Fish bone apatite for copper removal from stormwater runoff

Chris Hoff, Sherry Huang, & Jeff Nason

School of Chemical, Biological, and Environmental Engineering, Oregon State University

Introduction

Problem Statement

The dramatic increase in U.S. urban population and transportation has made stormwater runoff a major contributor to the contamination of waterways. Analysis of stormwater runoff from sites in Portland, OR. has shown that dissolved copper, Cu, and zinc, Zn, concentrations range from 12.8-22.7 and 43.8-193 (μg/L) respectively. Research by Sandahl et al. (2007) has shown that dissolved Cu at concentrations as low as 2 (μg/L) impair sensory physiology and predatory avoidance behavior in juvenile Coho. As a result of this research, regulators have significantly increased emphasis on the need to greatly reduce dissolved metals from stormwater runoff (Nason et al. 2009).

Figure 1. Storm water from roadways containing high levels of dissolved metals finds its way to streams and lakes were it posses a threat to salmonoids.

A Potential Solution

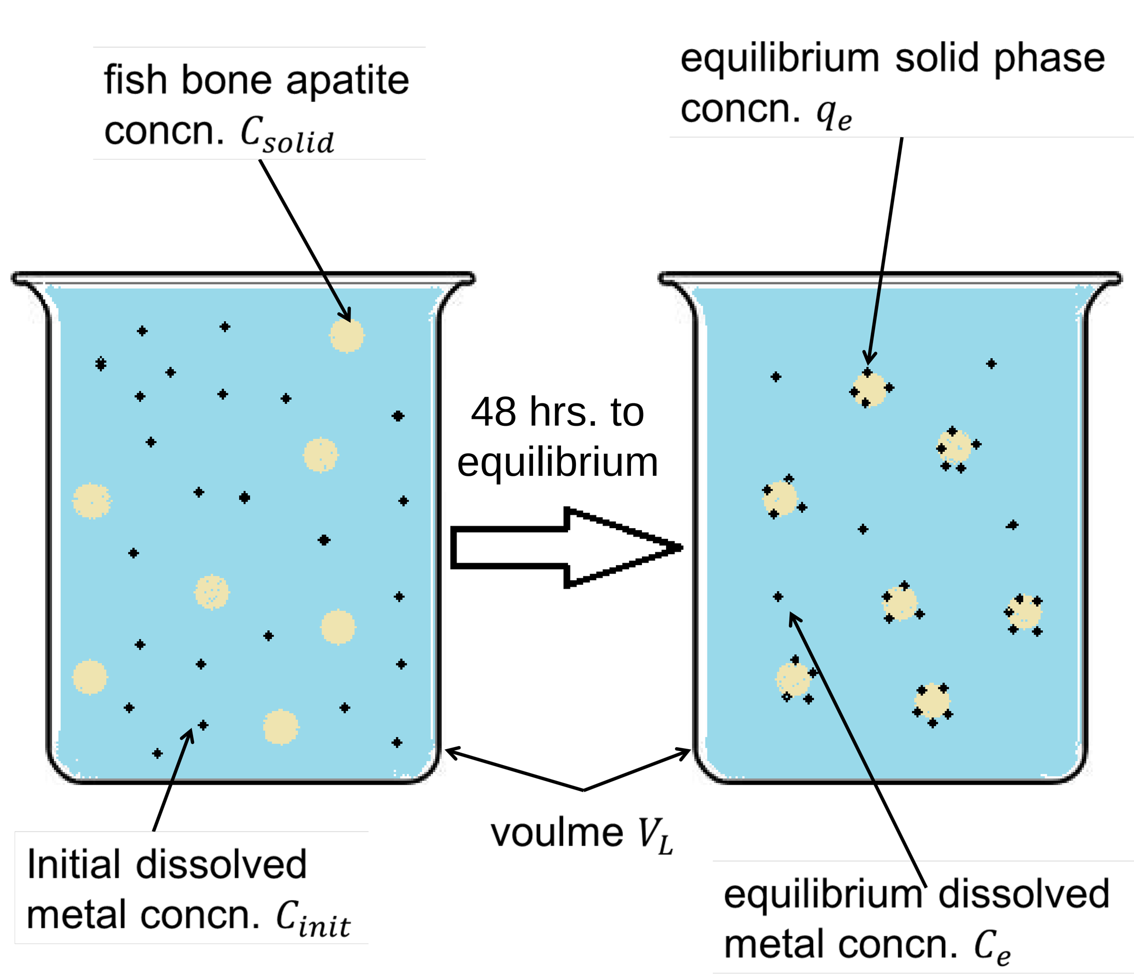
A potential solution is the use of fish bone apatite for the removal of dissolved metals from stormwater runoff. In comparison to current Best Management Practices (BMPs), preliminary tests on fish bone apatite indicate that it has a much greater adsorption capacity for dissolved metals.

Project Objectives

- Determine the adsorptive capacity of fish bone apatite for copper.
- Examine the competition between Cu and Zn for adsorption sites on the fish bone apatite.

Theory

Adsorption is the accumulation of a solute, the **adsorbate**, at the interface between two phases.



The **mass balance** for the adsorption process is written as:

$$\begin{pmatrix} Mass\ of\ adsorbate \\ in\ system\ initially \end{pmatrix} = \begin{pmatrix} Mass\ of\ adsorbate \\ in\ system\ at\ equilibrium \end{pmatrix}$$

$$C_{init}V_L + q_{init}C_{solid}V_L = C_eV_L + q_eC_{solid}V_L \quad [1]$$

For this experiment, the initial solid phase concentration and adsorption density, C_{solid} and $q_{initial}$, are 0 (μg/mg) and V_L is constant. Thus, the mass balance reduces to:

$$C_{init} = C_e + q_eC_{solid} \quad [2]$$

Materials and methods

Preparation of fish bone

Liquid phase transport processes are faster for smaller particles. To reduce the time required for the solutions to reach equilibrium, 40/50 mesh size fish bone was used. This also adds uniformity to the experiment. The bone was processed by grinding into small particles in a blender then sieving to achieve uniform particle size.

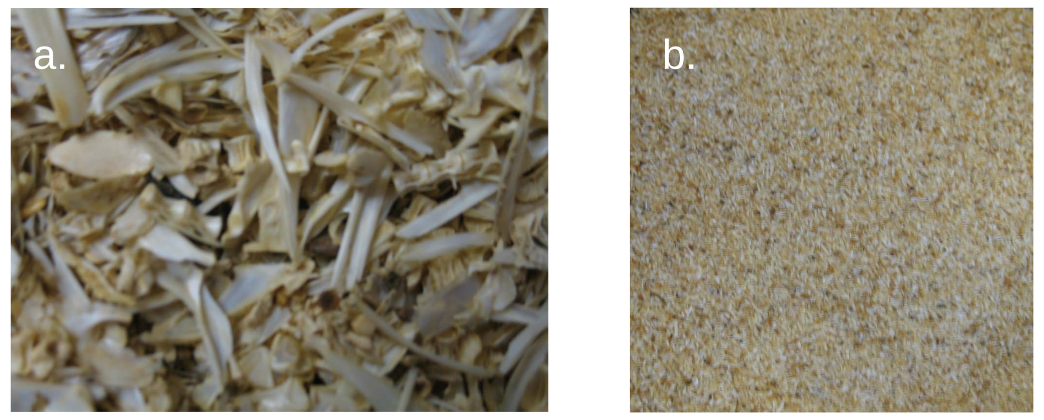


Figure 2. Bulk fish bone (a) and processed fish bone (b).

Bottle-Point Tests

The adsorptive capacity of fish bone apatite with respect to copper and zinc was determined through bench scale bottle point tests. The steps in this process are:

- Prepare solutions of varying Cu and Zn concentrations from stock solutions and mix with known masses of Apatite II.
- Equilibrate solutions for 48 hrs. in a tumbler.
- Measure final pH of solution.
- Ion Chromatography (IC) analysis to determine phosphate concentration of solutions.
- Inductively Coupled Plasma Mass Spectrometer (ICP-MS) analysis to determine Cu and Zn liquid phase equilibrium concentration, C_e, of solutions.
- Analysis of data

Table 1. Three batch experiments were performed. Batch #1 contained Cu only and was used to determine the adsorptive capacity for Cu on fish bone apatite. The remaining batches were used to determine the effect of Zn presence on the adsorptive capacity for Cu. The ratios of Cu:Zn vary from 1:1 to 1:8.

Batch #1		Batch #2		Batch #3	
$C_{cu,I}$ (ug/L)	$C_{Zn,I}$ (ug/L)	$C_{cu,I}$ (ug/L)	$C_{Zn,I}$ (ug/L)	$C_{cu,I}$ (ug/L)	$C_{Zn,I}$ (ug/L)
25	0	25	25	400	400
100	0	25	100	400	1600
400	0	25	200	400	3200
1600	0	100	100	1600	1600
3500	0	100	400	1600	3200
6400	0	100	800	1600	6400

Results and Discussion

Characterization of Cu adsorption onto fish bone apatite

The adsorption of Cu onto the fish bone apatite follows a linear isotherm as shown below (fig2a-b). The first sample from each triplicate set at each Cu initial concentration had a markedly higher C_e value. This trend appears to be a systematic error involving the ICP-MS machine. Removal of the outliers provides a better linear fit for the data. The slope of the linear fit for the data is 0.0126 L/mg.

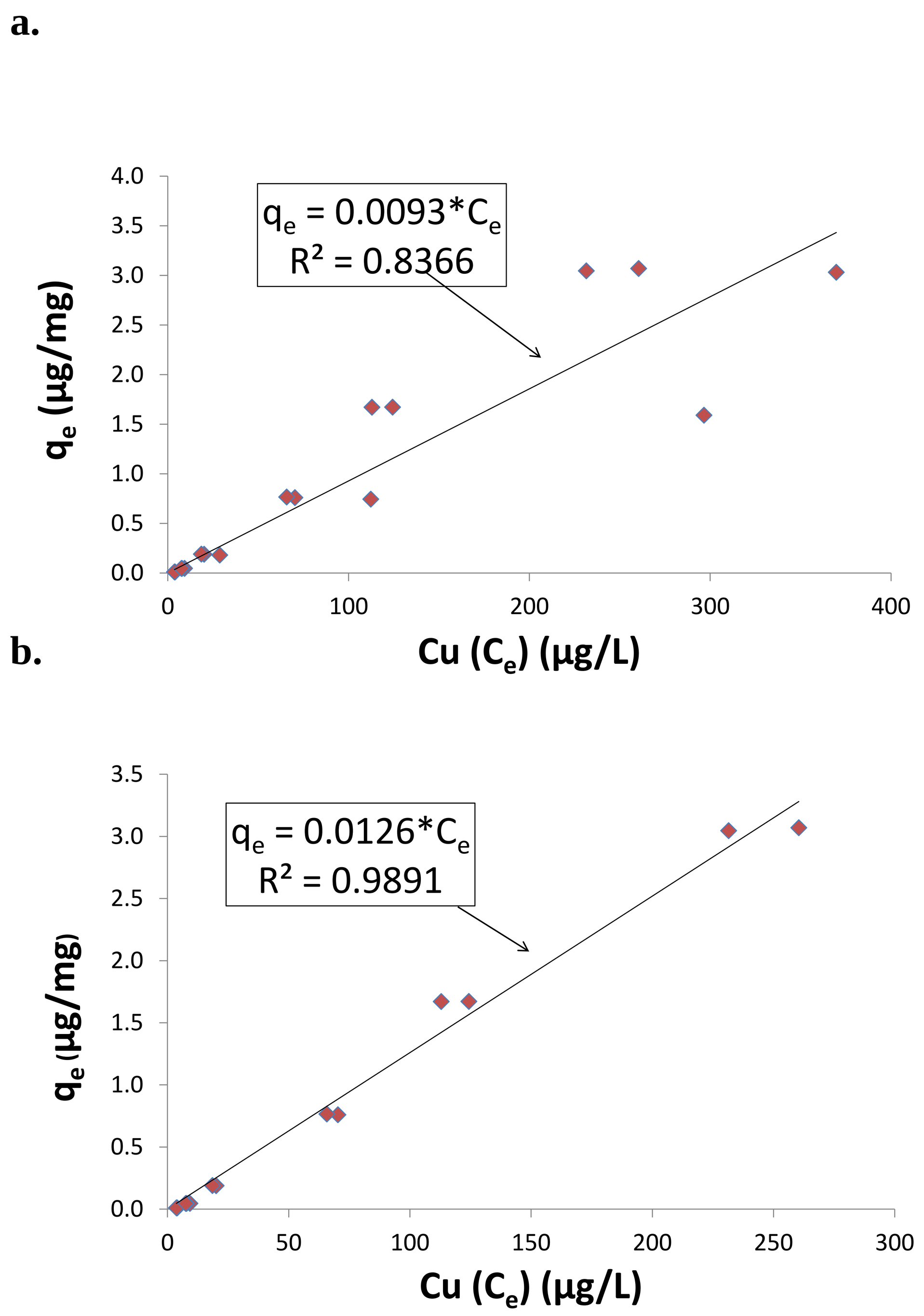


Figure 3. The isotherm created from analysis of data from batch #1. There was a probable systematic error in the ICP-MS analysis as can be seen in the outliers in fig. 2a. Figure 2b shows the improvement in the linear fit of the isotherm when these outliers are removed.

Cu and Zn competition

To determine whether the final Cu concentrations were significantly different due to the presence of Zn a Fischer's Least Significant Difference Test was performed for the different Cu concentrations from batches #2 and #3 (Table 1). The comparison of 100-100 to 100-800 and 100-400 to 100-800 from batch #2 showed a significant effect of initial Zn concentration at a 95% confidence level. The remainder of the comparisons showed no significant effect of initial Zn concentration. With only a minority of the comparisons showing a significant effect of initial Zn concentration, it cannot be said that the presence of Zn significantly effects the adsorption of Cu to the fish bone.

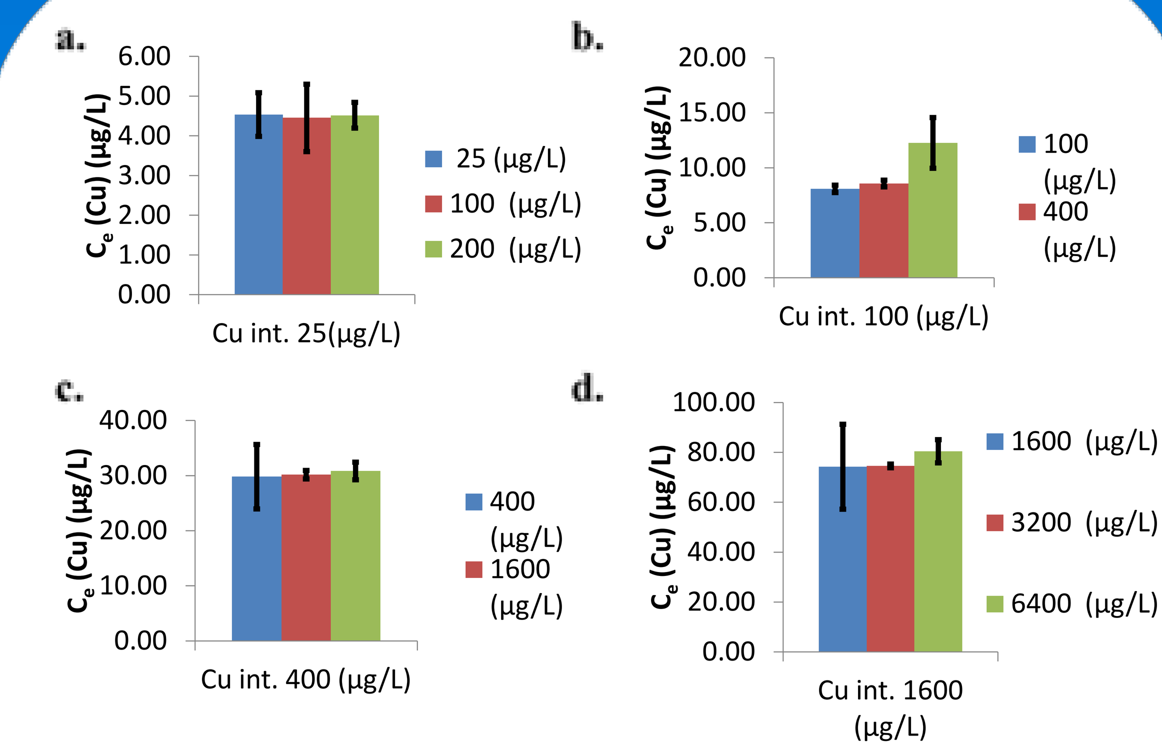


Figure 4. The bars on these charts represent the average C_e (Cu) (μg/L) for each combination of initial Cu and Zn concn. The error bars represent the 95% confidence interval. Only the average C_e values for Cu initial of 100 (μg/L) **(fig. b)** are significantly different. This indicates that the presence of Zn does not significantly effect Cu adsorption onto the fish bone.

Conclusions

- Adsorption of Cu onto fish bone apatite is characterized by a linear isotherm with a partitioning coefficient of 0.0126 (L/mg)
- Presence of Zn has no significant effect on Cu adsorption onto fish bone apatite.
- To reduce the Cu concentration of a liter of water containing an initial Cu concentration of 25 μg/L to a safe level for juvenile Coho (equilibrium Cu concentration of 2 μg/L), a fish bone concentration of 992.1 mg/L would be needed
- The fish bone releases phosphate, which could spawn algae blooms and lead to reduced oxygen levels in water.

Future research

- More bottle-point tests to develop isotherms and analyze the effect of the presence of Zn on Cu adsorption.
- Continuous flow column experiment to provide more useful information on Cu adsorption and phosphate release.

References

Sandahl, J.F.; Baldwin, D.H.; Jenkins, J.J.; and Scholz, N.L. *A Sensory System at the Interface between Urban Stormwater Runoff and Salmon Survival*. Environ. Sci. Technol. 2007;41:2998-3004

Nason, J.A.; Nelson, P.O.; Bloomquist, D.J.; and Sprick, M.S. *Copper Speciation in Highway Stormwater Runoff as Related to Bioavailability and Toxicity to ESA-Listed Salmon*. ODOT and FWHA, FWHA-OR-RD-11-11

Acknowledgements

Subsurface Biosphere Initiative for funding, Andy Ungerer for ICP-MS help, Mohammad Azizian for IC help, Sherry Huang for guidance and assistance, and Jeff Nason for guidance and assistance.

For Further Information

Please contact Chris: *hoffc@onid.orst.edu* or
Jeff: *jeff.nason@oregonstate.edu*