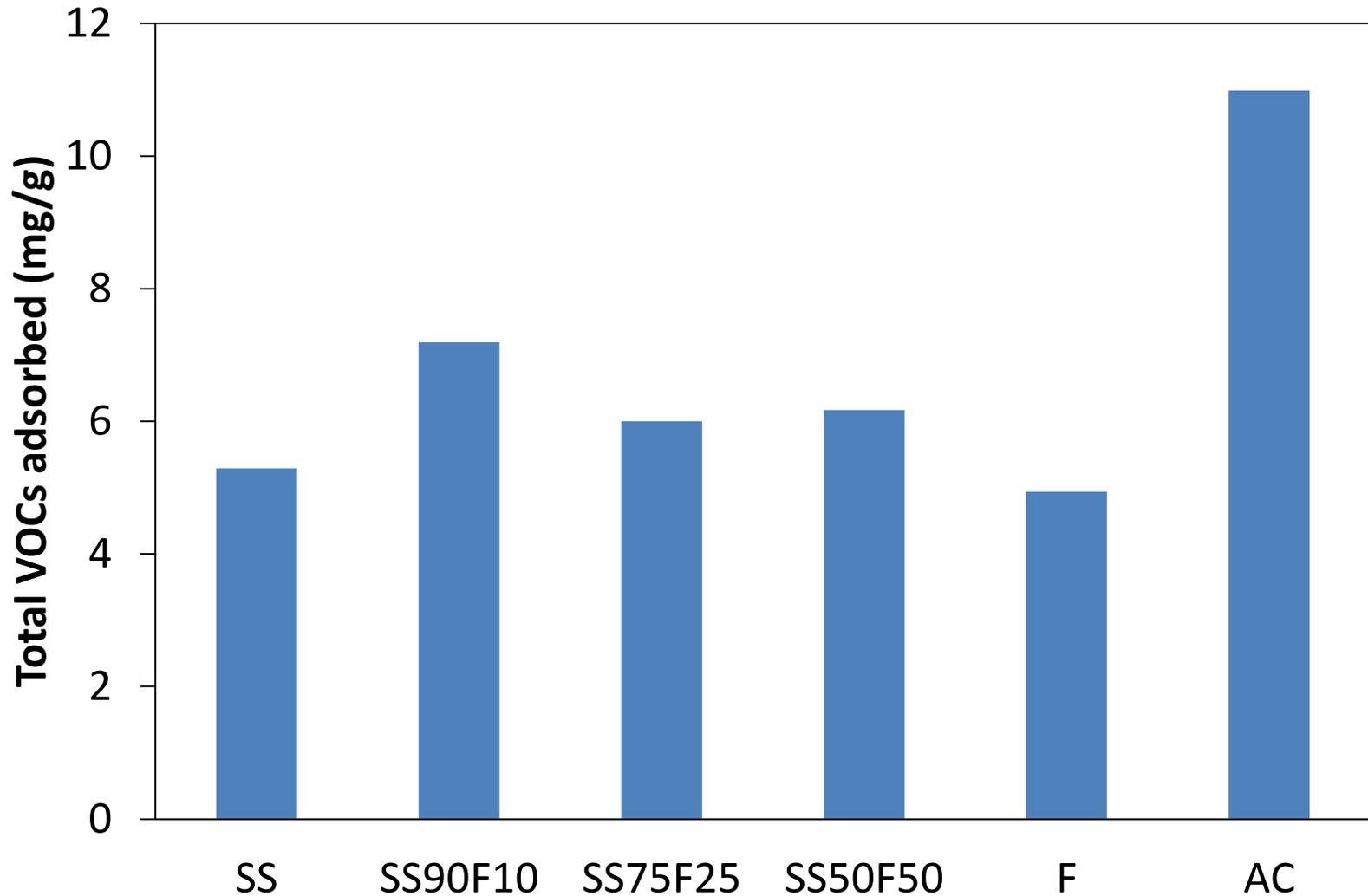
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- Batch adsorption experiments
- LC/MS/MS for pharmaceuticals and EDCs, and nitrosamines
- Headspace GC/MS for VOCs
- ICP/MS for metal analysis
- Material characterization using thermal analysis, XRD, XRF, SEM/EDX, sorption of nitrogen, FTIR, etc.



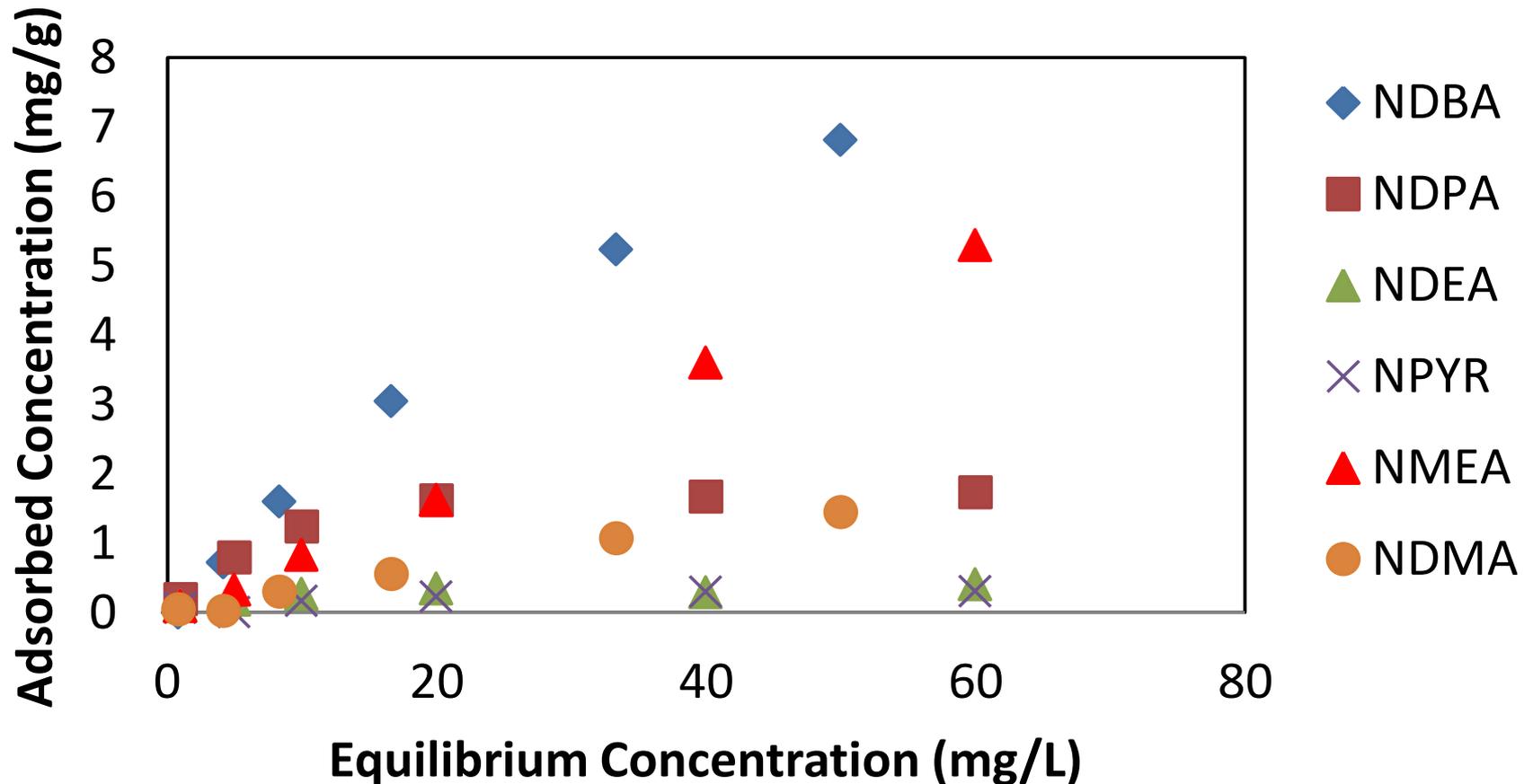
# Total maximum amount adsorbed

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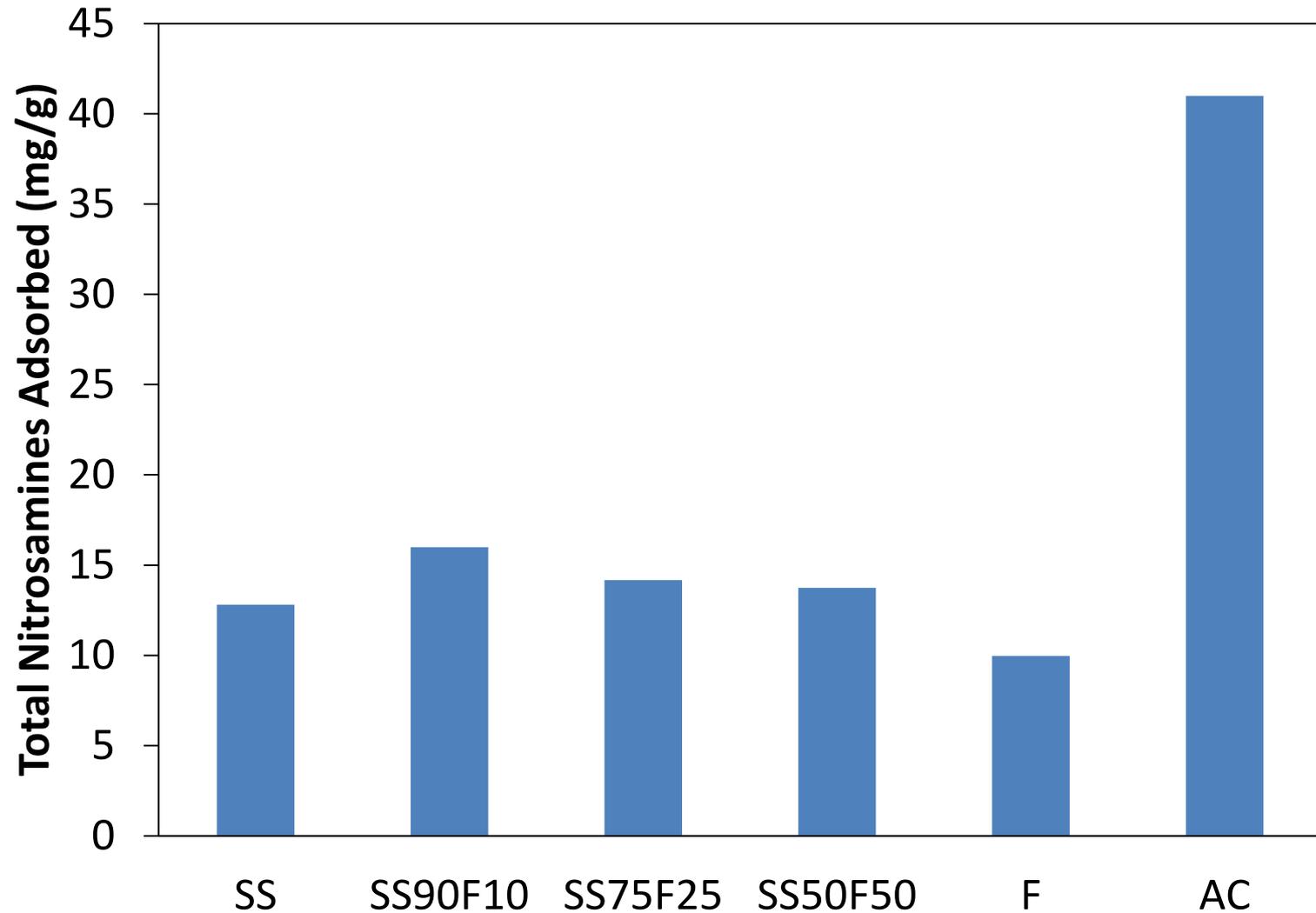
# Isotherms for nitrosamines

SS90F10

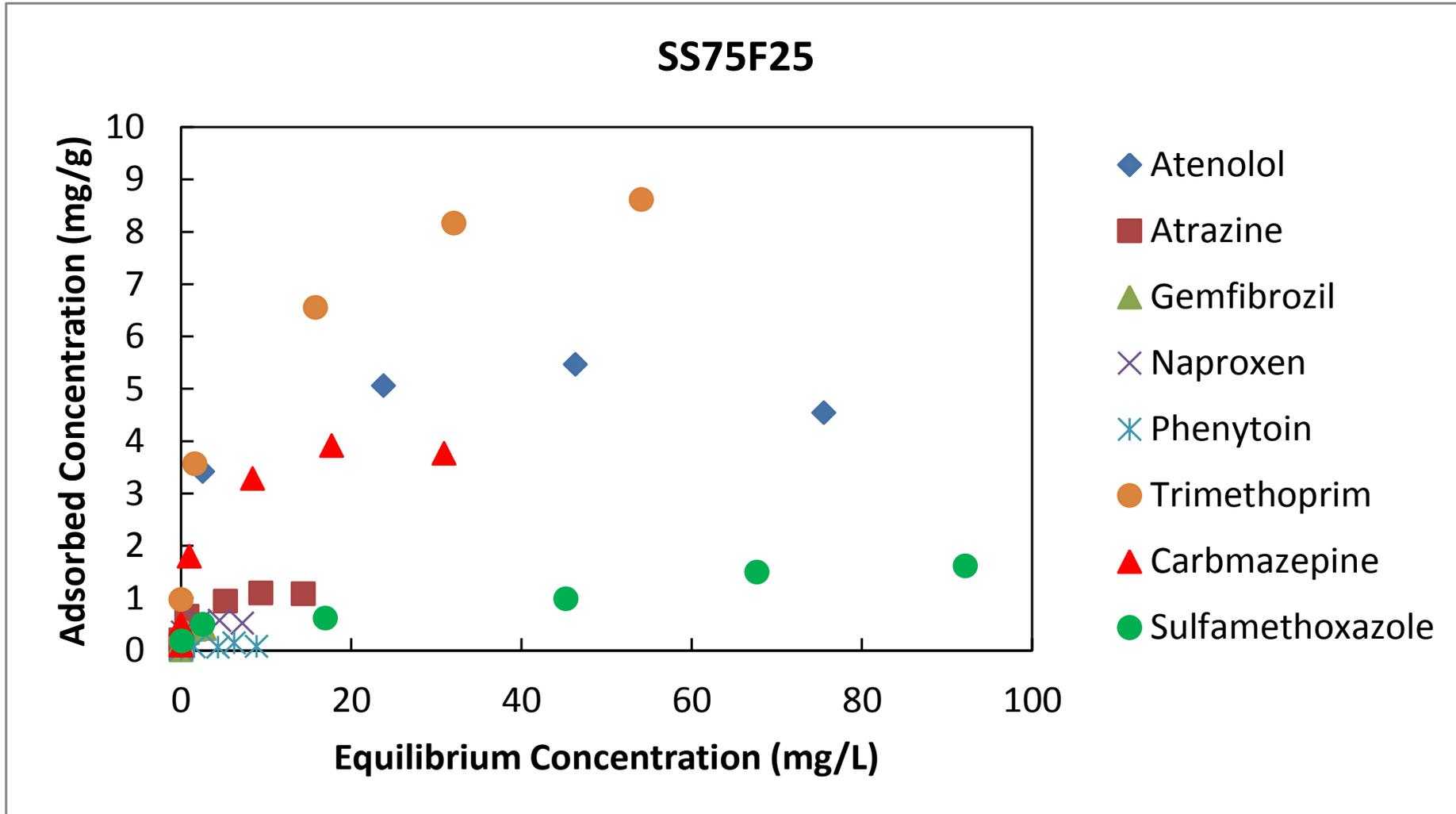


# Total maximum amount adsorbed

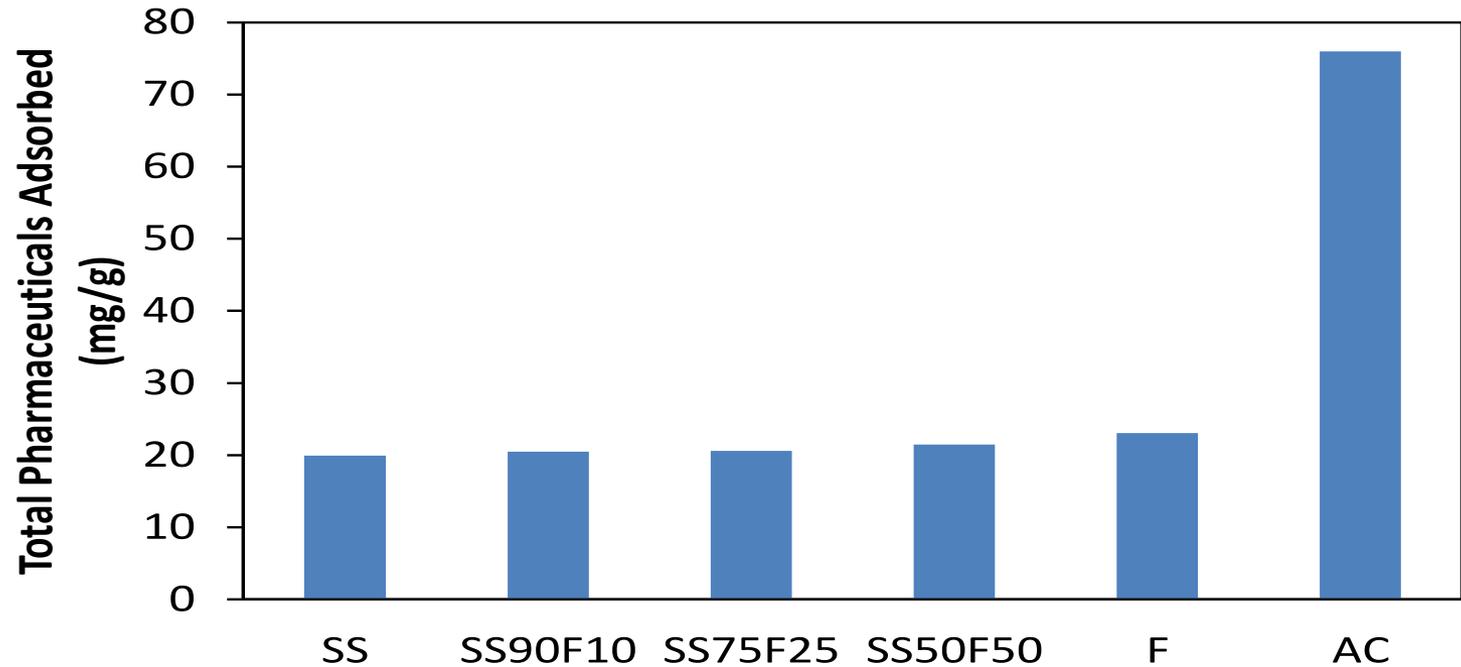
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# Isotherms for pharmaceuticals and EDCs

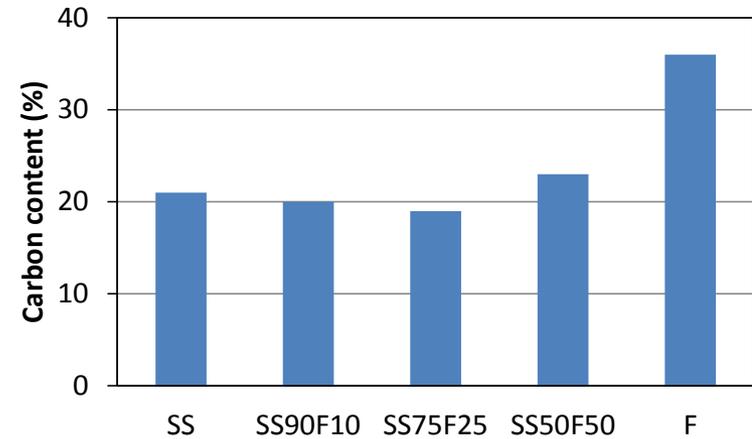
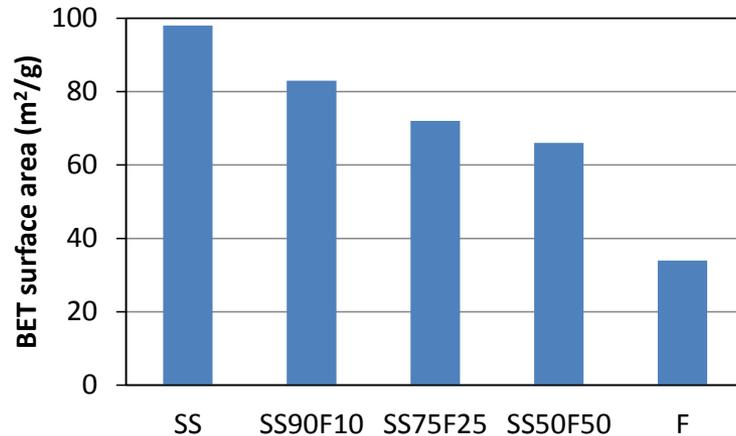


# Maximum amount adsorbed

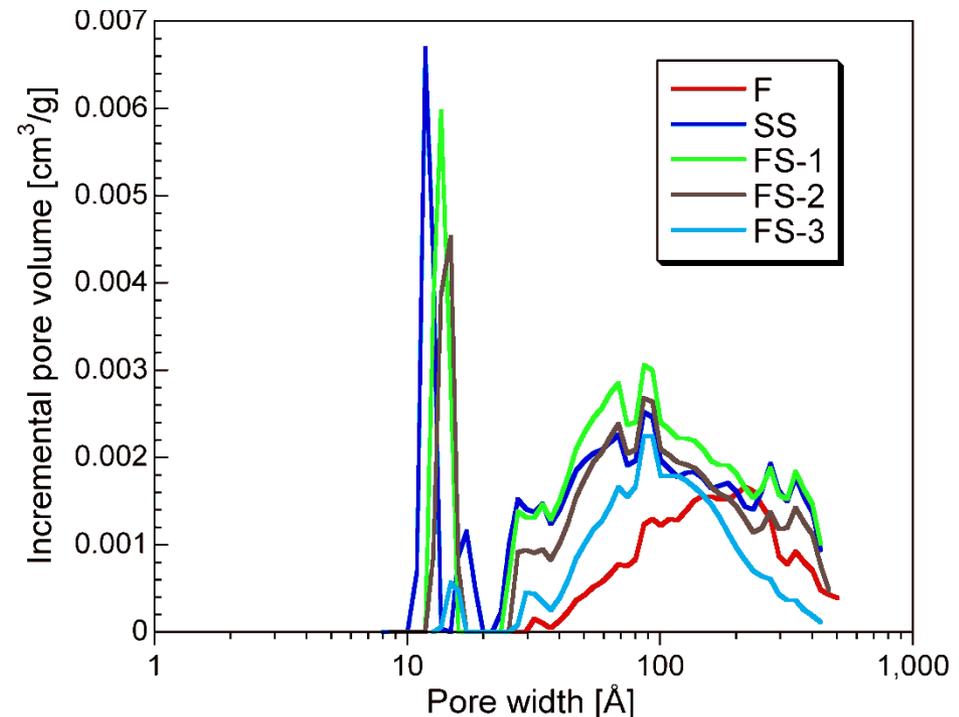


|                | Atenolol   | Atrazine   | Gemfibrozil | Naproxen   | Phenytoin  | Trimethoprim | Carbamazepine | Sulfamethoxazole | SUM  |
|----------------|------------|------------|-------------|------------|------------|--------------|---------------|------------------|------|
| SS             | 7.8        | 0.9        | 0.2         | 0.0        | 0.0        | 8.1          | 2.9           | 0.0              | 19.9 |
| SS90F10        | 7.8        | 1.1        | 0.2         | 0.0        | 0.0        | 8.3          | 3.1           | 0.0              | 20.5 |
| <b>SS75F25</b> | <b>4.5</b> | <b>1.1</b> | <b>0.4</b>  | <b>0.5</b> | <b>0.1</b> | <b>8.6</b>   | <b>3.8</b>    | <b>1.6</b>       | 20.6 |
| SS50F50        | 4.6        | 1.2        | 0.6         | 0.8        | 0.0        | 8.6          | 4.2           | 1.4              | 21.5 |
| F              | 6.8        | 0.8        | 0.4         | 0.8        | 0.2        | 9.0          | 3.4           | 1.7              | 23.0 |

# Material Characterization

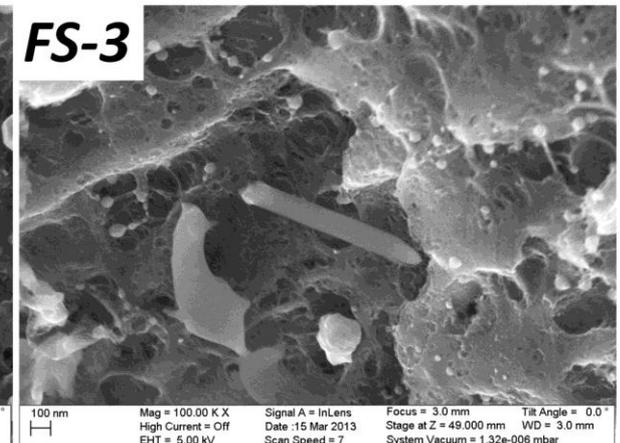
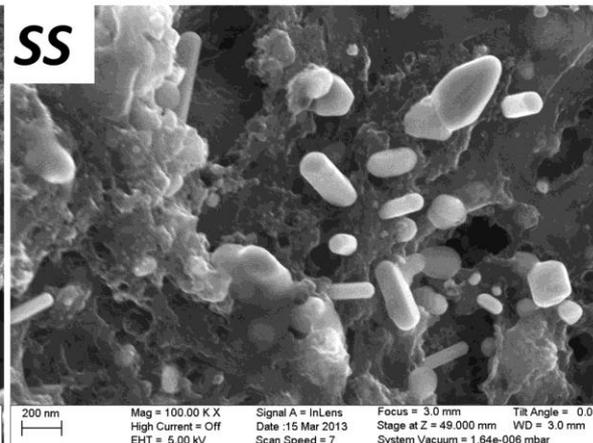
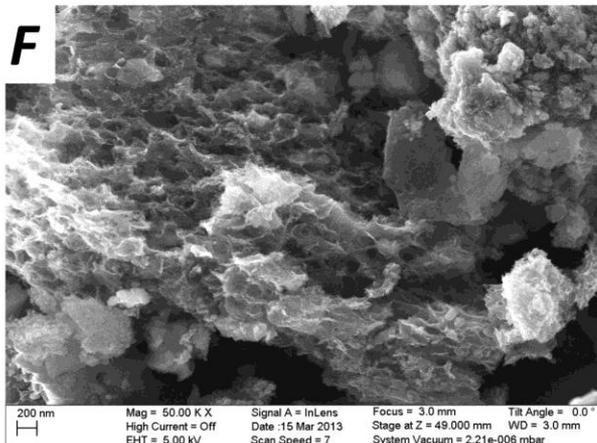


- Micropores of a carbonaceous origin – important sites for physical adsorption of non-polar compounds
- Mesopores predominated by a polar mineral phase – important sites for specific/reactive adsorption of polar compounds

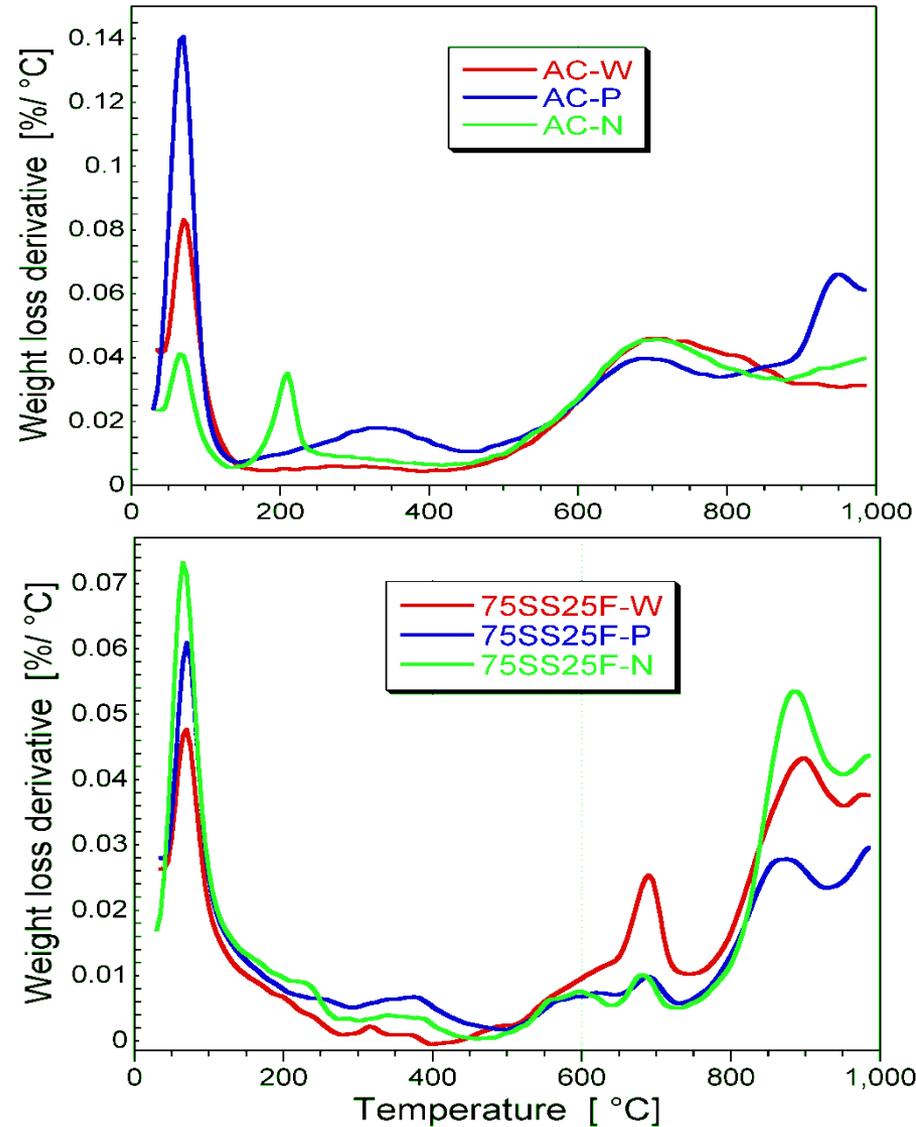


# Material Characterization

|    |   |   |   |   |
|----|---|---|---|---|
| F  | Halite<br>NaCl<br>Sylvite<br>KCl            | Sylvine<br>(K <sub>0.7</sub> Na <sub>0.3</sub> )Cl<br>Silicon<br>tetrachloride<br>SiCl <sub>4</sub> | Hydroxylapatite,<br>Chlorian<br>Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl <sub>0.5</sub> (OH) <sub>0.5</sub>   | Potassium Sodium Magnesium<br>Phosphate<br>Hydrate<br>(K,Na) <sub>4</sub> Mg <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> *5H <sub>2</sub> O  |
| SS | Quartz,<br>Cristobalite<br>SiO <sub>2</sub> | Barringerite<br>Fe <sub>2</sub> P<br>Berlinite<br>Al(PO <sub>4</sub> )                              | Ferroan<br>Ca <sub>2</sub> (Mg,Fe) <sub>5</sub> (SiAl) <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub><br>Ferrian<br>Fe <sub>5</sub> (PO <sub>4</sub> ) <sub>4</sub> (OH) <sub>3</sub> *2H <sub>2</sub> O<br>Feroxyhite<br>FeO(OH) | Beidellite<br>(Na,Ca) <sub>0.3</sub> Al <sub>2</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> *xH <sub>2</sub> O<br>Saponite<br>Ca <sub>0.5</sub> (Mg,Fe) <sub>3</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (O,H) <sub>2</sub> *4H <sub>2</sub> O<br>Nontronite<br>(Na,Ca) <sub>0.3</sub> Fe <sub>2</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> *xH <sub>2</sub> O |



# Material Characterization



DTG curves

# Summary

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- For VOCs, SS90F10, SS75F25 and SS50F50 materials performed better than the SS or F material suggesting some synergistic effects; maximum adsorbed amounts about  $\frac{1}{2}$  of the amount by AC
- For nitrosamines, SS90F10, SS75F25, and SS50F50 also performed better than the SS or F materials, maximum adsorbed amounts  $\sim \frac{1}{3}$  of the amount by AC
- For pharmaceuticals and EDCs, total maximum amounts adsorbed by the five materials were similar but adding fish waste increased the number of species adsorbed; maximum adsorbed amounts about  $\frac{1}{3}$  of those by AC

# Future work

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- Batch adsorption experiments with individual compound (selected) to understand mechanisms of removal (monitoring daughter products; DTG, FTIR, XRD/XRF analyses of virgin and spent materials)
- More leaching tests
- Column transport experiments
- Pilot scale column tests

# Publications to date

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## ➤ Journal articles:

1. Wallace, R., M. Seredych, P. Zhang and T.J. Bandosz, 2013. Municipal waste conversion to hydrogen sulfide adsorbents: Investigation of the synergistic effects of sewage sludge/fish waste mixture. *Env. Sci. Technol.* (revision under review)
2. Ding, R., P. Zhang, M. Seredych, and T. J. Bandosz. 2012. Removal of antibiotics from water using sewage sludge and waste oil sludge derived adsorbents, *Water Res.* 46, 4081-4090.

## ➤ Proceeding paper

1. Zhang, P, R. Ding, M. Seredych, and T. J. Bandosz. 2012. A sewage sludge derived composite material for adsorption of antibiotics – kinetics, *Advances in Materials Physics and Chemistry*, 2(S1), 35-38.

# Publications to date

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## ➤ Conference Presentations

1. P. Zhang, R. Ding, M. Seredych and T.J. Bandosz, 2012, Kinetics of antibiotics adsorption by a sewage sludge derived composite material, presented at the World Congress on Engineering and Technology (CET), Oct. 26-28, 2012, Beijing, China.
2. R. Ding, P. Zhang, M. Seredych and T.J. Bandosz, 2012, Simultaneous adsorption of multiple antibiotics on sludge derived materials, presented at the 2nd International Conference on Environmental Pollution and Remediation, Aug. 28-30, 2012, Montreal, Quebec, Canada, 28-30 August 2012.
3. R. Ding, P. Zhang, M. Seredych and T.J. Bandosz, Removal of antibiotics from water using sewage sludge derived composite material, presented at the American Chemical Society annual meeting, Aug. 19-23, Philadelphia, USA.
4. R. Ding, P. Zhang, M. Seredych and T.J. Bandosz, Simultaneous removal of multiple pharmaceuticals from water using sewage sludge derived adsorbents, presented at the American Water Resources Association (AWRA) 2012 Summer Specialty Conference on Emerging Contaminants of Concern in Water Resources, June 25-27, 2012, Denver, CO, USA.

# Acknowledgements

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