HW11 Explosives/Inorganics Remediation

10 points Due: Dec. 5

LIST ALL ASSUMPTIONS USED!

1. [3 pts] *TNT is treated in a two-stage biotreatment process: (1) an anaerobic fluidized-bed granular activated carbon (GAC) bioreactor (10-L with 1 kg GAC, recycle flow for 30% bed expansion, 0.34 d unexpanded empty bed HRT) in series with an (2) aerobic activated sludge reactor (17-L, HRT 15 days). The influent wastewater contained 100 mg/L TNT.*

a. What are the advantages of the selected FBR design versus a CSTR alternative?
keeping adapted biomass in the system, so not as much "growth" required to maintain high biomass concentrations in the reactor

b. What products would you expect in the effluent from the FBR?
products of anaerobic biodegradation: 2,4-dinitro-6aminotoluene; 2,6-dinitro-4-aminotoluene; 2-nitro-4,6-diaminotoluene; 2,6-diamino-4-nitrotoluene;

b'. from the activated sludge reactor? CO2, water, ...?

c. What is the SRT in the FBR? cannot determine since the biomass attached; VERY long
in the activated sludge reactor? 15 days (SRT = HRT)

d. What is the wastewater flow?
17-L/15 days = 1.13 L/d = 47.2 mL/hr

e. What other elements would need to be incorporated into the design?
the recycle flow in the FBR, the liquid volume in the FBR, the "biomass" in the FBR, the biomass in the activated sludge reactor, the oxygen addition rate to the activated sludge reactor and type of aerator, co-substrate addition to the FBR, nutrient addition to the FBR and CSTR, operating temperature of the reactors...

f. What parameters would you measure to characterize performance?
TNT and "metabolite toluene" concentrations in the effluent from the FBR
biomass in the effluent from the FBR
biomass and metabolite concentrations in the effluent from the CSTR (soluble TOC)

g. What parameters would you need to know in order to estimate the effluent concentration of TNT and the metabolites from each reactor?
biokinetics for degrading each compound (K and Ks) normalized to the total biomass consortia in the reactor, total biomass in each reactor, toxicity concentrations of each compound, interactive effects between compounds

2. [4 pts] Bioaccumulation of Metals by Phytoaccumulation
Given the following concentrations of heavy metals in "contaminated" site soil, design a phytomremediation system to remediate the site. Include in your design:

a. Type of plant selected and why
b. Selected soil "clean-up" criteria
c. Time to remediate site
d. "Fate" of the plants containing accumulated metals

Metal	Soil Conc mg/kg*	PLANT A			PLANT B			PLANT C		
		AC	TT	UR	AC	TT	UR	AC	TT	UR
Al	3200 2800	100	30000	1.2	5	20000	0.9	10	20000	0.3
As	80 100	20	5000	0.3	100	20000	0.2	50	10000	0.1
Cr	20 35	50	1000	0.3	20	5000	0.2	50	5000	0.1
Pb	50 40	20	8200	0.3	20	20000	0.2	50	20000	0.1
Mn	300 250	100	52000	0.1	5	90000	0.6	10	60000	0.3

* average meas conc from 2-4 ft deep/average meas conc from 10-12 ft deep
AC = accumulation coefficient; TT = toxicity threshhold, mg/kg;
UR = uptake rate = mg/kg-d (measured in lab tests as loss rate from completely rooted soil, during period when plant is alive)

assume no "interactive effects" of multiple metals uptake
assume site located in middle-America
PLANT A = grass; root depth approx. 10 ft; plant biomass ~800 g/m2 soil
PLANT B = deciduous tree; root depth >50 ft; PLANT C = conifer tree; root depth >50 ft
"tree" info: in 1 year on 1 acre grow approx. 5,520 lb plant material,
need approx. 660,000 gal water

First, consider that not all of the metal concentrations in soil listed in the Table may be hazardous or different than "background". Target concentrations for clean-up would likely be based on attaining near backgound concentrations. (In addition, regulation might be set to soil concentrations which would result in safe concentrations of metals leached into the groundwater.) The following information is pertinent to the toxicity associated with each of the metals:

Metal	Common Soil Range in U.S.	DW Std mg/L	Human health effects
Al	1000-3000	0.05*	neurotoxin
As	5-10	0.05	GI damage, vascular, teratogen; A carcinogen
Cr	1-25	0.1	+6 liver, kidney, resp disorders; A inhal carcinogen
Pb	10-30	0.005	anemia, kidney, cog and phys develop tox, B2 carcinogen
Mn	100-300	0.05	

First, I would recommend sampling in a "pristine" near-site area, in order to establish target clean-up levels. Based on the common ranges that I found (as listed in the Table), I set the clean-up criteria to the "max" of that common range. Therefore, manganese levels on site are O.K., as are the "deeper" concentration of aluminum and the shallow soil Cr. The greatest problem appears to be associated with the arsenic, since it is about 10x the clean-up criteria and has significant negative health effects.

Based on the given criteria, the "best" arsenic uptake rates over the 12 month growing season will occur with PLANT A in the shallow soil. However, at a removal rate of 0.175 kg/acre-year, >14,000 years would be required to reduce the Arsenic in the shallow soil to the selected clean-up level. With the trees, if the "mass" was allowed to accumulate due to growth without harvesting, greater biomass and therefore uptake would occur in subsequent years. Still, on the order of 600 years would be required to clean up both the shallow and deeper contamination, so phytoremediation doesn't appear to be a viable option for arsenic clean-up. Either different clean-up standards must be set, OR potentially interception of the arsenic-contaminated groundwater would be better options.

Therefore, ignoring arsenic the next most critical compound appears to be aluminum in the shallow soil. In this case, the best removal rates are achieved with PLANT A (in the first year). Natural aluminum levels are high, so assuming that only 200 mg/L aluminum removal is needed over a 2' band of soil, 80 years are still needed for aluminum removal using Plant B assuming uniform growth over an 80 year period. Again, this is a long period of time! In addition, 15,000 mg/kg is the maximum amount of aluminum that can partition into the tree based on the AC; after 78 years there is 195,312 kg tree/acre containing approx. 1233 kg aluminum = 6313 mg/kg Al, which is less than the maximum concentration due to AC partitioning and less than the 20,000 phytotoxicity maximum.

PLANT B is also better for As removal, at similar rates but greater overall equilibrium partitioning and toxicity tolerance than PLANT C.

However, additionally the Pb removal will take longer than Al removal, due to its presence above acceptable concentrations in BOTH shallow soil and deep soil. On the order of 200 years would be required. (Total biomass = 250,400 kg/acre; with 771 kg / 250400 = 3080 mg/kg in tree; AC max = 600 mg/kg; for Lead PLANT C is better).

3. [3 pts] Biosorption of metals
Your goal is to treat the following "acid mine drainage" effluents to meet drinking water standard (MCL or SMCL) concentrations.

waste stream
#1 = 50 mg/L Cu^{+2}, 50 mg/L Cd^{+2}, 50 mg/L Zn^{+2} pH = 4.0, temp 5-25°C
#2 = 100 mg/L Cd^{+2}, 10 mg/L Zn^{+2} pH = 5.0, temp 5-25°C

Given the following isotherms describing biosorption of metals to silica immobilized algae (SIA) and actinomycetes,
A) which of the two sorbents would you use in a packed bed to treat each of the given waste streams?
B) would you operate the system at the natural pH, or adjust the pH? what pH would you use?
C) what temperature would you operate the system at? (ambient or a selected constant temperature)

Test Conditions		SIA				Actinomycetes	
		<1 x E-4 M	ú	>1 x E-4 M	.		
		K	1/n	K	1/n	Q	b
20°C, pH 6	Cu	3.3	0.9	7.9	0.27	37	0.1
	Cd	1.4	0.7	3.9	0.36	21	0.07
	Zn	1.4	0.5	3.0	0.30	9	0.3
20°C, pH 5	Cu	3.2	0.94	7.9	0.25	35	0.1
	Cd	1.2	0.74	3.9	0.34	20	0.07
	Zn	1.3	0.54	3.0	0.27	9	0.3
20°C, pH 4	Cu	3.0	0.9	7.5	0.25	28	0.09
	Cd	1.0	0.7	3.5	0.34	15	0.05
	Zn	1.2	0.5	2.8	0.27	6	0.2
20°C, pH 3	Cu	0	0	0	0	3	0.09
	Cd	0.5	0.2	2	0.2	3	0.05
	Zn	0	0	0	0	3	0.2
10°C, pH 5	Cu	3.1	0.9	7.5	0.25	32	0.1
	Cd	1.1	0.7	3.4	0.34	18	0.07
	Zn	1.2	0.5	2.9	0.27	7	0.3

F = Freundlich isotherm; $\log q = \log K + (1/n) \log Ce$
L = Langmuir isotherm; $1/q = 1/(Q*b*Ce) + 1/Q$
where q = biosorbed quantity, mg metal/g dry mass sorbent
C = equilibrium liquid concentration of the metal

Assume that drinking water MCLs or SMCLs are the effluent criteria

Cu 1 mg/L smcl
Cd 0.005 mg/L MCL
Pb 5 mg/L smcl

First, knowledge of isotherms:
K and Q represent the maximum sorption capacity of the media, so higher values mean more metal can be biosorbed
1/n represents the adsorption bond, with higher n representing greater bond
Using the given information, one can reproduce sorbed concentration versus liquid concentration curves, for equilibrium conditions. This is important to look at all of the isotherms.

However, during continuous flow treatment, the system will not be at equilibrium.

mass sorbent exhausted * Qeq = Vol liq treated * Influent Conc
therefore, for the same Vol liq and influent conc, less mass sorbent is exhausted with larger Qeq at the influent concentration

In order to make the most optimal use of adsorption columns, they are typically run in series so that the sorbed capacity can be completely exhausted in the first, which can then be taken off-line for regeneration.

For example, with $\geq$ three columns in series each containing 50 kg media treating 5 L/min, with a fourth column off-line for regeneration and then cycled back into the sequence:

if Waste Stream #1, column #1 is FULLY exhausted after _ days (equil with inlet conc) and approx. time until effluent conc exceeded at effluent from first column

	SIA,		Actino,	
	d full exhaust	d >effl	d full exhaust	d >effl
Cu	2.76	0.42	3.18	0.32
Cd	1.81	0.0035	1.49	0.0006
Zn	1.12	0.37	0.76	0.42

SIA is clearly best, since full exhaustion from 1 metal will occur after 1.12 d instead of 0.76 days. Also, Cd breakthru after 5 minutes instead of 0.9 min. Would likely need more "polishing" reactors in series to maintain Cd below effluent limits, due to short "break-thru" time with respect to necessary effluent concentration.

Waste Stream #2

	SIA,		Actino,	
	d full exhaust	d >effl	d full exhaust	d >effl
Cd	1.30	0.0017	1.22	0.0005
Zn	3.88	2.15	4.69	3.75

For waste stream #2 under "ambient" pH of 5, and 20°C, the exhaustion times are similar for full exhaustion, but >3x longer for SIA with Cd. Therefoer, since the other differences are all closer to 50%, select SIA.

However, if looked at magnitude only, actinomycetes would be optimal.