Hydrothermal Carbonization of Glucose for the Production of Particles to Model S-PAC Membrane Breakthrough

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Introduction

Trace synthetic organic contaminants (SOCs) found in drinking water supplies are an increasing threat to public health.

Microfiltration (MF) membranes coated with adsorbents are a promising method of removing SOCs.[1]

- Superfine powder activated carbon (S-PAC) has large adsorption capacity due to its high surface area amplified by its porous network.[1]
- Due to S-PAC's small particle size (200-500 nm), the potential for S-PAC's passage into finished water after adsorption poses health risks.[2]

Hydrothermal carbonization of glucose can result in carbon nanospheres (CNS), which can have tightly controlled size and morphology.[3]

- By tailoring CNS to have a specific size distribution similar to S-PAC, they may be used to model S-PAC membrane breakthrough.

So far, CNS have been a poor system for adsorbing SOCs because they lack S-PAC's porosity.[3]

- S-PAC wet-milling synthesis approach requires high energy input.[1]
- With a proper method of activation, CNS may be a cheaper alternative to S-PAC.

Materials and Methods

Nanosphere Synthesis and Characterization

- Carbon nanosphere precursor: D(+) glucose monohydrate dissolved in DDI water.

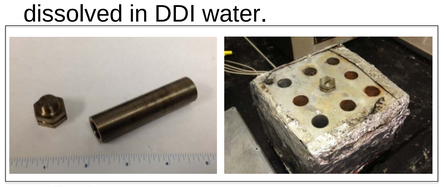

Fig. 1

Fig. 2

- Two hydrothermal reaction apparatuses: 5 mL titanium reaction vessels held in an aluminum heating block (Fig. 1) and a 300 mL Parr reactor vessel (Fig. 2) to scale up the reaction.
- Heating duration, temperature, and precursor concentration were varied.
- Dynamic light scattering (DLS) and scanning electron microscopy (SEM): size distribution of particle diameters and morphology characterization respectively.

Radiolabeled Nanosphere Synthesis and Breakthrough Measurement by Liquid Scintillation Counting (LSC)

- Radiolabelled spheres were filtered through various mixed cellulose ester (MCE) membranes and LSC estimated percent breakthrough.

Atrazine Adsorption Kinetic Experiments

- Radiolabelled atrazine was injected into solutions of S-PAC, as well as activated and non-activated hydrochar (HTC products) to evaluate each one's performance as adsorbents.[4] Percent atrazine removed was estimated with LSC.

Results and Discussion

Nanosphere Synthesis and Characterization

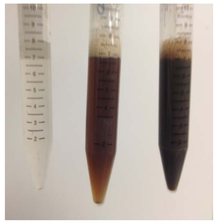

Fig. 3: Carbon hydrochar heated at 180 °C/2 hr using 0.25, 0.50, and 0.75 M glucose precursor concentration.

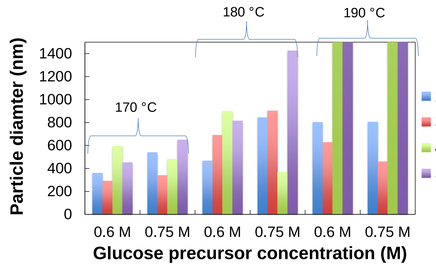

Fig. 4: Heating block particle size distribution results from DLS. (190 °C samples starting at 4 hr are larger than DLS could measure accurately, > 6 µm.)

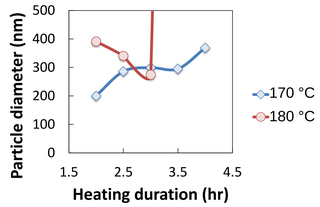

Fig. 5: Parr reactor particle size distribution results from DLS. (DLS could not get an accurate measurement for 180 °C samples heated longer than 3 hr due to the presence of large particles.)

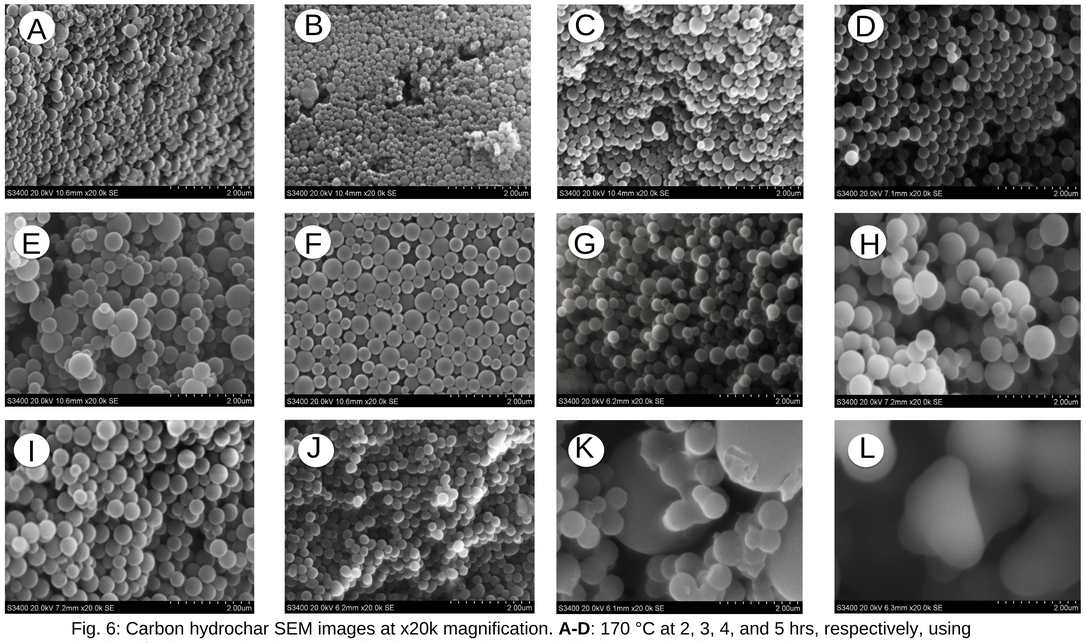

Fig. 6: Carbon hydrochar SEM images at x20k magnification. **A-D**: 170 °C at 2, 3, 4, and 5 hrs, respectively, using heating block. **E-H**: 180 °C at same durations as A-D. **I-L**: 190 °C at same durations as A-D.

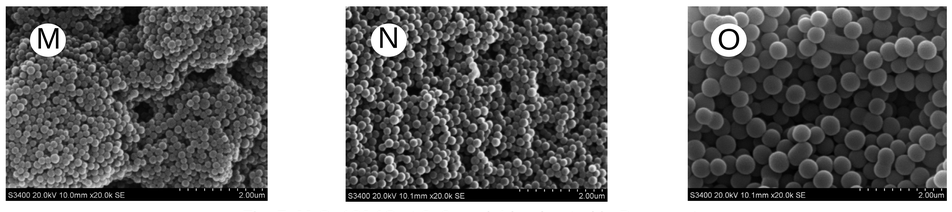

Fig. 7: **M-O**: 180 °C at 2, 3, and 4 hrs heated in Parr reactor.

Radiolabelled Carbon Nanosphere Membrane Breakthrough

Fig. 8: Left to right: Unfiltered CNS and CNS after filtration through 0.8, 0.22, 0.1, and 0.05 µm MCE membranes.

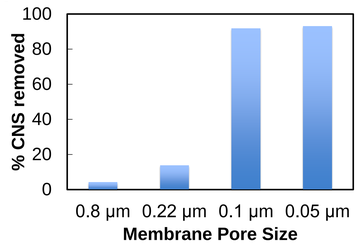

Fig. 9: 0.05 and 0.1 µm membranes removed ≈94% of CNS, while 0.8 µm removed only ≈4%. Smaller pore size will be necessary to remove S-PAC below detection limit. CNS also formed a caked layer on the membrane surface, a behavior observed in S-PAC. This further supports CNS as a useful model particle for S-PAC.

Results and Discussion

Hydrochar Activation and Atrazine Adsorption

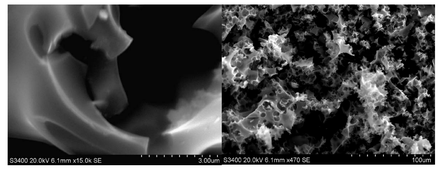

Fig. 10: Dried carbon hydrochar samples using Parr reactor at 180 °C/3 hr were ground with KOH pellets and heated to 750 °C/2 hr. The end result was a porous network, loss of spherical morphology, and larger particle size. Pictured left to right: activated hydrochar, x15k and x470 magnification.

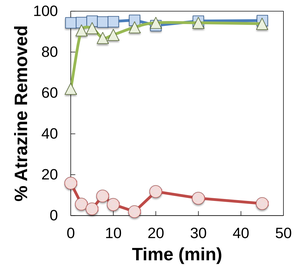

Fig. 11: Kinetic experiments using S-PAC (WC800, milled 1 hr), and activated and non-activated hydrochar (180 °C/3 hr). Activated hydrochar exhibits slower kinetics but shows promise as an adsorbent for water treatment.

Conclusions and Future Work

- CNS can be synthesized via hydrothermal carbonization to obtain particles of uniform size and morphology.
- Hydrothermal carbonization reaction was successfully scaled up from the 5 mL Ti vessels to the Parr reactor.
- The following reaction conditions sufficed for maximizing CNS yield with the target particle diameter: 0.75 M glucose heated at 180 °C/3 hr.
- CNS demonstrate that S-PAC likely exhibits a noticeable degree of membrane breakthrough even with a pore size of 0.05 µm.
- CNS become highly porous and lack spherical morphology after treatment with KOH at high temperatures.
- Activated carbon hydrochar may be a promising alternative to S-PAC as an SOC adsorbent.
- Tailoring activation conditions and changing atrazine concentration will be performed in the future to obtain more data on carbon-based adsorbent kinetics.

References

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Acknowledgements

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