COMPETITIVE ADSORPTION OF HEAVY METALS ONTO STRAW

Sandra Nunez[1], ***Robert W. Peters***[2], *Lisa Ann Blankinship*[3], *and Joseph J. Gauthier*[4]
Graduate Student[1], *Professor of Environmental Engineering*[2], *Instructor*[3], *and Associate Professor of Biology*[4]
[1,2]*Department of Civil and Environmental Engineering*
[3]*Department of Biological Sciences*
[4]*Department of Biology*
[1,2,4]*University of Alabama at Birmingham, Birmingham, AlabAma 35294*
[3]*University of Tennessee at Martin, Martin, Tennessee 38238*

ABSTRACT

Runoff from industrial sites may contain a variety of heavy metals that can adversely affect the ecosystem. One approach to this problem involves capturing the heavy metals onto an adsorbent, such as straw. The uptake of heavy metals [iron (Fe), lead (Pb), cadmium (Cd), and chromium (Cr)] was studied at various solution pH values. Batch adsorption tests of various concentrations of heavy metals in contact with straw were performed, and the adsorption of heavy metals on straw was modeled using the Langmuir and Freundlich isotherm models:

Langmuir Model: $q_e = (Q^o\ b\ C)/ [1 + bC]$

Freundlich Model: $q_e = k\ C^{1/n}$

The Langmuir isotherm provided a better description of the adsorption of iron, lead, cadmium, and chromium than did the Freundlich isotherm model. Heavy metals were allowed to pass through beds packed with straw for adsorption and uptake by straw. The breakthrough characteristics of passing the solutions through the straw were determined for single heavy metals systems involving iron and lead. These breakthrough curves were compared to those obtained for multimetal systems (involving iron and lead simultaneously). The results showed that at high concentrations, both iron and lead were removed to nearly the same efficiency.

RESULTS AND DISCUSSION

Batch isotherm experiments were performed in which the straw was loaded at a dosage of 10 g/L, and various heavy metal solutions (iron, lead, cadmium, zinc) with concentrations ranging from ~1 to ~12 mg/L. After contact with the straw, the residual concentration of each heavy metal remaining in solution was determined using atomic absorption spectrometer techniques. Linearized adsorption isotherms for each heavy metal using deionized water typically had correlation coefficients exceeding 0.8 for Langmuir isotherm and 0.7 for Freundlich isotherm as shown in Figure 1. This figure shows low residual concentrations could be achieved. Likewise, linearized adsorption isotherms for heavy metals in buffer solution have correlative coefficients above 0.9 for both isotherm models. The results are presented in the linearized form of the Langmuir and Freundlich isotherm models. The parameters for the two isotherm models (Langmuir and Freundlich) were obtained for each of these heavy metal systems; the results are summarized in Table 1. In Figure 1 for the Langmuir isotherms, lead is best adsorbed followed by iron, cadmium and chromium. In the Freundlich isotherm, lead is best adsorbed followed by iron, cadmium and chromium. The correlation coefficients for the adsorption models typically exceeded 0.7, and usually exceeded 0.85, showing the adsorption models provided a fairly good description for the adsorption of heavy metals by the straw. For any particular heavy metal, the correlation coefficients were usually higher for the Langmuir than for the Freundlich model, indicating that the Langmuir model provided a slightly better description for the adsorption of the heavy metals by the straw than the Freundlich model. Also there is not significant change in solution pH after contact with straw.

Iron and lead were chosen to show the competitive adsorption behavior. When iron and lead were combined using either deionized water or buffer solution, iron shows higher adsorptive capacity at higher equilibrium concentrations; however, lead has higher adsorptive capacities at lower equilibrium concentrations, for both of the isotherms (Langmuir and Freundlich) as shown in Figures 2 and 3. Also the intercept of the lines in Figures 2 and 3, showed similar adsorptive capacities for iron and lead at concentrations of approximately 2 mg/L in both isotherms Langmuir and Freundlich. There is not a significant change in solution pH after contact with straw.

From the results shown in these figures, the parameters for the Langmuir and Freundlich isotherm models were determined for each of the heavy metals systems and the combined of iron and lead system. These parameters are Q° and b for the Langmuir isotherm, and K_N and 1/n for the Freundlich isotherm. The highest adsorption capacity (Q°) using deionized water was: iron followed by lead, cadmium and chromium, and the highest adsorption capacity using buffer solutions was: iron followed by chromium, lead and cadmium. Because the value of 1/n was less than 1.0 for most of the heavy metals, the adsorption of these heavy metals onto straw appears to be very favorable. The results are summarized in Table 1.

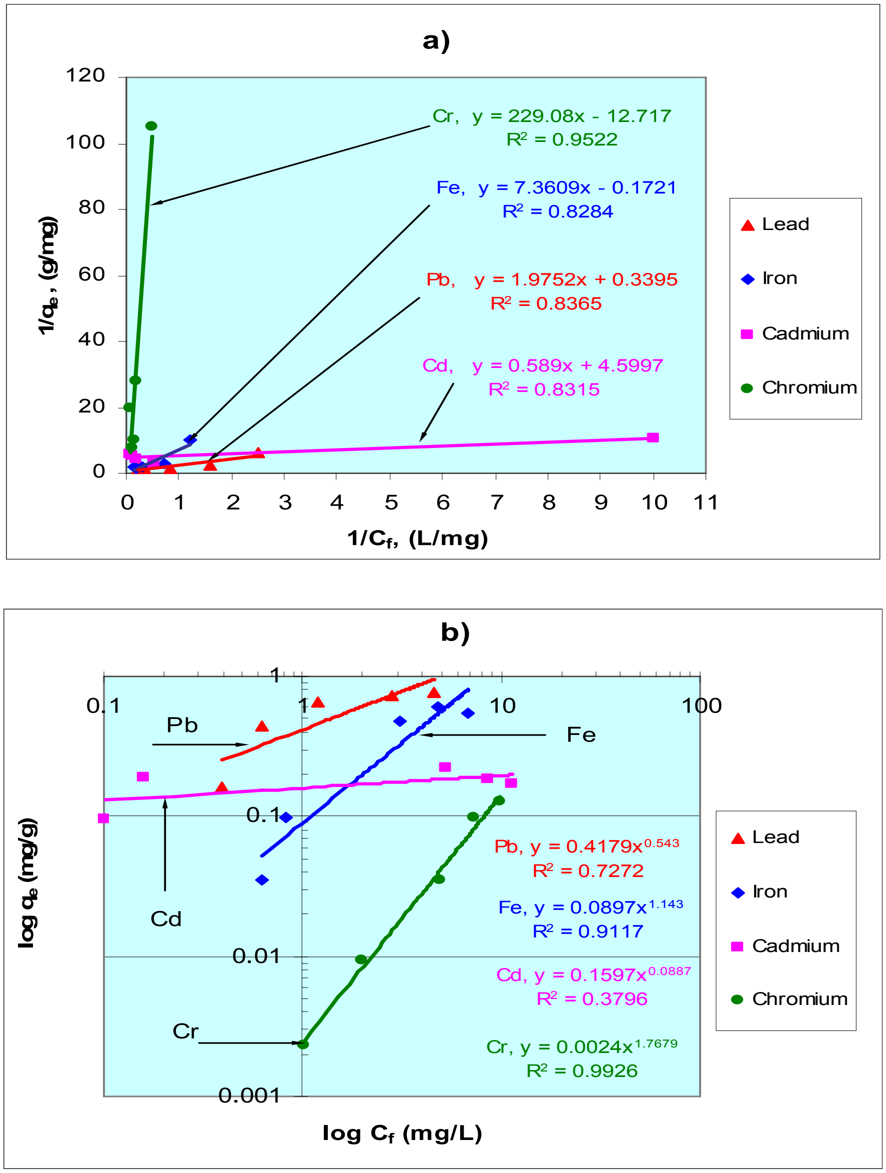
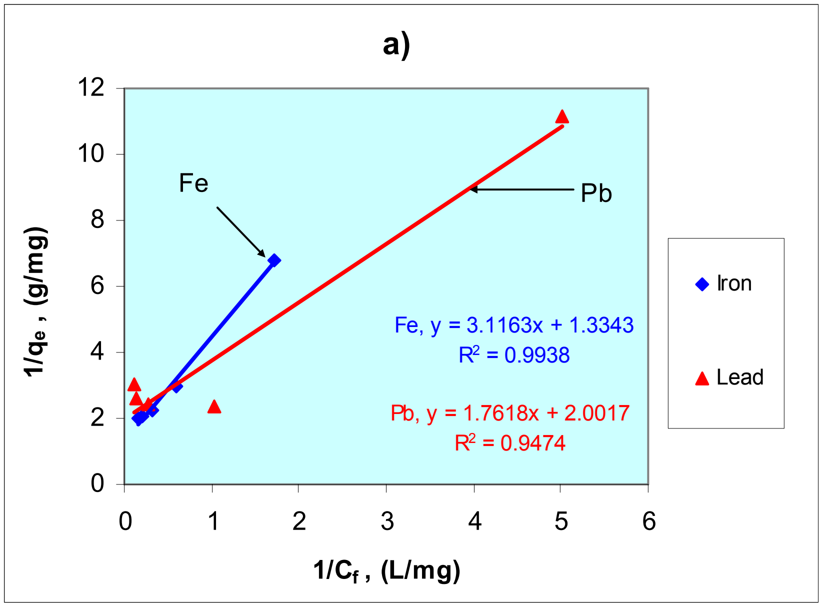


Figure 1. Langmuir and Freundlich Isotherms Using DI-Water for Selected Heavy Metals (Linearized Form).

a) Plot of Langmuir Isotherm for Selected Heavy Metals Showing $1/q_e$ versus $1/C_f$.
b) Plot of Freundlich Isotherm for Selected Heavy Metals Showing log q_e versus log C_f.



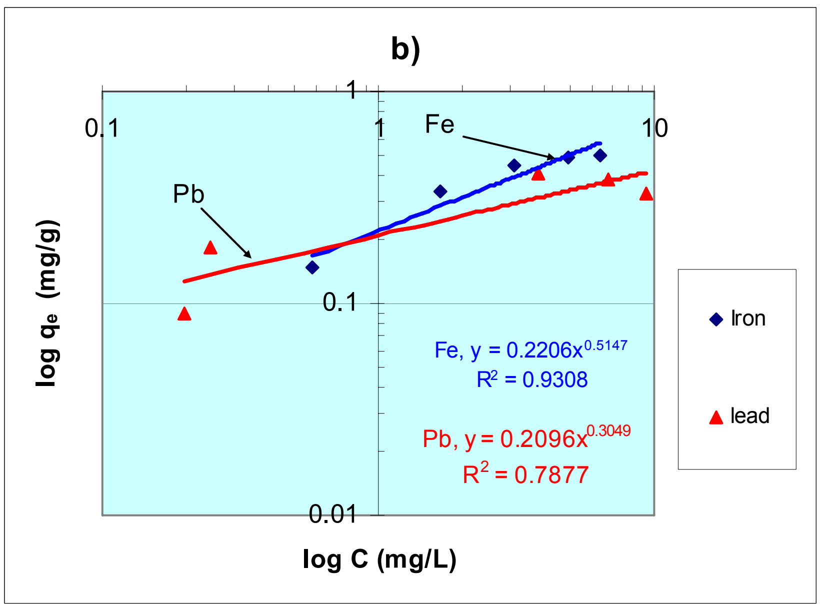
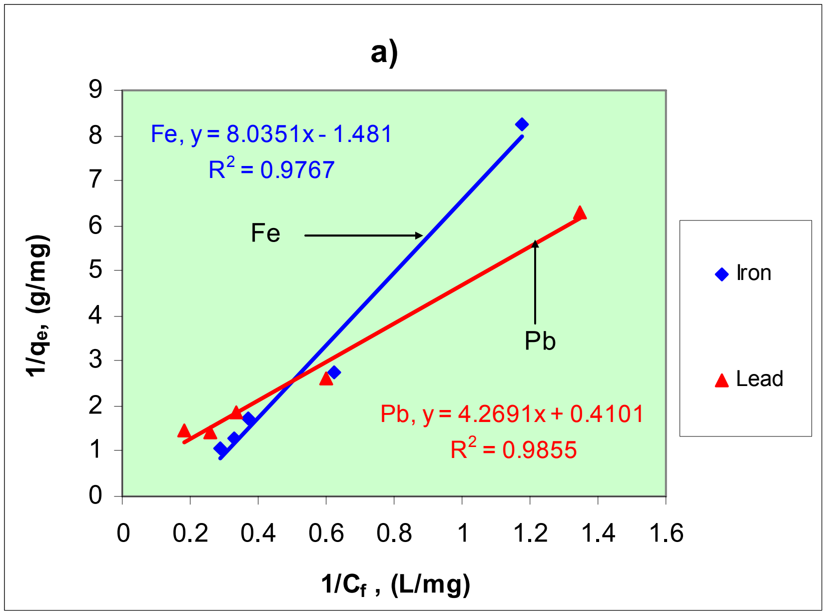


Figure 2. Competitive Adsorption Langmuir and Freundlich Isotherm for Iron and Lead Using Deionized Water (Linearized Form)

a) Plot of Langmuir Isotherm (at pH 2.64) for Iron and Lead Showing $1/q_e$ versus $1/C_f$.
b) Plot of Freundlich Isotherm (at pH 2.64) for Iron and Lead Showing log q_e versus log C_f.



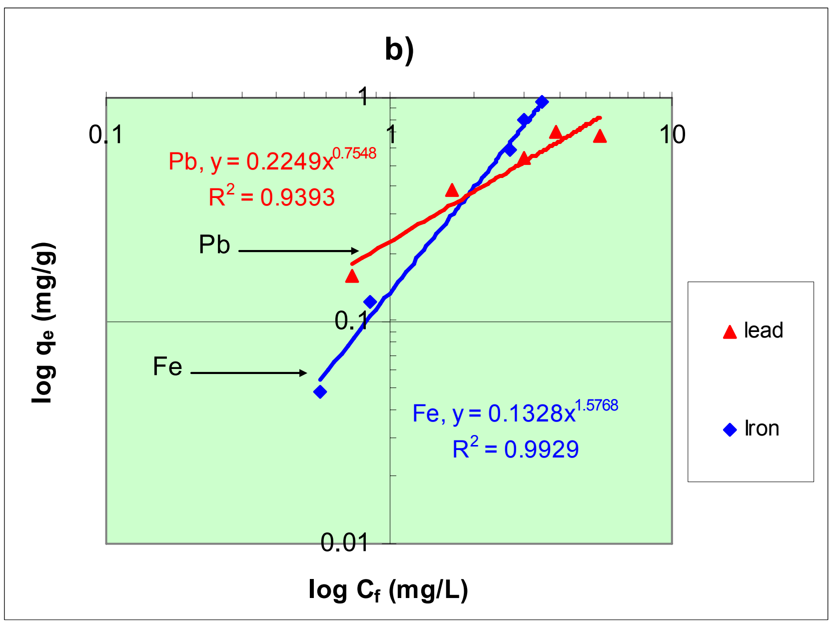


Figure 3. Competitive Adsorption Langmuir and Freundlich Isotherm for Iron and Lead Using Buffer Solution (Linearized Form).

a) Plot of Langmuir Isotherm (at pH 4.30) for Iron and Lead Showing $1/q_e$ versus $1/C_f$.
b) Plot of Freundlich Isotherm (at pH 4.30) for Iron and Lead Showing $\log q_e$ versus $\log C_f$.

Table 1. Summary of Langmuir and Freundlich Isotherm Constants.

Deionized Water and Buffer Solution	Heavy Metals and pH		Langmuir Isotherm Model			Freundlich Isotherm Model		
			Q^o	b	r^2	K_N	1/n	r^2
Deionized Water	Iron at pH 3.56		[5.811]	[0.023]	0.8284	0.090	1.143	0.9117
	Lead pH= 3.72		2.946	0.172	0.8365	0.418	0.543	0.7272
	Cadmium at pH= 3.79		0.217	7.809	0.8315	0.160	0.089	0.3796
	Chromium at pH= 4.19		[0.079]	[0.056]	0.9522	0.002	1.768	0.9926
	Iron and Lead combine	Iron at ph= 2.64	0.749	0.428	0.9938	0.221	0.515	0.9308
		Lead at pH= 2.64	0.500	1.136	0.9474	0.210	0.305	0.7877
Buffer Solution. (Acetic Acid and Sodium Acetate)	Iron at pH= 4.10		5.244	0.028	0.9989	0.155	1.081	0.9929
	Lead pH= 4.36		1.276	0.368	0.9943	0.327	0.600	0.9521
	Cadmium at pH= 4.33		0.863	0.046	0.9983	0.035	0.862	0.9948
	Chromium at pH= 4.39		2.626	0.003	0.9493	0.010	0.805	0.9941
	Iron and Lead combine	Iron at pH= 4.30	[0.675]	[0.184]	0.9767	0.133	1.577	0.9929
		Lead at pH= 4.30	2.438	0.096	0.9855	0.225	0.755	0.9393

From bed depth-service time experiments (continuous flow through packed columns), the low adsorptive capacities of lead and iron result in fairly rapid breakthrough characteristics (less than 5-10 bed volumes for lead and iron onto straw). However, at high concentrations, both lead and Iron were removed to nearly the same efficiency, while lower heavy metals concentrations allowed the breakthrough curve to be shifted to the right achieving greater time before breakthrough. In addition, when iron and lead were combined, iron was adsorbed and retained more effectively by the straw than lead, resulting in a preferential adsorption of the iron; thus, lead breaks through the column before iron, indicating a competition for the site.

From the bed depth-service time analysis, the straw exhaustion rate was calculated using the slope, the cross section of the column, and the density of the straw. When iron and lead were combined, the straw exhaustion rate was higher compared to that for iron alone and lead alone. Iron and lead exhibit similar straw exhaustion rates. From knowledge of the bed depth-service time parameters, the system can be scaled to handled large throughput system and thereby be applicable for field demonstrations.

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