Zinc Removal using Biogenic Iron Oxides

By

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Abstract

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More stringent regulations coupled with increasing cost for popular sorbents has created a demand for new, cost effective sorption technologies to remove Zn from regulated surface waters. This research explored the capability of biogenic iron oxides to remove Zn utilizing batch equilibrium experiments. Biogenic iron oxide kinetics followed a pseudo-first order model reaching equilibrium after 24 hours with $k = -0.0051 \text{ min}^{-1}$ and $R^2 = 0.930$. Langmuir and the Redlich Peterson sorption isotherms were most effective at modeling sorption. Langmuir R^2 values varied between 0.860 and 0.972 with a mean value of 0.940 ± 0.031 (n=7). Redlich Peterson R^2 values varied between 0.891 and 0.982 with a mean value of 0.948 ± 0.024 (n=7). Maximum sorption varied greatly between samples with values ranging between 0.89 to 20.81 mg Zn/g solids. Increasing the pH from 6.54 to 9.0 increased Zn removal four fold from 5.93 to 23.32 mg/g. Zn removal using biogenic iron oxides was comparable to other experiments that investigated natural and engineered sorbents. The use of biogenic iron oxides for agricultural or tertiary wetland treatment to "polish" waste streams is a potential application.

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1.0 Introduction

Human activities have introduced (zinc)Zn into water supplies at toxic levels. The toxic effects of Zn paired with their propensity to accumulate in organisms have led the U.S. Environmental Protection Agency (U.S. EPA) to develop surface and ground water regulations. Such concern has led the U.S. EPA to list Zinc as one of the 126 priority pollutants. Common industrial sources of Zn include mineral processing, electroplating, porcelain enameling, paper manufacturing processes, steel works with galvanizing lines, fiber production, and battery manufacturing (Malkoc, et al., 2005; Mohan, et al., 2002). As a drinking water contaminant, however, Zn is rarely a concern with a secondary drinking water standard of 5 mg/L (U.S. EPA, 2004). Zn toxicity issues are often associated with mining activities and poor management practices. For example, the Bunker Hill Superfund site in the Coeur d'Alene River Basin (Idaho) is one instance where industrial mining activities have jeopardized water bodies. Years of mining and inadequate management practices have allowed Zn to dissolve in runoff waters contaminating regional water supplies (U.S. EPA, 2000). Combating this issue has led to the implementation of strict total maximum daily loads (TMDL's), which often places the responsibility for Zn removal on local municipalities.

Zn cannot be degraded or destroyed like many organic pollutants. Instead, many removal techniques have been developed and implemented to prevent Zn from reaching critical receptors. These methods focus on making soluble Zn insoluble and include: chemical precipitation, oxidation/reduction, reverse osmosis, dilution, ion exchange, filtration, sedimentation, flocculation, and carbon adsorption (Bailey, et al., 1999; Pentari, et al., 2009). The most popular of these methods are precipitation and adsorption (Al-Degs, et al., 2006; Mohan, et al., 2002;

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Minceva, et al., 2008). Although these methods have been shown to remove various dissolved heavy metals most of them are not cost-effective (Bailey, et al., 1999). With both local and federal agencies tightening regulations, more economical removal methods are needed. Bailey et al. (1999) examined various low-cost organic and inorganic sorbents and suggested that more research is needed to further understand the technology life cycle of low-cost sorbents. Additionally, Mohan et al. (2002) determined that issues surrounding regeneration and reuse of many low cost sorbents often act as deterrents to their use. Sorbent technology that is both financially viable and environmentally sustainable is imperative to the future of heavy metal removal.

The use of iron oxidizing bacteria to remove pollutant ions from water may present an alternative removal method. Biogenic iron oxides are produced by auto-lithotrophic microbes that oxidize soluble Fe^{2+} to Fe^{3+} creating a hydrated iron hydroxide precipitate in an organic matrix (Weiss, 2004; Edwards, et al., 2004). Iron oxidizing bacteria grow at anoxic/oxic interfaces that retain circumneutral pHs (Emerson, et al., 1994; Emerson, et al., 1997; Roden, et al., 2004), making them ideal candidates to remove contaminants in wetland systems. Emerson et al. (1994) determined that the oxidized form of iron was amorphous ferrihydrite, which is known to remove Zn and other heavy metals from solution (Jambor, et al., 1998). Additional research has shown that the organic matrix produced by these bacteria has Zn removal capabilities (Bhaskar, et al., 2006) . Furthermore, previous investigations have shown that biogenic iron oxides have the ability to remove PO_4^{3-} and Cu^{2+} from solution (Rentz, et al., 2009; Rentz Unpublished 2009).

The objective of this research was to quantify the ability of biogenic iron oxides to remove aqueous Zn using batch equilibrium experiments, and to evaluate conditions that affect

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Zn adsorption. To our knowledge this research represents the first time that biogenic iron oxides have been investigated for Zn removal.

2.0 Methods

2.1 Sample collection

Biogenic iron oxide samples were collected from Spring Lake near Pomeroy, WA (46°18'21.28"N, 117°39'9.21"W), Moose Creek Reservoir near Bovill, ID (46°52'24.54"N 116°25'10.55"W), and Myron Lake near Yakima, WA (46°37'22.65"N, 120°32'59.24"W). Samples were taken from microbial mats using 50 ml pipettes and the fluid was placed into one liter Nalgene glass jars. The sampling site water conditions were characterized in the field by dissolved oxygen (D.O.) (YSI Model 55 Dissolved Oxygen Meter), pH (Oakton pHTestr Basic), Fe (II) (1, 10 Phenanthroline method), and temperature (YSI Model 55 Dissolved Oxygen Meter). Samples were placed in a cooler and transported on ice to the lab where they were stored at 4°C. At the lab, samples were settled for approximately six hours. Once settled, supernatant was removed and discarded using a 50 ml pipette. A 0.1 M NaCl solution equal to the discarded supernatant volume was added to wash the sample, replacing between 40 and 60% of the total volume. The samples were mixed and allowed to sit over night.

2.2 Sample characterization

Standard laboratory procedures were used to further characterize the samples. Solids density and organic density were determined gravimetrically (n=4). Solids content was determined by dehydrating 10 ml of sample for 24 hours at 110°C. Heating the dehydrated samples at 440°C for an additional 24 hours yielded the organic density. Total iron was determined by first digesting 1 mL of sample in 49 mL of 0.25M oxalic acid overnight (Rentz, et al., 2007). Following digest, samples were buffered with 1M NaHCO₃ and total iron was

measured using the 1, 10 Phenanthroline method. The pH of the buffered sample was measured using a Denver Instruments pH meter (model UB-10). Site Zn concentration was determined by extracting 10 mL of supernatant, stabilizing it in a 2% nitric acid solution and analyzing the solution by Inductively coupled plasma mass spectrometry (ICP-MS). A morphological evaluation was conducted with a Leica DMLB light microscope with SPOT software (Diagnostic Instruments Inc.).

2.3 ICP-MS analysis

ICP-MS analysis was carried out using an Agilent 7500 (Santa Clara CA) in full quant mode. The ICP-MS was tuned with stock trace metal tuning solutions that were provided by the manufacturer. ICP-MS mass to charge ratios (m/z) were checked to ensure proper operating ranges for heavy metal analysis. Ranges, by average, were m/z 7: 1000 – 2000, m/z 205: 2000-3000, and m/z 156/140: < 1% as suggested by the manufacture. All samples were introduced into the ICP-MS by an auto sampler. Between each ICP-MS sample the peristaltic tubing was rinsed with 18 M Ω nanopure water for 30 seconds. If Zn was expected to be present in high concentrations, the peristaltic tubing was rinsed for an extra 30 seconds with ~5% (v/v) trace metal grade nitric acid. Standard curves were developed both pre and post ICP-MS run to ensure the integrity of the data. A typical standard curve is seen in Figure 1. Furthermore, each time the ICP-MS was tuned, a new standard was created. This was done because tuning the ICP-MS created new instrument operating conditions.



Figure 1. Typical standard curve produced by ICP-MS analysis. Zn concentrations (0.01, 0.1, 1.0, and 10.0 mg/L) were created by dissolving $ZnCl_2$ in 2% trace metal grade nitric acid.

2.3 Batch equilibrium procedure

Sorption kinetics where carried out to determine time to equilibrium for zinc to adsorb onto the biogenic iron oxides. A standard stock Zn solution was made by dissolving 2.084 g of zinc chloride (ZnCl₂) in one liter of water to create a 1 g/L solution. Fifty milliliter Falcon reactor tubes where filled with 20 mL of sample, 29 mL of DI water, and 1 mL of 1 g/L Zn stock solution (n=2). Reactors were immediately rotated. At 5 minute intervals reactors were centrifuged and 1.0 mL of supernatant was removed, diluted with 8.7 mL of DI water, and stabilized by 300 μ L of 2% trace metal grade nitric acid solution

Biogenic iron oxide sorption potential was determined by performing batch equilibrium experiments. The stock solution was used to achieve Zn concentrations ranging between 1.0 and 60 mg/L in 50 ml Falcon tubes (n=2). Previous laboratory experiments indicated that between

5.0 to 15 mg of iron were required in the 50 mL reactor to observe desired sorption isotherms. The Falcon tubes were rotated for a 24 hour period to allow them to reach equilibrium. After equilibrium was reached the Falcon tubes were centrifuged at 4100 rpm for 10 minutes. Once centrifuged, 1.0 mL of supernatant was removed, diluted with 8.7 mL of DI water, and stabilized with 300 μ L of 70% trace metal grade nitric acid solution. The samples were analyzed by an ICP-MS for dissolved Zn concentration. A pH altered batch equilibrium experiment was accomplished by adding 0.588g NaHCO₃ to a saline washed biogenic iron oxide sample. This followed by the incremental addition of NaOH in order to bring the pH up to 9.0.

2.4 Determining removal potential at various pHs

Biogenic iron oxide sorption potential was also observed at various pHs. One liter of saline washed sample was buffered with 0.588g NaHCO₃. Six Erlenmeyer flasks were filled with 110 mL of buffered sample. Each flask had its pH altered by adding one of the following: (1) 3.0mL of 100 mM NaOH, (2) 1.5 mL of 100 mM HNO₃, (3) 3.1 mL of 100 mM HNO₃, (4) 8.1 mL of 100 mM HNO₃, (5) 11 mL of 100 mM HNO₃, and (6) 15.4 mL of 100 mM HNO₃. Solutions were capped with a rubber stopper and vortexed two times for five minutes each. Ten milliliters of sample was pipetted from each Erlenmeyer flask into a 50 ml Falcon tube along with 39 mL of DI water (n=5). After the pH was recorded, one milliliter of 1 g/L dissolved Zn stock solution was added to each Falcon tube. The reactors were allowed to reach equilibrium and Zn removal was determined as previously stated.

2.5 Isotherm and kinetic analysis

Zn sorption kinetics to biogenic iron oxides were quantified by (7) pseudo first order, (8) pseudo second order, and the (9) power function models.

$$\frac{c}{c_o} = 1 - a * \exp[(-k * t)]$$
(7)

$$\frac{C}{C_o} = \frac{t}{\frac{t}{a*b^2} + \frac{t}{b}}$$
(8)

$$\frac{c}{c_o} = a * t^b \tag{9}$$

For these equations, $\frac{c}{c_o}$ was the ratio between observed sorption (C mg/g) to maximum sorption (Co mg/g), k (min⁻¹) was the first order rate constant, t (min) was time and both a and b were both fitting coefficients.

Sorption isotherm data was fit with five different models: (1) Langmuir, (2) Freundlich, (3) Temkin, (4) Redlich-Peterson, and (5) Langmuir-Freundlich.

$$\Gamma = (\Gamma_{\text{Max}} bC) / (1 + bC)$$
 (1)

$$\Gamma = K_{\rm f} \, C^{\wedge}(1/n) \tag{2}$$

$$\Gamma = A_1 + B_1 \ln C \tag{3}$$

$$\Gamma = A_2 C / (1 + B_2 C^n) \tag{4}$$

$$\Gamma = (\Gamma_{\text{Max}} b C^{1/n}) / (1 + b C^{1/n})$$
(5)

 Γ was the sorbed Zn concentration (mg Zn/ g solids), Γ_{max} was the maximum sorption potential (mg Zn/ g solids), b was the Langmuir equilibrium constant, C was the equilibrium concentration (mg Zn/ L), K_f was the Freundlich sorption capacity, n was the Freundlich sorption intensity constant, and both A and B were fitting parameters. C was determined experimentally; all other variables were determined by curve fitting along with 95% confidence intervals (Igor Pro ver.

5.05A, Wavemetrics). Γ was indirectly determined by ICP-MS and was explained by the following equation:

$$\Gamma = \frac{(C_o - C_e) * V}{M} \qquad (6)$$

where C_0 was the initial concentration of dissolved Zn in a reactor, C_e was the dissolved Zn concentration in a reactor after 24 hrs, V was the reactor volume, and M was the mss of solids. Pearson R^2 was determined for the fitting isotherm equations to determine the how well the isotherms fits the data (Microsoft Excel 2007). The Langmuir isotherm model predicted maximum sorption potential and therefore the isotherm model was used to compare sorption potential against other investigated sorbents.

3.0 Discussion

3. 1 Site characteristics

Visually inspecting sample sites revealed orange mats and bulbous orange biofilms near seeps. This is indicative of iron oxidizing bacteria (Figure 2a). The presence of iron oxidizing bacteria was further confirmed by evaluation of the sampling site. Favorable growth conditions were quantified by a microaerobic environment with a mean sample site D.O. of 1.41 ± 0.45 mg/L and a circumneutral pH of 7.16 ± 0.16 (Emerson, et al., 1994) (Table 1). Dissolved Fe²⁺ was 9.32 ± 5.74 mg/L, indicating sufficient dissolved iron to fuel the metabolic processes of the iron oxidizing bacteria. Furthermore, a morphological evaluation suggested that *Leptothrix*, a known iron oxidizing bacteria, was present as the sampling sites (Figure 2b).



Figure 2. A. Typical image of a biogenic iron oxide sampling site. Site was located near a wetland and has bulbous, orange mats present. B. Microscopic image of sample. Long sheaths suggest that *Leptothrix* was present at the sampling site.

Characteristics of biogenic iron oxides between samples were variable. For Spring Lake samples the total iron varied significantly with values between 99.2 and 936 mg/L and a mean value of 485 ± 386 mg/L (Table 1). Variation between the evaluated solids content and organic content was less significant among the Spring Lake samples with mean values of 1.89 ± 0.63 mg/L and 0.90 ± 0.12 mg/L, respectively. Moose Creek samples contained significantly higher

solids than other sample sites. Total iron, solids content, and organic content were 2034 ± 109 , 7.34 ± 1.30 , and 2.32 ± 0.41 mg/L respectively (Table 1). Differences between samples were attributed to sample age. Newly formed samples had a gelatinous appearance with large volume per solids content. New iron oxide formations also had bulbous structures giving biofilms very apparent three dimensional shapes. Aged samples lacked gelatinous texture, were condensed in structure, and typically yielded a high organic content per volume in unaltered newly collected sample. Moose Creek samples were "aged" which was why they had significantly more solids. Yakima sample characteristics resembled those of Spring Lake with respect to total iron and solids content, but had notably lower organic content (Table 1).

Table 1. Site characteristics from the seven different samples. Organic density, solids density, and total iron vary notably between samples. MC: Moose Creek, SL: Spring Lake, YK: Yakima (Myron Lake). Blank values were not recorded during field measurements. Values are reported with 95% confidence intervals.

	Organ	nic D	ensity	Solids Density			Total Iron				
	(mg/L)			(mg/L)			(mg/L)			pH	D.O.
MC1	2.03	±	0.09	6.42	±	0.29	2111	±	101	7.4	1.25
MC2	2.61	±	0.08	8.26	±	0.20	1957	±	49.8	-	1.5
SL1	0.98	±	0.16	1.24	±	0.23	99.2	±	13.4	7.1	1.65
SL2	0.81	\pm	0.23	1.5	\pm	0.18	236	\pm	8.75	7	1.9
SL3	1.03	\pm	0.18	2.22	\pm	0.10	668	\pm	18.2	7.3	1.73
SL4	0.78	\pm	0.05	2.6	\pm	0.05	936	\pm	26	7	0.42
YK1	0.45	\pm	0.02	1.23	\pm	0.07	490	\pm	32	-	-

3.2 Kinetic experiments

Zn adsorption to biogenic iron oxides occurred rapidly. Sixty three percent of sorption occurred within the first five minutes, and maximum sorption occurred after 24 hours (Figure 3). Sorption kinetics most closely followed the pseudo-first order model with an R^2 of 0.930 and a k of -0.0051 min⁻¹. Power function and second order models yielded R^2 values of 0.929 and 0.583 respectively (Table 2). These values compared well with other Zn sorption experiments. When lignites were used as a sorbent, equilibrium occurred after 20 min (Pentari, et al., 2009).

Furthermore, Al-Degs et al. (2006) modeled Zn sorption to natural sorbents with both pseudofirst order and pseudo second order models and concluded, due to rapid Zn removal, kinetic sorption was best represented by pseudo-first order kinetics. The pseudo-first order rate constant for these natural sorbents was 0.00507min⁻¹ at an initial Zn concentration of 4.05 mmol/ L, which agrees well similar to the 0.0051min⁻¹ reaction rate constant for biogenic iron oxides.



Figure 3. Zn sorption kinetics of biogenic iron oxides (Yakima 2 sample). Pseudo-first order kinetic model shown. Maximum sorption was 8.40 mg Zn/L at 24hrs. Other removal models are reported in Table 2.

				h			\mathbf{R}^2
	a			U			K
Pseudo-2nd order	0.500	<u>+</u>	0.184	0.844	<u>+</u>	0.027	0.538
Power Function	0.554	±	0.554	0.082	±	0.007	0.929
	а			k (min ⁻¹)			
Pseudo-1st order	-0.005	±	0.017	-0.337	±	0.001	0.930

Table 2. Kinetic coefficients for Zn sorption to biogenic iron oxides (Yakima 2 sample).

3.2 Batch experiments

Zn sorption to biogenic iron oxides followed expected isotherms. The Redlich Peterson isotherm had the best mean R^2 value at 0.948 ± 0.024. The Langmuir isotherm had a similar R^2 of 0.940 ± 0.031. Freundlich, Temkin, and the Langmuir Freundlich had mean R^2 of 0.881 ± 0.062, 0.905 ± 0.040, and 0.886 ± 0.065, respectively, demonstrating that they were less effective at predicting characteristics of Zn sorption to biogenic iron oxides. Freundlich, Temkin, Redlich Peterson, and the Langmuir Freundlich sorption coefficients are reported in Table 3 with corresponding R^2 values.

Table 3. Langmuir, Freundlich, Temkin, Redlich Peterson, and Langmuir-Freundlich isotherms for samples. Coefficients are presented with a 95% confidence interval.

	L	angmuir		F	reundlich		Temkin		
	Γ_{\max}	В	\mathbf{R}^2	\mathbf{K}_{f}	n	\mathbf{R}^2	A1	B1	\mathbf{R}^2
MC1	20.81 ± 2.01	0.09 ± 0.03	0.972	$3.55{\pm}0.39$	2.37 ± 0.19	0.982	3.95 ± 0.99	3.03 ± 0.37	0.915
MC2	0.89 ± 0.05	0.46 ± 0.14	0.959	0.36 ± 0.05	3.97 ± 0.67	0.924	0.36 ± 0.03	0.14 ± 0.01	0.888
SL1	10.18 ± 0.64	0.25 ± 0.07	0.958	3.13 ± 0.59	3.13 ± 0.61	0.911	2.53 ± 0.52	1.93 ± 0.20	0.950
SL2	13.11 ± 1.00	0.36 ± 0.15	0.908	4.99 ± 1.18	3.90 ± 1.14	0.793	4.43 ± 0.95	2.23 ± 0.35	0.868
SL3	$5.93{\pm}0.55$	0.11 ± 0.03	0.950	1.19 ± 0.31	2.61 ± 0.53	0.890	0.58 ± 0.37	1.13 ± 0.13	0.925
SL4	18.50 ± 0.67	0.47 ± 0.10	0.975	7.51 ± 0.87	4.00 ± 0.66	0.925	7.28 ± 0.51	3.01 ± 0.19	0.977
YK1	7.52 ± 0.78	0.24 ± 0.12	0.860	2.46 ± 0.76	3.51 ± 1.17	0.741	1.75 ± 0.77	1.42 ± 0.28	0.815

		Redlich Pete	erson	Langmuir Freundlich					
	A2	B2	n	\mathbf{R}^2	Γ_{\max}	b	n	\mathbf{R}^2	
MC1	4.61 ± 0.61	0.72 ± 0.03	0.72 ± 0.95	0.982	13.10 ± 1.43	0.87 ± 0.54	0.88 ± 0.95	0.728	
MC2	0.6 ± 0.07	0.92 ± 0.03	0.92 ± 0.95	0.940	0.89 ± 0.22	0.93 ± 0.24	0.93 ± 0.95	0.939	
SL1	4.73 ± 0.77	0.84 ± 0.95	0.84 ± 0.95	0.952	8.15 ± 0.64	0.67 ± 0.37	0.67 ± 0.95	0.825	
SL2	2.7 ± 1.1	0.09 ± 0.10	1.21 ± 0.20	0.928	13.05 ± 1.72	0.35 ± 0.16	0.98 ± 0.38	0.909	
SL3	0.43 ± 0.12	0.02 ± 0.03	1.31 ± 0.30	0.961	5.7 ± 0.96	0.10 ± 0.05	0.92 ± 0.29	0.951	
SL4	13.89 ± 4.60	1.05 ± 0.50	0.91 ± 0.05	0.982	20.63 ± 1.75	0.47 ± 0.08	1.38 ± 0.23	0.984	
YK1	1.00 ± 0.40	0.37 ± 0.06	1.33 ± 0.30	0.891	7.10 ± 1.04	0.149 ± 0.14	0.80 ± 0.39	0.866	

Differences in the Langmuir maximum sorption capacity between samples were significant and the source of the differences was difficult to identify (Table 3; Figures 4 and 5). Moose Creek 1 sample had the largest sorption capacity with a maximum sorption of 20.81 ± 2.01 mg/g. Moose Creek 2 sample had the smallest maximum sorption, with a value of 0.89 ± 0.05 mg/g. The sample characteristics between Moose Creek 1 and 2 were very similar (Table 1), but maximum sorption varied by three orders of magnitude. Conversely, Spring Lake samples showed less variability with a mean maximum sorption of 11.91 ± 5.18 mg/g. Yakima sample were similar to Spring Lake samples in their ability to remove Zn, but it had significantly less organic content. Despite these obvious differences, the reasons for the variability between samples were difficult to assess. No correlations were found between maximum sorption of the samples and organic density, solids density, or total iron ($\mathbb{R}^2 < 0.038$). Normalizing organic density and total iron by total solids also showed no significant correlations between samples and maximum sorption values ($\mathbb{R}^2 < 0.035$). This evidence suggested that no single removal mechanism was responsible for Zn removal between the different biogenic iron oxide samples.



Figure 4. Langmuir sorption isotherms for Zn onto biogenic iron oxides that were taken from Moose Creek. Duplicate values are shown. Additional isotherms and fitting parameters are listed in Table 2. Initial batch pH was 6.21 in Moose Creek 1 and 6.29 in Moose Creek 2.



Figure 5. Langmuir sorption isotherms for Zn onto biogenic iron oxides collected at Spring Lake and Yakima. Additional isotherms and fitting parameters are listed in Table 2. Initial pH varied from 6.54 to 6.83 between Spring Lake samples. Initial reactor pH for Yakima sample 6.63.

Both single and multilayer sorption was probable during batch experiments. Superior Langmuir isotherm fit implied that saturated monolayer sorption occurred on a homogenous sorbent surface (Al-Degs, et al., 2006), which would be governed by maximum sorption capacity, sorption site affinity for Zn, and H^+ and Zn exchange on the surface of the biogenic iron oxides (Altin, et al., 1998). When compared to the evaluated isotherms the Langmuir isotherm fit the sorption data quite well, but the mean R^2 of 0.94 was insufficient in predicting

single monolayer surface sorption (Kinniburgh, et al., 1983). At low equilibrium Zn concentrations, monolayer sorption was probable because the ratio of Zn to sorption sites was low. The implication here is that there were enough sorption sites on the surface of the iron oxides for just monolayer sorption to occur. Alternatively, at high equilibrium Zn concentrations, the ratio of Zn to sorption sites resulted in multilayer removal since the monolayer sorption sites are likely occupied. The occurrence of multilayer sorption was examined by calculating the heterogeneity coefficient β ($0 < \beta < 1$) (Altin, et al., 1998). A β close to one represented a homogenous surface (Altin, et al., 1998), and a small β suggests a heterogeneous where multilayer sorption is likely. β can be determined from the Freundlich isotherm in which $\beta = 1/n$. The mean β for all experiments was 0.31 ± 0.05 which depicts a heterogeneous surface and explains the unfavorable Langmuir R² for predicting monolayer sorption.



Figure 6. Idealized schematic of a heterogeneous surface. A: Represents an area of the surface where no defects are present and the iron oxide is uniform. B - D are imperfections in the surface. B: niche or recession C: raised surface/corner D: raised surface (Brown, et al., 1999).

While monolayer and multilayer sorption was probable in the batch equilibrium experiments, specific removal pathways were difficult to identify without advanced spectroscopic techniques. Ambiguity exists in the literature as to which sorption mechanisms are present at the iron oxide surface (Brown, et al., 1999). This interaction is further complicated by the biogenic nature of these iron oxides (Emerson, et al., 1997) and the existence of an organic matrix that is produced by the iron oxidizing bacteria. It is understood that heterogeneous surfaces create electrostatically favorable sorption sites on surfaces. Niches (recessions), corners, and elevated surfaces are examples of surface imperfections that create sorption sites (Brown, et al., 1999) (Figure 6). These sites can be generated by imperfections during crystal formation, broken surface bonds, and chemical reactions with other constituents in solution. Surface imperfections become an increasingly dominant sorption mechanism where high Zn concentration is present, and as stated previously, leads to less favorable Langmuir R² values.

3.3 pH effect on sorption

Increasing initial batch reactor pH increased Zn removal. Maximum sorption in the Spring Lake 3 sample was elevated to 26.78 ± 1.09 mg/g when initial pH of the reactors was increased to 9.01. This was significantly higher than the circumneutral Spring Lake 3 sample, had a maximum sorption of 5.93 ± 0.55 mg/g at a pH of 6.66 (Figure 7). Increasing the pH also increased the R² value from 0.975 in pH 6.66 sample to 0.995 in pH 9.01 sample. Experiments that observed average sorption over a variety of pHs showed that sorption could be increased to 34.6 mg/g by raising the pH to 9.0 (Figure 8). A pH below 4.35 showed a mean sorption of 0.47 \pm 0.29 mg/g (Figure 8), indicating that decreasing pH significantly inhibited the amount of Zn that could be removed.

Increasing pH in experiments added another removal mechanism to the system, principally $Zn(OH)_2$ precipitation, which is described by the solubility equation (10). Relating $Zn(OH)_2$ solubility to [OH] (Eq 11) and pH yielded equation (13), which estimates the theoretical pH that precipitation occurred in the batch reactors.

$$K_{sp} = [Zn^{2+}]^*[OH^-]^2$$
 (10)

$$pH + pOH = 14 \tag{11}$$

$$pH = \log\left(\sqrt{\frac{K_{sp}}{[Zn^{2}+]}}\right) + 14 \tag{12}$$

Moore et. al. (2005) reported a K_{sp} of 4.5×10^{-17} and the initial Zn²⁺ concentration for these experiments was 20mg/L (0.3059 mM). Under these assumptions and conditions, precipitation occurred at a pH greater than 7.58. As seen in Figure 6 the initial pH for five of the reactors was 9.0, suggesting that precipitation, coprecipitation acted as a removal mechanism. This observation was further supported by Baltpurvin, et al., (1996) who observed Zn(OH)₂ precipitation from an ionic solution that occurred between the pHs 7.5 and 8.



Figure 7. Langmuir isotherms revealed increased sorption at elevated pH. After 24 hours, the pH altered Spring Lake 3 sample had a pH ranging from 6.21 at low equilibrium concentration to 6.51 at high equilibrium concentrations. Maximum sorption was $26.78 \pm 1.09 \text{ mg/g}$ for the pH altered Spring Lake 23 sample and $5.93 \pm 0.55 \text{ mg/L}$ for the unaltered Spring Lake 23 sample. Duplicate values are shown.



Figure 8. The ability of biogenic iron oxides to remove Zn from solution was dependent on the batch reactor pH. Initial Zn concentration was 20 mg/L. Optimal removal occurred at a pH of 9, while a pH below 4.35 reduced average removal to 0.47 ± 0.29 . Based on the solubility of Zn and hydroxide, precipitation started to occur at pH=7.58.

Further increasing the pH has been shown to complex the precipitated $Zn(OH)_2$ with OH⁻ and resolubalize the zinc as $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ (Equations 13 and 14) (Reichle, et al. 1975; Baltpurvin, et al., 1996).

$$Zn(OH)_{2} + OH^{-} \leftrightarrow Zn(OH)_{3aq} \qquad K_{sp @25^{\circ}C} = 1.32x10^{3} (13)$$
$$Zn(OH)_{2} + 2OH^{-} \leftrightarrow Zn(OH)_{4aq} \qquad K_{sp @25^{\circ}C} = 6.47x10^{2} (14)$$

According to the solubility constants for $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ this will occur at a pH near 12. Resolubalizing Zn as $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ would facilitate removal by surface sorption, but these conditions where never experienced during experiments. At near neutral pH, the Zn in the batch reactors was divided between the both Zn^{2+} and $Zn(OH)^{-}(K_{sp} = 2.54 \times 10^{11})$ ions, resulting in both species being sorbed to biogenic iron oxides (Brady, et al., 1999; Reichle, et al., 1975).

Metal oxide chemistry also suggests that the Zn cation removal benefited from a basic solution when precipitation was not occurring. This relationship was established by electrostatic forces between the water molecules that surrounded the biogenic iron oxides (Brown, et al., 1999). An increased OH⁻ concentration means more anions will be electrostatically bonded to biogenic iron oxide surfaces. The presence of these anions on the surface of the biogenic iron oxide results in electrostatically negative regions where Van der Waal Forces facilitated cation binding (Figure 9). This increase in the number of sites to which ionic Zn can bind led to the increased sorption that was seen in the pH varied experiment where biogenic iron oxides sorbed 25.71 ± 0.53 mg/g at a pH of 7.26. Theoretically at this pH no precipitation should have occurred leaving sorption to biogenic iron oxides as the most likely removal mechanism. Advanced spectroscopic methods would be needed to confirm this occurrence.

High pH iron oxide sample

Figure 9. Zn electrostatically benefits from a high pH. At a low pH Van der Waal forces between anions, water molecules and iron oxides (Fe(OOH)x) create area for Zn cations to bind. When the pH is increased the hydroxide ion makes even more electrostatically favorable site for Zn to bind. This was caused by an overall decrease surface charge characteristic by the presence of the hydroxide anion on the iron oxides surface. Adopted from Brown et al. (1999).

3.4 Sorption comparison

Biogenic iron oxides compared well with other organic and inorganic sorbents. In many instances, biogenic iron oxides outperformed these investigated sorbents (Figure 10). Larsen et al. (1981) conducted heavy metal removal studies and found that 5.3 mg Zn/ g of barley straw could be removed in a batch reactor. Other organic substrates such as coir, coniferous bark, factory tea waste and peat have shown to remove 8.6 (Conrad, et al., 2007), 7.4 (Seki, et al., 1997), 10.18 (Wasewar, et al., 2008), and 11.71 mg Zn/g (McKay, et al., 1997) respectively.

Inorganic sorbents have also been investigated. Natural soils such as natural zeolite, lignite, bentonite and orera-sepiolite have been shown to adsorb 3.93 (Minceva, et al., 2008), 10.71 (Pentari, et al., 2009), 8.27 (Kaya, et al., 2005) and 5.73 mg Zn/g (Garcia-Sancheza, et al., 1999) respectively. Furthermore, *Pseudomonas aeruginosa* was investigated as a sorbent in column studies and yielded a maximum sorption of 37.0 mg/g after nine days (Orhan, et al., 2006). Moose Creek 1 and Spring Lake 2 and 4 samples outperformed all of these sorbents (9). Activated carbon, which is currently the most common sorbent used for pollutant removal, was studied by Minceva, et al., (2008) and showed that activated carbon had a maximum Zn sorption capacity of 10.70 mg/g. This resembled the sorption capacity of unaltered Spring Lake samples, with mean sorption capacities of 11.91 ± 5.18 mg/g.



Figure 10. Maxium sorption values for a variety of experimental sorbents. Moose Creek 1 and Spring Lake 2 and 4 at circumneutral pH sorbed better than other studies sorbent. Natural zeolites (Minceva, et al., 2008), Bentonite (Kaya, et al., 2005), Lignite (Pentari, et al., 2009), and orera-sepiolite (Garcia-Sancheza, et al., 1999) are all clays. Coir was derived from coconut (Conrad, et al., 2007). Tea factory waste (Wasewar, et al., 2008), coniferous bark (Seki, et al., 1997), peat (McKay, et al., 1997), and barley straw (Larsen, et al., 1981) are all organic waste sorbents.

4.0 Conclusion

The investigation into Zn sorption to biogenic iron oxides yielded the following four conclusions. (1) Zn kinetics were described well by a pseudo-first order model ($R^2 = 0.930$) and a first order rate constant of 0.0051 min⁻¹. (2) The Langmuir isotherm was sufficient in describing sorption in equilibrium batch experiments and a maximum sorption value of 20.81 ± 2.01 mg/g was obtained. (3) Increasing initial reactor pH increased Zn removal, while decreasing the pH decreased Zn removal. (4) Multiple sorption mechanisms were attributed to Zn removal including precipitation and monolayer sorption.

The use of biogenic iron oxides presents a unique potential to remove Zn from solution. Biogenic iron oxides are naturally produced in the environment and therefore could be used in conjunction with treatment wetlands for pollutant removal. This could be cost effective by eliminating operating cost and eliminating the need to physically alter sorbents. To accomplish this, future research would have to be conducted to better understand long term fate of both the biogenic iron oxides and the sorbed pollutant.

Further research needs to be conducted before implementation of biogenic iron oxides can become feasible. Quantifying the age of the biogenic iron oxides may give insight to sorption mechanisms. Although visual inspection and sight conditions yields an arbitrary age of the biogenic iron oxides, being able to quantify sample age may give insight into which sorption mechanism, are dominate for a particular sample. With the knowledge of specific sorption mechanism the long term fate of the Zn can be further explored. This will be especially important for wetland implantation, where pH, DO, and chemical composition of the water change seasonally and spatially.

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Exploiting the structure of the biogenic iron oxides may shed light on maximum sorption capacities. As seen in Figure 11 the microscopic organization of these biogenic iron oxides creates a large surface area to water interface which can create favorable micropore flow regimes. This would facilitate increased sorption interactions and is supported by the notably increased sorption that occurs with newly formed iron oxides, although current research cannot confirm this occurrence. Further microscopic evaluation needs to be conducted on the structure of the biogenic iron oxides to determine if there is a direct correlation between "well structured" biofilms and sorption capacities. This research should be coupled with surface area experiments to quantify if better structure correlates to more interfacial surface area for sorption to occur.



Figure 11. SEM image of a Leptothrix biofilm. Arrows point to elevated surfaces that are stacked in the biofilm. The particular structure of the Leptothrix biofilm creates a large surface area that is exposed to the water, which increases sorption site - sorent interaction. Arrows point to elevated surfaces in the biofilm. Image taken from (Schieber, et al., 2007).

5.0 Bibliography

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