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We use this protocol and it's working

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pH-Dependent Adsorption of Chemicals by Biochar (Adsorption Edges)

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ABSTRACT

This is a protocol for determining the pH-dependent adsorption of chemicals by biochar. The resulting product is a plot of adsorbed concentration, or adsorbed fraction of added sorbate, as a function of pH. These plots are typically referred to as "adsorption edges" for cations or "adsorption envelopes" for anions. In cases where the exact adsorption mechanism is unknown, the general term "sorption" is substituted for "adsorption". Variables such as initial sorbate concentration, ionic strength of the background solution, and biochar:solution ratios need to be considered beforehand for the results to be practically useful.

The reagents, concentrations, and reaction times in this protocol will refer to those detailed in Padilla et al., (2024). However, there is much flexibility with these variables, so please see the "Guidelines & Warnings" tab before starting.

Reference:

Padilla, J.T., Watts, D.W., Szogi, A.A., Johnson, M.G. (2024). Evaluation of a pH- and time-dependent model for the sorption of heavy metal cations by poultry litter-derived biochar. Chemosphere 347, 140688.

ATTACHMENTS

Evaluation of a pH- and time-dependent model for the sorption of heavy metal cations by poultry litter-derived biochar.pdf

Adsorption Edge - Lab Notes Template.docx

MATERIALS

1. Disposable 50 mL polypropylene tubes.
2. Calibrated pH-Meter
3. Biochar
4. Balance
5. Spatula for transferring materials
6. Background Electrolyte (In this case, KCl)
7. Sorbate (In this case, CdCl2)
8. 10 mL pipette, 1000 uL pipette, 100 uL pipette and corresponding pipette tips
9. 5% HCl (referred to as HCl-W in "Steps")
10. 5% HCl in the background electrolyte (referred to as HCl-E in "Steps")
11. Platform Shaker
12. Disposable 10 mL syringe
13. 0.45 um syringe filter
14. Tubes for ICP
15. Parafilm
16. Adsorption Edge - Lab Notes Template (Included in "Attachments")

SAFETY WARNINGS

Be mindful of safety if performing experiments with hazardous materials (certain heavy metals, etc.).

BEFORE START INSTRUCTIONS

Concentration of Sorbate:
Review the literature for relevant concentrations of the sorbate and medium of interest. For example, contaminant concentrations in wastewater are typically orders of magnitude greater than those in soil pore-water. Multiple initial concentrations are recommended if experimental results are to be modeled.

Background Electrolyte:
The purpose of using a background electrolyte in adsorption experiments is to maintain (relatively) constant ionic strength. As such, the concentration of the background electrolyte is typically 10-20x the initial concentration of the sorbate so that the removal of the sorbate from solution has little effect on the ionic strength. Interactions between the background electrolyte and sorbent should also be minimal - salts containing Na, K, NH4, Cl, and NO3 are typically chosen. Interactions between the background electrolyte and sorbate should also be minimized - i.e. CaCl2 for PO4 experiments would be a poor choice.

Sorbent:Solution Ratio:
Choose a sorbent:solution ratio that is realistic. Here we use 0.1 g biochar to 20 mL solution, corresponding to a 5 g/L dosage. Multiple dosages are recommended if experimental results are to be modeled.

Reaction Time:
Adsorption edges describe the system at chemical equilibrium. While 24 hours of reaction time is typical, preliminary experiments should confirm that your reaction time is sufficient for equilibrium.

Prepared Materials Before Starting

1 Print out "Adsorption Edge - Lab Notes Template" (Lab Notes).

1.1 Label 50 mL polypropylene tubes and fill in "Tube/Trt." column in the Lab Notes accordingly. I typically use at least 12 points for each adsorption edge.

1.2 Weigh each EMPTY 50 mL tube and record the weight under the "Mass Tube" column in the Lab Notes.

1.3 Transfer 0.1 g of biochar to each 50 mL tube. Reweigh the tubes with the added biochar and record the weight under the "With Char" column in the Lab Notes.

1.4 Label the ICP tubes accordingly. Weigh the ICP tubes and record their weight under the "Mass ICP Tube" column in the Lab Notes.

2 Prepare 1 L of 10 mM KCl (BGE):
Weigh out 0.7455 g of KCl and quantitatively transfer to a 1 L volumetric flask. Bring up to volume.

3 Prepare 100 mL of 10 mM stock solution of Cd (Cd Stock Solution):
Weigh out 0.1833 g of $CdCl_2$ and quantitatively transfer to 100 mL volumetric flask using BGE. Add about 50 mL of BGE and swirl until dissolved. Bring to volume with BGE.

Starting the Experiment

4 Transfer an appropriate amount of the BGE to a beaker. Connect the appropriate pipette tips to their corresponding pipettes.

5 Remove caps from 50 mL tubes with biochar. Transfer 19 mL of BGE to each tube. Replace caps. Weigh each tube and record their weight under the "With KCl" column in the Lab Notes.

6 Remove caps from tubes. Using the 100 uL pipette, add a small volume of HCl-E to each tube. Each tube receives a different volume of HCl-E. For example, the first tube receives no HCl-E, the second receives 10 uL HCl-E, the third recieves 20 uL HCl-E, etc. The total volume of HCl-E should not exceed 200 uL. Replace caps and gently swirl to mix. Weigh each tube and record their weight under the "With HCl" column in the lab notes.

7 Remove caps from tubes. Using the 1000 uL pipette, transfer 1000 uL of the Cd Stock Solution to each tube. RECORD THE TIME AT THIS STEP (i.e. 9:30 AM). Replace caps, weigh, and record weight under the "With Spike" column in the Lab Notes.

8 Transfer the tubes to a platform shaker and constantly shake for 24 hours (or whatever time is needed for equilibrium).

Taking Samples

9 Calibrate a pH meter. After 24 hours of shaking (from step 7), remove tubes from platform shaker. Remove caps from tubes. Using a 10 mL disposable syringe, remove about 2 mL of the supernatant from the tube, attach a 0.45 um syringe filter, and transfer the solution into a ICP tube. Do this for all samples.

10 Weigh the ICP tubes and record the weight under the "With Sample" column in the Lab Notes. Add 1 mL of HCl-W to each tube, and bring the final volume up to about 10 mL using BGE. Weigh each tube again and record under the "With Dil." column in the Lab notes. Cap each tube with parafilm and invert to mix.

11 Measure the pH of the remaining solution in the 50 mL tubes. Record this value in the "pH Final" column in the Lab Notes.

12 FOR HAZARDOUS WASTE: Dispose of hazardous waste (left over solution, spent syringes/filters, etc.) appropriately.

Calculations

13 Determine solution concentrations using ICP (Measured Con.). Measure the actual concentration of the Cd Stock Solution (Stock Con.).

14 I recommend doing the following in an excel sheet.
Dilution Factor, DF:

DF=(With Dil. - Mass ICP Tube)/(With Sample - Mass ICP Tube)

Corrected Concentration (Cor. Con.):

DF x Measured Con.

Adsorbed Concentration (S):

(((With Spike - With HCl) x Stock Con.) - ((With Spike - With Char) x Cor. Con.)) / (With Char - Mass Tube)

Fraction Adsorbed (F):

F=1-((With Spike - With Char) x Cor. Con.))/((With Spike - With HCl) x Stock Con.)

15 Plot S or F vs pH Final to obtain sorption edge.