

Treatment of zinc-contaminated water using a multistage ferrihydrite sorption system

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Abstract

Previous studies demonstrated the environmental and economic benefits of treating lead(II)-contaminated water streams with ferrihydrite in multiple equilibrium sorption stages. In this work, multistage ferrihydrite sorption systems were evaluated for their effectiveness in reducing single-solute zinc(II) (Zn(II)) concentrations in contaminated water streams to very low levels. As for lead(II) (Pb(II)), experimental data and modeling results indicate that a multistage sorption system can significantly reduce Zn(II) effluent concentrations for the same total amount of sorbent or, alternatively, dramatically lower total sorbent consumption for the same effluent Zn(II) concentration. Compared to Pb(II), however, Zn(II) removal requires on the order of 10 times more sorbent to achieve the same target effluent concentration for the same pH and number of stages. Model predictions were made using a steady-state, multistage, equilibrium adsorber model that was previously developed for and integrated into OLI Systems' Environmental Simulation Program (ESP). The modified triple-layer model was used to simulate Zn(II) surface-liquid equilibria within the adsorber model. Engineering screening evaluations again indicate that a 2- to 3-stage sorption process can provide significant economic savings when compared to a 1-stage process operating with the same target effluent Zn(II) concentration. Additional equilibrium stages beyond 2 or 3 provide diminishing economic returns. The major economic driver for multiple contacting stages is reduced capital investment and operating costs for sludge handling, dewatering, and disposal.

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1. Introduction

Trace metal discharges from industrial manufacturing processes are being increasingly scrutinized and regulated as new, revised, and proposed regulations are pushing metal effluent limits to parts per billion (ppb) and lower levels [1–5]. Alkaline precipitation has historically been the technology of choice for meeting parts per million (ppm) regulatory levels for trace metals (e.g., Pb(II), Ni(II), Cd(II), Zn(II)) in direct-discharge wastewater point sources; however, this technology is limited to ≥ 1 ppm effluent concentrations be-

cause of the finite solubility of amorphous metal hydroxide phases (PbO, Ni(OH)₂, Cd(OH)₂, Zn(OH)₂, etc.) and inefficiencies in commercial solid-liquid separation devices [6]. On the other hand, much lower effluent levels are possible by taking advantage of the large sorptive capacity of amorphous, high-surface-area solids, such as hydrous iron and aluminum oxides.

As previously reviewed by Dyer et al. [7], the scientific and engineering literature is devoid of experimental and modeling studies demonstrating the use of a high-surface-area sorbent, such as ferrihydrite, to treat metals-contaminated wastewater streams to ppb levels in a multistage cross-flow or countercurrent-flow reaction system. Previous research by other groups has focused on one-stage treatment using amorphous metal oxides [8–10] or multi-

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equilibrium-stage treatment in fixed-bed columns using a granular sorbent that can be regenerated over many cycles [11–15]. More background on these previous studies can be found in Dyer et al. [7]. The various technologies for sorbing trace metals onto metal–oxide sorbents each fill a niche, and each technology offers its own advantages and disadvantages. The niche for multistage sorption onto ferrihydrite appears to be for the *ex situ* treatment of contaminated wastewater streams in existing or new wastewater treatment facilities that must comply with ppb regulatory levels for trace metals. Treatment at the process source, prior to dilution with the rest of the manufacturing site’s wastewater, will result in a more economical treatment process with less sludge generation and a smaller environmental footprint.

Dyer et al. [7] showed for lead(II) (Pb(II)) that treatment with a high-surface-area sorbent, such as ferrihydrite, in a cross-flow arrangement containing two or more equilibrium contacting stages will (i) reduce metal effluent concentrations to much lower levels than can be achieved in one stage using an equivalent amount of sorbent; or (ii) reduce total sorbent consumption and disposal for the same target effluent concentration. In theory, then, equilibrium staging can be used in a cross-flow or countercurrent flow configuration to optimize the removal of several trace metals and metalloids whose pH ranges for optimum treatment are much different. Experience in the chemical engineering field has shown that two to four contacting stages in a cross-flow or countercurrent-flow configuration often provide significant improvement over a single contacting stage in chemical reaction, leaching, and extraction systems, while additional stages beyond four or so often lead to diminishing economic returns [16–18]. A decision on the number of contacting stages often becomes an economic tradeoff between the incremental capital investment for the additional equipment and the savings in raw material, energy, and waste disposal costs.

In this study, one-, two-, three-, and four-stage ferrihydrite sorption systems were evaluated for their effectiveness in reducing single-solute zinc(II) (Zn(II)) concentrations to very low levels in contaminated water streams. The objectives of the research were threefold. First, to demonstrate for another trace metal how a multistage sorption process can significantly reduce trace metal effluent concentrations for the same total amount of sorbent or, alternatively, dramatically lower total sorbent consumption for the same metal effluent concentration. Second, to develop and validate a steady-state, multistage adsorber model for treating a Zn(II)-contaminated water stream to parts per billion levels, and in the process, demonstrate the integration of a surface complexation model (SCM), such as the modified triple-layer model (TLM), into a steady-state equilibrium process flow sheet simulator to predict metals removal efficiency and sorbent requirements. Third, to conduct engineering screening evaluations to verify the economic drivers for equilibrium staging.

2. Methods

2.1. Ferrihydrite preparation

The two-line ferrihydrite was synthesized, washed, and aged for 48 h according to the procedures described in Trivedi et al. [19].

2.2. Multistage Zn(II) sorption experiments

Sorption studies were conducted with preformed ferrihydrite solids at room temperature in a N₂ glovebox using well-mixed 1-l reaction vessels containing a 0.01 M NaNO₃ background electrolyte solution. All studies were conducted in triplicate at the same time using the same batch of ferrihydrite. Equilibration time was 4 h for each contacting stage, and pH was controlled at 6.5 using 0.1 M HNO₃ or NaOH. Zinc was added as Zn(NO₃)₂ using a 1 M stock solution. All chemicals were ACS reagent grade; ultrapure water (Micropore SA) was used throughout. Equilibrated ferrihydrite solids were separated from the aqueous phase using a RC5 Sorvall centrifuge operating at 12,000 rpm for 20 min. Graphite furnace atomic absorption spectroscopy (Perkin–Elmer Analyst 800) was used to analyze the centrates for total soluble Zn(II). The multistage, cross-flow sorption experiments were batch equilibration studies; the experimental conditions for each case are summarized in Table 1. For example, in a two-stage system, such as case 1B, 0.5 g of “fresh” ferrihydrite sorbent was first equilibrated with 0.6 mmol of Zn(NO₃)₂ dissolved in 1 l of a 0.01 M NaNO₃ background solution (39.23 ppm Zn). After 4 h, the mixture was centrifuged, and the resulting centrate was analyzed for residual Zn(II) in solution. The bulk of the remaining centrate (~0.9 l) was then added to a second 1-l reaction vessel, where it was equilibrated again for 4 h with 0.5 g/l of “fresh” ferrihydrite sorbent. The resulting centrate was analyzed for residual Zn(II). More background on the experimental protocol used in this study can be found in Trivedi et al. [20]. A N₂ atmosphere was chosen to be consistent with the macroscopic and spectroscopic studies reported in this companion paper [20].

2.3. Chemical equilibrium modeling software

The OLI Software (OLI Systems Inc., Morris Plains, NJ) was used to perform the multistage, steady-state simulations. Details on the thermodynamic databank and framework, the equation solvers, and the SCMs used in the OLI Software are presented in Dyer et al. [21]. More specifically, the Environmental Simulation Program (ESP) was used for this study, because it is designed for steady-state simulation of vapor, liquid, and solid interphase and intraphase equilibria occurring within multistage chemical process flow sheets. The modified TLM (as developed by Davis et al. [22] and Davis and Leckie [23], later modified by Hayes and Leckie [24,25], and finally extended by Sverjensky and Sahai [26])

Table 1
Definition of and results for Zn(II)/ferrihydrite (fh) multistage sorption case studies^a

Case	Stage	g of fh/l in each stage	Stg. 1 Zn(II) feed concn. (ppm)	Zn(II) effluent measured ^b	95% CI Zn(II) effluent measured ^c	Zn(II) effluent model	95% CI Zn(II) effluent model ^c
1A	1	1.0	39.23	1.2 ppm	1.1–1.3 ppm	1.4 ppm	0.73–2.6 ppm
1B	1	0.5	39.23	3.4 ppm	3.2–3.5 ppm	3.2 ppm	1.8–5.9 ppm
	2	0.5		108.6 ppb	102–117 ppb	189.2 ppb	55–426 ppb
2A	1	5.12	1.63	8.3 ppb	7.8–9.0 ppb	9.6 ppb	5.1–18.6 ppb
2B	1	0.34	1.63	110.7 ppb	106–114 ppb	136.5 ppb	76–249 ppb
	2	0.34		7.1 ppb	6.9–7.4 ppb	11.2 ppb	3.4–24.9 ppb
2C	1	0.15	1.63	301.4 ppb	293–309 ppb	283.9 ppb	169–491 ppb
	2	0.15		50.3 ppb	49.4–51.0 ppb	48.1 ppb	17.8–97.1 ppb
	3	0.15		7.3 ppb	7.0–7.4 ppb	8.1 ppb	1.6–18.5 ppb
3A	1	0.4	16.35	1.2 ppm	1.1–1.2 ppm	1.4 ppm	0.76–2.5 ppm
3B	1	0.2	16.35	3.4 ppm	3.39–3.41 ppm	2.9 ppm	1.8–4.9 ppm
	2	0.2		413.1 ppb	408–418 ppb	402.4 ppb	140–848 ppb
3C	1	0.1	16.35	6.2 ppm	6.1–6.3 ppm	5.9 ppm	4.2–8.4 ppm
	2	0.1		1.8 ppm	1.7–1.8 ppm	1.6 ppm	0.8–2.9 ppm
	3	0.1		425.4 ppb	422–430 ppb	391.8 ppb	111–808 ppb
	4	0.1		82.3 ppb	81.7–83.4 ppb	92.4 ppb	19–210 ppb

^a All experiments were conducted at room temperature in a N₂ glovebox using a 0.01 M NaNO₃ background electrolyte solution. The pH in each stage was controlled at 6.5 using 0.1 M HNO₃ or NaOH.

^b Mean of triplicate studies.

^c See Dyer [34] for more details on how the 95% confidence intervals (CI) were generated. CI for the measured values reflect “same-batch” variation displayed by the triplicate studies. CI for the model values reflect “between-batch” uncertainties in input parameters (i.e., pH, Zn(II), ferrihydrite, and NaNO₃ feed concentrations, and mass H₂O) as well as uncertainties in the thermodynamic parameters (i.e., surface complexation *K* values).

was utilized in this work, having provided best fits of the Zn(II)/ferrihydrite isotherm and pH edge data presented and analyzed in Trivedi et al. [20] and Dyer et al. [27]. The experimental data and TLM calibrations presented in this previous work cover the pH range 4.0–8.0.

2.4. Surface complexation models

Over the years, a variety of SCMs have been developed and utilized for predicting trace metal sorption onto mineral oxides. These include the nonelectrostatic model (NEM), the constant capacitance model (CCM), the diffuse-layer model (DLM), the generalized two-layer model (GTLM), and the modified TLM. SCMs attempt to explicitly account for the reaction processes occurring at the solid–water interface; they assume that metal ions form complexes with surface functional groups in a manner similar to metal–ligand complexation reactions in solution [28]. They are thermodynamic models that differ in their physical descriptions of the solid–water interfacial region (i.e., the location of sorbed species with respect to the surface as well as the description of surface charge–potential relationships across the interfacial region) and in their assumptions regarding the number of site types and the structure and composition of the sorbed species. More background on SCMs can be found in Hayes and Katz [28].

2.5. Modeling protocol

Examples of two-stage cross-flow and two-stage counter-current-flow sorption systems for treating a metals-contaminated wastewater stream are shown schematically in

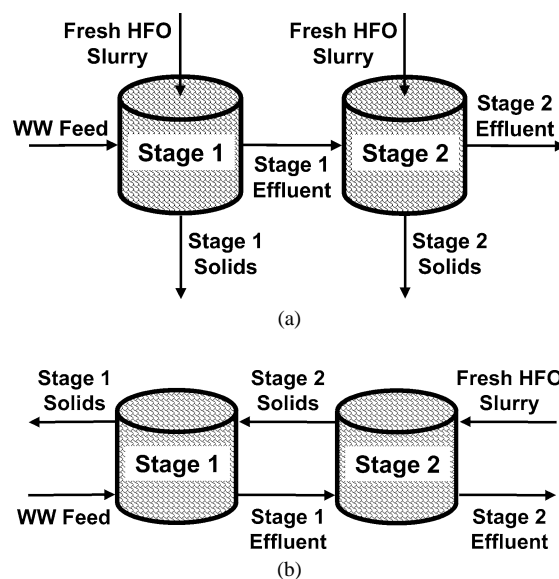


Fig. 1. Schematic flow diagrams for two-stage cross-flow (a) and counter-current-flow (b) sorption systems.

Figs. 1a and 1b, respectively. In a cross-flow system, fresh sorbent is added to each reaction vessel or stage, equilibrated with the contaminated wastewater, and then removed for dewatering and disposal. This contrasts with a true counter-current-flow system (Fig. 1b), where fresh sorbent is added to the final sorption stage, and partially spent sorbent is subsequently reused in the upstream stages (i.e., the flow of sorbent is counter-current to the flow of wastewater). A true counter-current-flow system represents the minimum-sorbent-consumption case for a specified metals

effluent concentration. For solids handling reasons, a cross-flow arrangement will probably be more practical for amorphous materials, such as ferrihydrite, in most industrial situations. In addition, to simplify the process, most full-scale industrial systems would likely be operated in a coprecipitation mode, rather than a sorption (onto preformed floc) mode as shown in Fig. 1. Operation in a coprecipitation mode would likely lead to lower Zn(II) effluent concentrations and sorbent requirements; however, the benefits of a staged process will be seen in either case. Finally, the experimental and modeling studies in this work are based on Zn(II) sorption onto preformed ferrihydrite at chemical equilibrium in order to utilize the TLM results from Dyer et al. [27]. This means that the kinetics of ferrihydrite particle formation and zinc sorption onto ferrihydrite are not included in the process model. Liquid holdup times in typical industrial reactor/clarifiers used to conduct multistage sorption, however, will be on the order of 2–4 h. As reported in Trivedi et al. [20], batch studies were performed initially to determine the kinetics of Zn(II) sorption onto the external surfaces of ferrihydrite particles as a function of pH using the same boundary conditions employed in the constant-pH isotherm studies. The kinetic studies found that substantial change in sorption did not occur after 1–2 h; therefore, a contact time of 4 h was more than adequate for equilibration of Zn(II) with the external surface as well as with the macropore walls of the ferrihydrite particles. As a result, model predictions based on equilibrium sorption onto preformed ferrihydrite floc will most probably be conservative for environmental compliance purposes.

Steady-state process flow sheets were constructed in ESP using the appropriate combination of unit operations (separator, pH controller, acid/base manipulator, and sensitivity blocks) and feed/effluent streams (wastewater feed, sorbent feed, NaOH feed, stage 1 effluent, stage 1 solids, etc.). Separator blocks served as the isothermal reaction vessels. The

efficiency of the solid–liquid separation was also specified in this block. An acid/base manipulator block and a pH controller were linked to each separator block to regulate the flow of mineral acid or base to each reaction vessel, so as to control pH at 6.5. The sensitivity block was used to perform multiple-case runs. The TLM functioned within all blocks containing sorbing solids. An example of a block flow diagram for a two-stage ESP cross-flow sorption model is shown in Fig. 2.

The TLM parameters used in this work are summarized in Table 2. The TLM parameters, along with the corresponding mass law expressions and Zn(II) surface speciation assumptions, were obtained from Dyer et al. [27]. These assumptions and parameters are valid over the pH range 5.5–7.5 as noted in the table. The choice of a bidentate surface complex is based on spectroscopic data reported and analyzed previously [20,27]. Benjamin [29] discusses several approaches for estimating the concentration of available bidentate surface sites for use in equilibrium mass law expressions for bidentate species. To be consistent with the thermodynamic framework for the modified TLM in the OLI Software [27,34], the bidentate sites were assumed to be nonoverlapping and the number of available bidentate sites was assumed to be proportional to the number of monodentate sites to the first power. These assumptions provided excellent fits of the constant-pH isotherm data as reported in Dyer et al. [27]. ESP simulations were made for each of the cases listed in Table 1. The objective was to compare model predictions based on the single-solute Zn(II) sorption data reported in Trivedi et al. [20] to the results of the bench-scale multistage experiments. In theory, the results should not be statistically different when taking into account experimental and model uncertainties. In addition, generalized sensitivity studies were conducted over the pH range 5.5–7.5 to understand the impact of pH, Zn(II) feed concentration, number of stages, perfect versus imperfect solid–liquid separations,

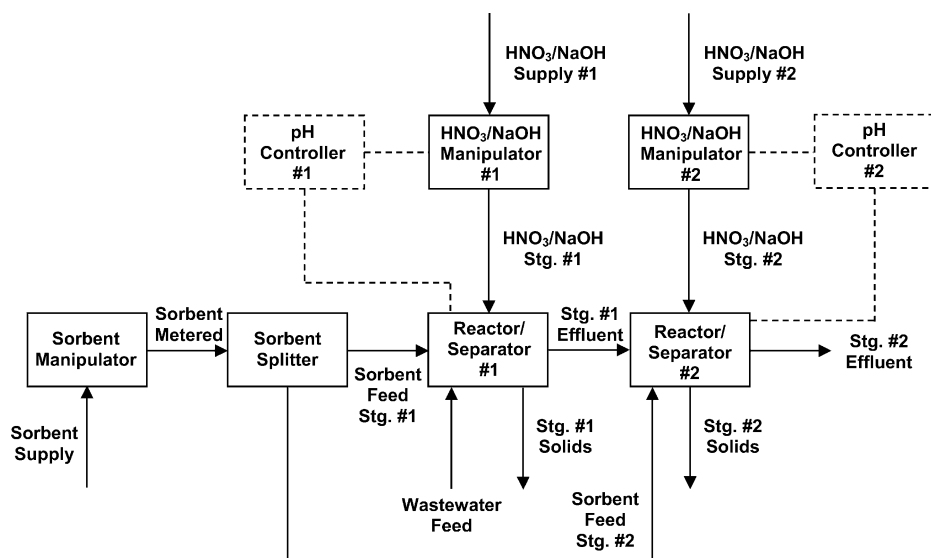


Fig. 2. Block flow diagram for a two-stage ESP cross-flow sorption model.

Table 2
Triple-layer model parameters used in ESP simulations^a

Parameter	Value
Zn(II) surface species	(≡FeO) ₂ Zn
N_s for H ⁺ (mol/mol)	1.2
N_s for Zn ²⁺ (mol/mol)	0.3, 0.65, 1.2 (pH 5.5, 6.5, 7.5)
A_s (m ² /g)	600
C_1 (faraday/m ²)	0.6
C_2 (faraday/m ²)	0.2
$\log K_{a1}^{\text{int}}$	-5.41
$\log K_{a2}^{\text{int}}$	-10.41
$\log K_{\text{NO}_3^-}^{\text{int}}$	-7.46
$\log K_{\text{Na}^+}^{\text{int}}$	8.48
$\log K_{(\equiv\text{FeO})_2\text{Zn}}^{\text{int}}$ at 1 g of solids/l ^b	4.95, 7.15, 9.52 (pH 5.5, 6.5, 7.5)
γ_s	$\gamma_s = \gamma_{\text{Zn}^{2+}}$

^a Refer to Tables 1 and 2 in Dyer et al. [27] for details on the chemical reactions and mass law expressions corresponding to each of the equilibrium constants given above. Definitions for each of the parameters can also be found in Dyer et al. [27].

^b For bidentate surface complexes, K^{int} is really a conditional K that depends on sorbent solids concentration. The value for K in this table is based on 1 g of ferrihydrite/l. See Table 2 in Dyer et al. [21,27] for additional explanation.

and cross-flow versus countercurrent-flow arrangement on the predicted Zn(II) effluent concentration at a fixed sorbent dose and the predicted sorbent requirement at a specified Zn(II) effluent concentration.

2.6. Engineering evaluations

Preliminary engineering screening evaluations ($\pm 30\%$ accuracy) were completed for each of the cases in Table 1 to assess the relative economic incentive/penalty for additional equilibrium sorption stages. The volumetric flowrate of contaminated wastewater was assumed to be 6.3 l s^{-1} (100 gal min^{-1}). There are two key differences between the treatment process assumed in the engineering evaluations and that used in the experimental and modeling studies—use of FeCl_3 , rather than $\text{Fe}(\text{NO}_3)_2$, and operation in a coprecipitation mode, rather than a sorption mode. Investment, costs, and economics in this manuscript can be safely used for a relative ranking of the multistage process alternatives; however, they should not be used on an absolute basis to compare to costs for other technologies, such as ion exchange and alkaline precipitation, that are published in other sources. In other words, alternative technologies should be compared to each other by the same evaluator on the same basis using the same estimation techniques and assumptions.

The evaluations are based on the 10-step engineering evaluations methodology outlined in detail in Mulholland and Dyer [30]. For each case, a process flow diagram was developed, showing the necessary equipment pieces (pumps, tanks, clarifiers, filter presses, etc.) and process interconnections. From the process flow diagrams, facility scopes of

work (i.e., description of the physical facilities required to build the process) were developed, and operating requirements were defined (annual requirements for 50 wt% NaOH, 30 wt% FeCl_3 , electricity, sludge disposal, etc.). On the basis of the facility scopes of work, capital investment was then estimated for each case using a factored research guidance appraisal technique that is widely used within the chemical industry. Finally, with estimates for new capital investment and operating requirements, a 10-y cash flow analysis was completed for each case to estimate annual cash operating cost and net present cost at both a 12% and a 25% discount rate. Net present cost (NPC) was the economic measure of merit used to rank alternatives, because it incorporates the effects of both new capital investment and ongoing cash operating costs over the life of the facility. A discount rate of 25% was chosen to rank the alternatives, because it better reflects the opportunity cost of capital in situations where the supply of capital dollars is limited and other viable projects are competing for the same dollars (which is almost always the case in the chemical industry).

The major assumptions used in the engineering evaluations are summarized in Table 3. Bare equipment, raw material, utility, and waste disposal costs were obtained from various reliable sources ([30–33] and personal communication with DuPont Sourcing Dept.). A process flow diagram for a two-stage, cross-flow, coprecipitation process is shown in Fig. 3. A slightly to moderately anionic polyacrylamide emulsion polymer is added to the clarifier to improve solid–liquid separation. A complete set of process flow diagrams, facility scopes of work, operating requirements, factored investment estimates, and 10-year cash flow analyses can be found in Dyer [34]. In addition, the supporting information provided by Dyer et al. [7] contains a similar set of engineering evaluation results for Pb(II) sorption onto ferrihydrite.

3. Results and discussion

3.1. Multistage sorption case studies

Experimental data (Zn(II) Effluent Measured) and ESP modeling results (Zn(II) Effluent Model) for the multistage sorption case studies are summarized in Table 1. Experimental data are the arithmetic average of the effluent Zn(II) concentrations measured in the three replicate studies for each stage of each case. Model data are ESP predictions based on the modified TLM and the parameters summarized in Table 2. To better assess the agreement between the measured and the model data, 95% confidence intervals (CI) were generated for each data point and are reported in Table 1. Details on the statistical tools, methodology, and uncertainty assumptions used to calculate the 95% CI are described in Dyer [34].

Briefly, confidence intervals for the measured values reflect the variation in or, more specifically, the *repeatability* of the three replicate studies for each stage of each case.

Table 3
Major assumptions and bases used in engineering evaluations

Assumption/basis	Value	Assumption/basis	Value
Raw Material Costs		Cash Flow Analysis	
30% FeCl ₃	\$0.33/kg ^a	Plant utility	90%
50% NaOH	\$0.33/kg ^a	Escalation rate	2.5%/yr
Emulsion polymer	\$3.30/kg ^a	Years of operation	10 yr
Filter aid	\$0.36/kg ^a	Income tax rate	40%
Filter cloth	\$1.00/m ²	Creep investment	1.5%
Filtered water	\$0.04/m ³	NPC ^b discount rates	12% and 25%
Hazardous waste landfill disposal	\$0.19/kg wet sludge	Depreciation (6-year)	20%, 32%, 19%, 12%, 12%, 5%
Electricity	\$0.045/kWh	Δ Working capital	60 days cash costs
Other Cash Costs		Capital Investment Factors	
General plant overheads	0.5% replacement inv. +24% salaries, wages, and benefits	Misc. equipment/foundations, supports, platforms	5%/7%
Maintenance	4% replacement inv.	Field material, labor, insulation	17%
Property taxes and insurance	0.75% replacement inv.	Piping/instrument/electrical	45%/16%/11%
Operations (round-the-clock shift coverage)	\$430,000/yr	Minor changes/working conditions	2%/10%
Technical exempt	\$160,000/yr	PG&S ^c /D&R ^d	10%
Startup/project liaison	10%/2% new inv.	Contingencies	25%
		MCC/ICR/ECR ^e	6%
		Freight/QA/sales tax/procurement	11%
		Engineering and home office/field indirects	20%/8%

^a 100% basis.
^b Net present cost.
^c Power, general, and service facilities.
^d Dismantlement and rearrangement.
^e Motor control center/instrument control center/electrical control center.

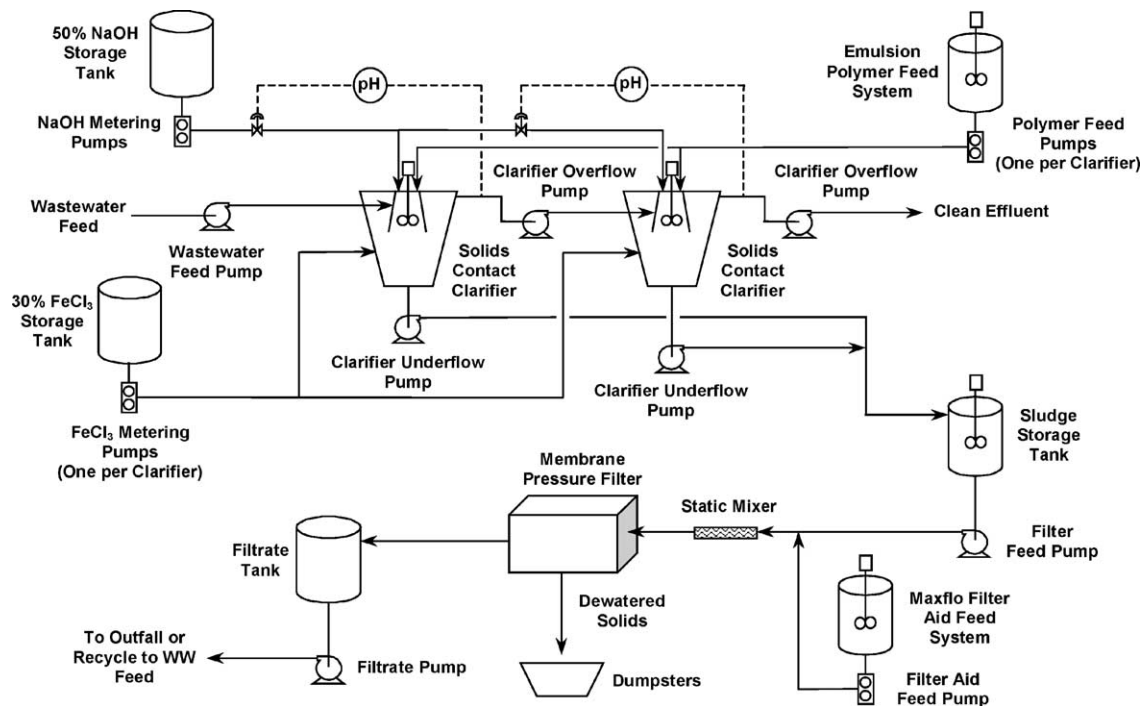


Fig. 3. Process flow diagram for a two-stage cross-flow ferrihydrate coprecipitation process used in the engineering evaluations.

Hence, the confidence intervals account for “within-the-same-batch” uncertainties in analytical/experimental procedures and equipment for the same operator conducting experiments with the same batch of ferrihydrate on the same

day. These include analytical equipment, sample collection, sample handling, and sample processing errors as well as errors in pH calibration/control, reagent doses, etc. The Resampling Stats for Windows software (Resampling Stats,

Inc., Arlington, Virginia) was used to estimate the 95% CI for the measured values. This software uses a bootstrap procedure [35,36] to randomly generate, *with replacement*, N new samples of size n directly from the original sample. The number of new samples (N) is usually set at 10,000 or more, while the sample size (n), in this case, was 3. For this study, N was set equal to 10,000. The bootstrap procedure effectively creates a hypothetical “infinite” population that represents one’s best guess about the real population.

The 95% CI for the ESP model predictions, on the other hand, attempt to account for “between-batch” uncertainties in the model input parameters (i.e., pH, Zn(II) feed concentration, ferrihydrite dose, NaNO₃ concentration, and the mass of H₂O) as well as uncertainties in the regressed thermodynamic parameters (i.e., surface complexation equilibrium constants). Examples of between-batch uncertainties include differences in sorbent properties, reagent concentrations, and pH measurement equipment as compared to the original isotherm and edge studies used to determine the best-fit model parameters. Hence, the confidence intervals attempt to reflect the reproducibility of Zn(II)/ferrihydrite sorption studies on different days using different batches of ferrihydrite/reagents as well as the quality of the model fits of the acid–base titration and Zn(II) sorption data used to estimate the thermodynamic parameters in the first place. As detailed in Dyer [34], the OLI Software’s error analysis tool was first used to propagate input and thermodynamic parameter uncertainties through the multistage sorption model, yielding local extrapolation models that approximated the value of each output parameter of interest (i.e., effluent Zn(II) concentration and Zn(II) surface loading). Monte Carlo simulations ($N = 10,000$) of the OLI-generated local extrapolation models were then conducted with the Resampling Stats software to estimate the 95% CI for the model predictions.

In principle, the greater the overlap of the confidence intervals for the measured and model values, the higher the probability that the two values are the same. That is, one cannot say with confidence that the model and the measured values are statistically different. On the basis of the 95% CI reported in Table 1 (i.e., when model and experimental uncertainties are taken into account), the agreement between the model-predicted and measured effluent Zn(II) concentrations is excellent. In all cases, there is significant overlap of the 95% CI. More rigorous hypothesis testing using Resampling Stats indicated that the difference between the measured and the model values was not statistically significant ($P < 0.05$) in any cases. On the basis of these results, the ESP model does a satisfactory job of predicting the expected Zn(II) removal efficiency in a multistage operation.

Another useful product of the error analysis tool in the OLI Software is a quantitative analysis of which input/thermodynamic parameter uncertainties dominate the uncertainty in the output variables [34]. In all cases, the output uncertainty in effluent Zn(II) concentration (Zn_{aq}) from the first equilibrium sorption stage was dominated

by the input uncertainty in $\log K_{(=FeO)_2Zn}^{int}$ (i.e., 60–70% of the output coefficient of variation squared). The balance was split between input uncertainties in pH and total ferrihydrite concentration. The importance of total ferrihydrite concentration relative to pH increased as Zn(II) surface loading increased. On the other hand, the output uncertainty in Zn_{aq} from the second and subsequent stages was dominated by the input uncertainty in total Zn(II) feed concentration (i.e., 45–75% of the output coefficient of variation squared). The balance was mainly due to input uncertainties in $\log K_{(=FeO)_2Zn}^{int}$, followed by pH and total ferrihydrite concentration. Due to error propagation downstream, the dominance of total Zn(II) feed concentration increased with stage number. Quantitative uncertainty analysis results for the multistage cross-flow sorption case studies are summarized in Table 4. The results in Table 4 are based on the same input/thermodynamic parameter uncertainty assumptions reported in Dyer [34] for Zn(II) and Pb(II).

3.2. Generalized multistage sensitivity studies

Figure 4 shows the effects of influent Zn(II) concentration, pH, and number of equilibrium stages on the predicted effluent Zn(II) concentration from a multistage cross-flow adsorber operating with a total ferrihydrite dose of 1 g/l, equally split across the stages (i.e., 1 g/l in a one-stage system vs 0.5 g/l in each stage of a two-stage system). Figure 4a assumes perfect solid–liquid separations, while Fig. 4b highlights the impact of 20 ppm suspended solids in the clarified effluent and 30 wt% solids in the settled iron sludge on effluent Zn(II) levels at pH 6.5. In both scenarios, the combined impact of pH and number of stages on Zn(II) removal is significant. For example, as shown in Fig. 4a, a 10 ppm Zn(II)-containing water stream can be treated to only 300 ppb Zn(II) using a one-stage adsorber at pH 6.5; however, the addition of a second and third stage at the same pH will reduce the effluent Zn(II) concentration to approximately 35 and 7 ppb, respectively. On the other hand, raising the pH from 6.5 to 7.5 at a constant number of stages will lower the effluent Zn(II) concentration from 300 ppb to only 200 ppb for a one-stage process and from 35 ppb to only 20 ppb for a two-stage process. In this case, the beneficial impact of adding equilibrium stages is more significant than the impact of raising the pH from 6.5 to 7.5. The benefit realized from adding a second stage is most significant at low Zn(II) feed concentrations and at pH 6.5 and 7.5, where sorption of Zn(II) is highly favored. For pH 6.5 and 7.5, adding a second stage lowers the effluent Zn(II) concentration 4- to 15-fold for a Zn(II) feed concentration of 100 ppm or less. This is substantially lower than the 30- to 100-fold reduction realized for Pb(II) at pH 5.5 and 6.5 [7]. The diminishing impact of additional equilibrium stages at high Zn(II) feed concentrations (>100 ppm) is the result of operating closer to site saturation (i.e., the systems are closer to being sorbent-limited). The results above are to be contrasted with a cocurrent contacting arrangement, where the sorbent

Table 4
Input/thermodynamic parameters dominating output uncertainty in Zn_{aq} (ppm) for multistage sorption case studies (pH 6.5, 0.01 M NaNO₃)

Case	Stage	Zn outlet concn. (ppm) ^a	Surface loading (mol Zn/mol Fe)	Fraction of output COV ^b squared for Zn _{aq}			
				Total Zn	Total ferrihydrite	pH	log K ^{int} _{(=FeO)₂Zn}
1A	1	1.38	0.0514	–	0.10	0.14	0.74
1B	1	3.21	0.0979	–	0.15	0.13	0.70
	2	0.189	0.0082	0.51	0.04	0.07	0.38
2A	1	0.0096	4.3E-04	–	0.08	0.15	0.77
2B	1	0.136	0.006	–	0.08	0.15	0.77
	2	0.011	5.0E-04	0.50	0.04	0.07	0.39
2C	1	0.284	0.012	–	0.08	0.14	0.76
	2	0.048	0.0021	0.50	0.04	0.07	0.39
	3	0.008	3.6E-04	0.67	0.02	0.05	0.26
3A	1	1.36	0.05	–	0.10	0.14	0.74
3B	1	2.9	0.091	–	0.14	0.13	0.71
	2	0.402	0.017	0.49	0.04	0.07	0.39
3C	1	5.89	0.142	0.02	0.21	0.12	0.63
	2	1.61	0.058	0.45	0.06	0.08	0.41
	3	0.392	0.0166	0.63	0.03	0.05	0.28
	4	0.092	0.0041	0.73	0.02	0.04	0.21

^a ESP model prediction.
^b Coefficient of variation.

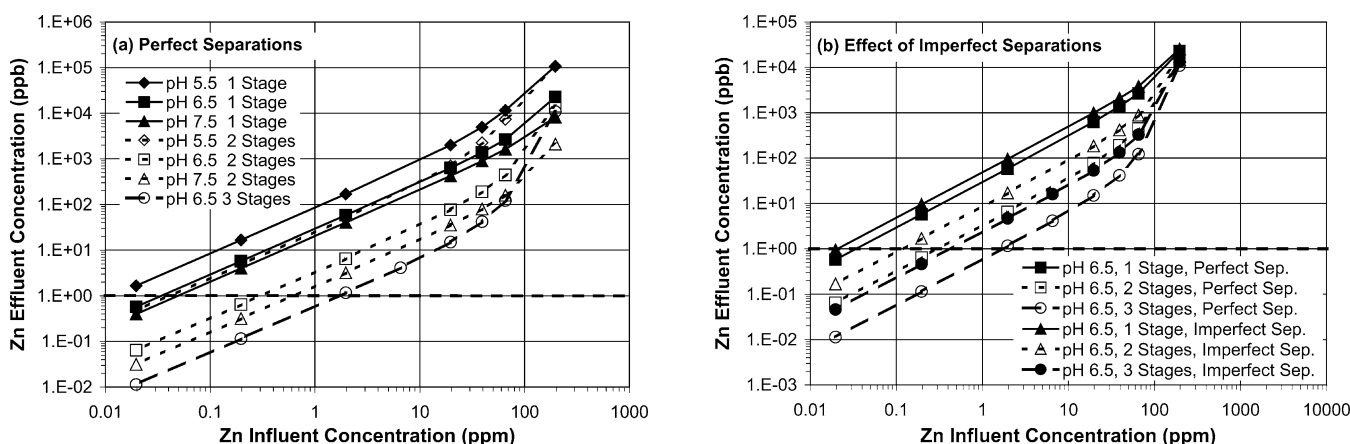


Fig. 4. Impact of influent Zn(II) concentration, pH, and number of equilibrium stages on the effluent Zn(II) concentration in one- and two-stage cross-flow adsorbers operating with a fixed total ferrihydrite dose of 1 g/l (1 g/l equally split between stages in two-stage system). In (a), perfect solid–liquid separations are assumed. In (b), the impact of imperfect solid–liquid separations (20 ppm suspended solids in clarified effluent and 30 wt% solids in the settled sludge) on Zn(II) removal at pH 6.5 is shown. Model predictions are based on the modified TLM using a 0.01 M NaNO₃ background electrolyte solution and parameters summarized in Table 2.

and contaminated wastewater are flowing in the same direction. In this case, additional removal of zinc would occur only if the pH is changed, the sorption reactions are reaction rate limited, and/or the availability of sorption sites is limited. In a cross-flow design, on the other hand, the fresh sorbent added to each stage will lower the trace metal(s) concentration to a new point on the equilibrium curve (i.e., the constant-pH isotherm). This occurs even if the pH is the same, the process reaches equilibrium, and the sorption sites are in excess.

The impact of solids carryover in the clarified effluent is to reduce Zn(II) removal efficiency. As shown in Fig. 4b, predicted effluent Zn(II) concentrations at pH 6.5 increase by 1.5- to 4-fold compared to the model predictions based on perfect solid–liquid separations. As might be expected,

the benefit gained by adding a second equilibrium stage is diminished as solids carryover increases. Consider the same 10-ppm Zn(II)-containing water stream discussed above for Fig. 4a. On the basis of Fig. 4b, the predicted effluent Zn(II) concentration for a two-stage adsorber operating at pH 6.5 is about 95 ppb (instead of 35 ppb) when more realistic solid–liquid separation efficiencies are assumed (20 ppm suspended solids in the clarified effluent and 30 wt% solids in the settled iron sludge).

Similarly, Figs. 5a and 5b display the impacts of influent Zn(II) concentration, pH, and number of equilibrium stages on the total required ferrihydrite dose in multistage cross-flow Zn(II) adsorbers operating with a fixed effluent Zn(II) concentration of 1 ppb. Figure 5a assumes perfect solid–liquid separations; Fig. 5b highlights the impact of 20 ppm

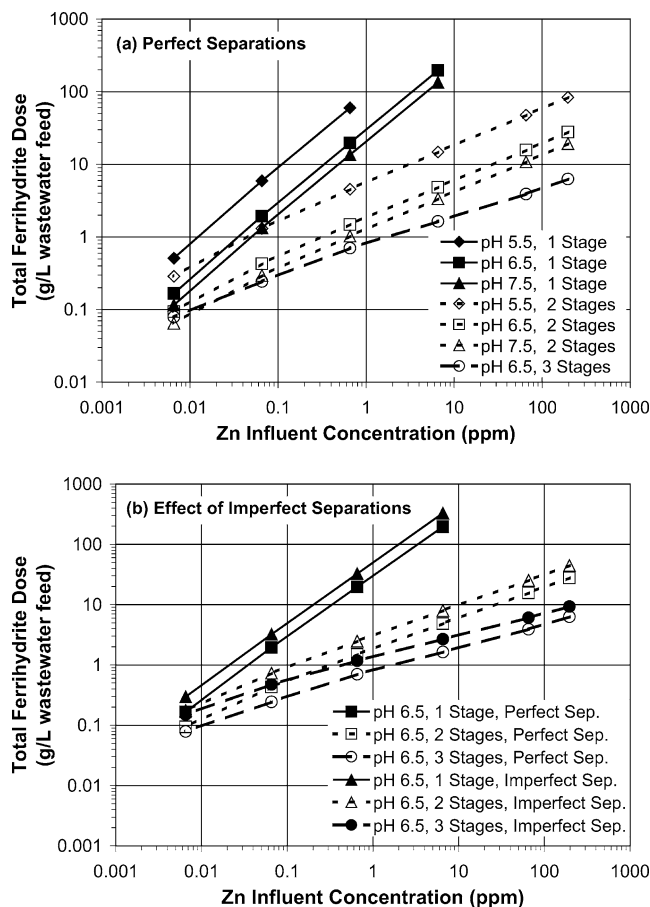


Fig. 5. Impact of influent Zn(II) concentration, pH, and number of equilibrium stages on total ferrihydrite consumption in one- and two-stage cross-flow adsorbers operating with a fixed effluent Zn(II) concentration of 1 ppb. Ferrihydrite is equally split between stages in the two-stage system. In (a), perfect solid–liquid separations are assumed. In (b), the impact of imperfect solid–liquid separations (20 ppm suspended solids in clarified effluent and 30 wt% solids in the settled sludge) on ferrihydrite consumption at pH 6.5 is shown. Model predictions are based on the modified TLM using a 0.01 M NaNO₃ background electrolyte solution and parameters summarized in Table 2.

suspended solids in the clarified effluent and 30 wt% solids in the settled iron sludge on effluent Zn(II) concentration at pH 6.5. As in Fig. 4, the combined impact of pH and number of stages on Zn(II) removal efficiency is significant. For example, as shown in Fig. 5a, total ferrihydrite consumption for the same hypothetical 10-ppm Zn(II)-containing water stream can be reduced from ~300 g/l using a one-stage adsorber at pH 6.5 to ~6 g/l using a two-stage adsorber at pH 6.5. Further reductions in ferrihydrite consumption can be achieved by raising the pH in a two-stage adsorber to 7.5 (~4 g/l) or, alternatively, by adding a third stage at pH 6.5 (~2 g/l). In this case, the beneficial impact of adding a second stage is most significant at higher Zn(II) feed concentrations and is uniform with pH. An approximately two-orders-of-magnitude reduction in ferrihydrite dose was also seen for Pb(II) in moving from a one-stage system at pH 5.5 to a two-stage system at pH 6.5 [7].

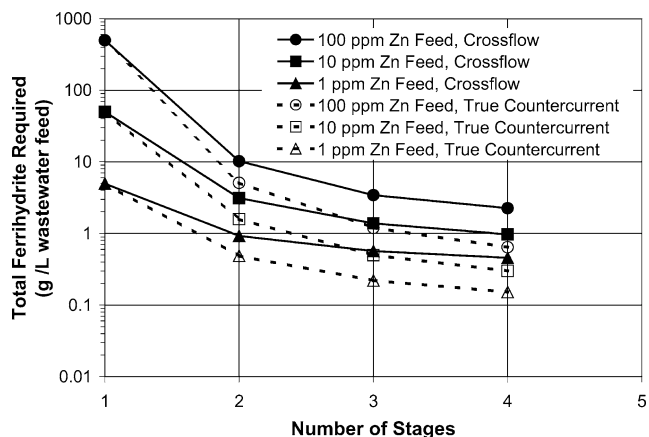


Fig. 6. Impact of the number of equilibrium stages and influent Zn(II) concentration on total ferrihydrite consumption in cross-flow and true countercurrent-flow adsorbers operating at pH 6.5 with a fixed effluent Zn(II) concentration of 10 ppb, 20 ppm suspended solids in clarified effluent, and 30 wt% solids in the settled sludge. Ferrihydrite is equally split between stages in the multistage systems. Model predictions are based on the modified TLM using a 0.01 M NaNO₃ background electrolyte solution and parameters summarized in Table 2.

The negative impact of solids carryover in the clarified effluent is also displayed in Fig. 5b. Predicted total ferrihydrite doses at pH 6.5 increase by 1.5- to 2-fold when compared to the predicted doses assuming perfect solid–liquid separations. For the same 10 ppm Zn(II)-containing water stream discussed above for Fig. 5a, the required total ferrihydrite dose for a two-stage adsorber operating at pH 6.5 is about 10 g/l (instead of 6 g/l) when more realistic solid–liquid separation efficiencies are assumed.

Finally, Fig. 6 shows the impact of number of equilibrium stages on total ferrihydrite dose as a function of Zn(II) feed concentration for both cross-flow (Fig. 1a) and true countercurrent-flow (Fig. 1b) arrangements. Figure 6 assumes operation at pH 6.5, 10 ppb Zn(II) total in the clarified effluent, 20 ppm suspended solids carryover, and 30 wt% solids in the iron sludge. It is apparent from Fig. 6 that the benefits of staging diminish as the number of equilibrium stages increases. By three to four stages, the dose curves begin to level out. This agrees with the results for multistage Pb(II) sorption as well [7]. Figure 6 also highlights the ferrihydrite consumption penalty realized by operating in a cross-flow arrangement instead of a true countercurrent-flow arrangement. As was the case for Pb(II), total ferrihydrite doses are 2–4 times higher for the cross-flow arrangement for two or more equilibrium stages.

3.3. Economic benefits of staging

Table 5 presents the results of engineering evaluations for the multistage sorption case studies summarized in Table 1, assuming a volumetric wastewater flow rate of 6.3 l s⁻¹. A key principle of engineering evaluations is that process flow sheets and scopes of work should be based on equivalent outcomes (i.e., the same effluent Zn(II) concentration)

Table 5
Engineering evaluation results for multistage sorption case studies (6.3 l s⁻¹ flowrate)

Case	Stage	g of fh ^a /l in each stage ^b	Zn(II) feed concn. (ppm)	2002 invest- ment (\$1000)	2004 cash operating cost (\$1000/yr)	2002 NPC ^c at 12% (\$1000)	2002 NPC ^c at 25% (\$1000)
1A	1	1.0	39.23	2,300	690	4,800	3,100
1B	2	0.5	39.23	2,800	760	5,500	3,600
2A	1	5.12	1.63	4,300	2,360	13,500	7,900
2B	2	0.34	1.63	2,600	600	4,600	3,100
2C	3	0.15	1.63	2,900	580	4,800	3,300
3A	1	0.4	16.35	1,900	420	3,300	2,200
3B	2	0.2	16.35	2,400	490	4,000	2,700
3C	4	0.1	16.35	3,300	620	5,300	3,600

^a Ferrihydrite.

^b Total ferrihydrite consumption equals the ferrihydrite dose in each stage times the number of stages (e.g., for case 3C, total ferrihydrite consumption is 0.1 g/l × 4 stages = 0.4 g/l total).

^c Net present cost.

in order to fairly compare alternatives. Case studies 2A–2C adhere to this principle, having been designed to achieve an effluent Zn(II) concentration of ~10 ppb from the final stage. For this reason, NPC_{25%} values for each of these cases can be compared to choose the most cost-effective alternative(s). In other words, they can provide insight on the economic benefit of additional equilibrium stages. Case studies 1 and 3, on the other hand, are not based on equivalent outcomes (i.e., the effluent Zn(II) concentration varies between alternatives). However, they do provide valuable insights on the incremental investment and net present cost associated with adding equilibrium stages to lower the effluent Zn(II) concentration at a fixed total ferrihydrite dose.

The results for case studies 2A–2C in Table 5 clearly show that the addition of a second equilibrium stage makes economic sense (NPC_{25%} of \$3,100,000 for two stages versus \$7,900,000 for one stage). The additional investment and ongoing operating costs associated with handling, dewatering, and disposing of an order of magnitude more iron sludge (5.12 g/l total for case 2A vs 0.68 g/l total (0.34 g/l per stage × 2 stages) for case 2B) are substantial. On the other hand, the addition of a third stage just about breaks even (NPC_{25%} of \$3,300,000 for three stages versus \$3,100,000 for two stages); therefore, the additional operational complexity associated with three stages versus two is probably not justified. In this case, the reduction in sludge from case 2B to case 2C is only about 33% (0.68 g/l total for case 2B vs 0.45 g/l total (0.15 g/l per stage × 3 stages) for case 2C). The use of four or more stages would almost certainly result in an NPC_{25%} > \$3,300,000. Very similar results were obtained for the multistage Pb(II) sorption studies [7].

The results for case studies 1 and 3 indicate that the incremental investment and NPC_{25%} for moving to a multistage operation are both on the order of \$450,000–\$500,000 per added stage. This compares to one-stage (i.e., base case) NPC_{25%} values of \$3,100,000 and \$2,200,000 for case studies 1A and 3A, respectively. In other words, the incremental NPC_{25%} for an additional stage is approximately 15–20% of the base-case NPC_{25%}. For case study 1, a second stage at

the same total ferrihydrite dose results in an order of magnitude reduction in effluent Zn(II) concentration. For case study 3, each incremental stage provides a 4- to 8-fold reduction in effluent Zn(II) concentration on the basis of the experimental data reported in Table 1.

4. Summary

Chemical equilibrium modeling is an important engineering tool because it enables one to predict the removal of contaminants, such as Zn(II) and Pb(II), from aqueous streams under different environmental conditions and at different sorbent concentrations. More importantly, the modeling approach used in this research is consistent with the macroscopic and spectroscopic findings for these closed systems that have been discussed in detail in Trivedi et al. [20]. Similar results would be expected in systems open to the atmosphere. As regulated trace metal concentrations in water discharges are pushed to parts per billion and lower levels, multistage contacting schemes will likely provide substantial economic benefits when sorption onto or coprecipitation with amorphous materials, such as ferrihydrite, is being considered. The results of this research have confirmed that:

1. A multistage sorption process can significantly reduce trace metal effluent concentrations for the same total amount of sorbent or, alternatively, dramatically lower total sorbent consumption for the same metal effluent concentration. For a fixed total ferrihydrite dose at pH 6.5 and 7.5, adding a second equilibrium stage will lower the effluent Zn(II) concentration by 4- to 15-fold for a Zn(II) feed concentration of 100 ppm or less. Similarly, adding a second equilibrium stage at a fixed pH will reduce the total ferrihydrite dose by as much as two orders of magnitude for the same target effluent Zn(II) concentration.
2. A 2- to 3-stage sorption process can provide substantial capital investment and operating cost savings when

compared to a 1-stage process operating with the same target effluent Zn(II) concentration as shown in case study 2 in Table 5. This corroborates the findings reported in Dyer et al. [7] for multistage Pb(II) sorption as well.

3. A steady-state process flow sheet simulator, such as OLI Systems' ESP software, can adequately predict Zn(II) removal in a multistage ferrihydrite adsorber using the triple-layer surface complexation model calibrated with macroscopic and spectroscopic Zn(II) sorption data. While wastewater streams with a more complex speciation may limit the practicality of the triple-layer model, the methodology and economic drivers for multistage sorption remain the same regardless of the surface complexation model chosen.

Finally, the collective body of work presented in Trivedi et al. [19,20], Dyer et al. [7,21,27], Dyer [34], and this paper helps to show how fundamental macroscopic and spectroscopic metal sorption data, coupled with surface complexation models, can be practically used to help solve industrial trace metal emissions problems.

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Appendix A. Nomenclature

A_s	specific surface area of sorbent (m^2/g)
C_1	inner-layer capacitance term for triple-layer model ($\text{faraday}/\text{m}^2$)
C_2	outer-layer capacitance term for triple-layer model ($\text{faraday}/\text{m}^2$)
K_i^{int}	intrinsic or thermodynamic equilibrium constant
K_{a1}^{int}	intrinsic acidity constant for surface deprotonation reaction: $\equiv\text{FeOH}_2^+ = \equiv\text{FeOH} + \text{H}^+$
K_{a2}^{int}	intrinsic acidity constant for surface deprotonation reaction: $\equiv\text{FeOH} = \equiv\text{FeO}^- + \text{H}^+$
N	number of resamples
n	sample size
N_s	surface site density (mol of sites/mole of sorbent)
$\gamma_{\text{Zn}^{2+}}$	activity coefficient for the Zn^{2+} ion in the bulk solution
γ_s	lumped surface activity coefficient used in OLI model to account for nonidealities of the surface complex species per Dyer et al. [21,27]

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