Soil Washing to Remove Mixed Wastes

Objective
The goal of this laboratory exercise is to acquaint students with some of the chemical reactions that result in the binding of inorganic and organic pollutants in subsurface materials. Extractants used by engineers to release contaminants at hazardous waste sites (where mixtures of both types of contaminants are present) may or may not prove effective, depending upon their mechanism of action. In this laboratory exercise, students will test the efficacy of a variety of proposed extractants in the removal of a mixture of an inorganic metal cation, and an organic compound from a contaminated porous medium.

Introduction
Many Superfund site soils are contaminated with a mixture of contaminants including toxic metals and organic compounds. A pressing environmental problem is to devise clean-up strategies that can effectively remove mixed wastes. Many kinds of contaminants bind to soils and aquifer media (collectively referred to here as porous media). Binding reactions limit the effectiveness of “pump and treat remediation” in which a contaminated porous medium is flushed with water to remove contaminants. In such cases, it can prove useful to engineer the properties of the aqueous phase to improve the mobility of the pollutants of interest.

In the case of toxic metals, release of medium-bound or “adsorbed” metals can be enhanced by introduction to the pore solution of a dissolved compound that will bind to the metal in the aqueous phase and form a dissolved “complex”. Such compounds are referred to as “ligands”, and ligands that bind metals very strongly are called “chelating agents”. Metal solubility and adsorption can also be strongly influenced by the oxidation state of the metal, and use of oxidants or reductants to alter the redox conditions in a porous medium can modify metal mobility both directly and indirectly. Direct effects would be observed if oxidized and reduced metal species have different adsorption characteristics (ex. Cr$_2$O$_7^{2-}$ vs. Cr$^{+3}$). Indirect effects would be observed if a metal were bound to a solid phase that would be dissolved under different redox conditions (ex. Fe(OH)$_3$ may dissolve under reducing conditions). Addition of acids or bases could also alter metal mobility. Adsorption of metals is very sensitive to pH shifts, with a decrease in pH favoring the release of cationic metal species (ex. Cd$^{+2}$, Pb$^{+2}$) and an increase in pH favoring release of anionic species (ex. Cr$_2$O$_7^{2-}$, SeO$_3^{-2}$).

Organic cations and anions will have a pH dependent adsorption behavior similar to that described above for metal ions. However, many organic pollutants of interest are nonionic and their binding to the matrix of the porous medium is not greatly influenced by pH. “Hydrophobic interactions” of nonionic organic compounds with organic matter in porous media appear to be a major driving force for their binding. The addition of surfactants to the pore solution can help to release sorbed nonionic organic pollutants. Under suitable conditions many organic pollutants can be degraded by addition of oxidants or by indigenous or added bacteria [i.e.; given that
the bacteria have the necessary genetic capabilities, nutrients (N, P, etc.) and a suitable electron acceptor. Metals, however, are elements and cannot be degraded.

Porous media is not inert. The mineral and organic constituents of the porous matrix can react with added ligands, acids, bases, oxidants, reductants, and surfactants. A consequence, in some cases, is that a desired addition may be rendered impractical.

Given the variability and possible dissimilarity of conditions that influence the mobility of metal vs. organic pollutants, it is a challenging task to identify a remediation strategy that will successfully treat a given medium that is contaminated with mixed wastes. In this laboratory exercise, students will evaluate the utility of several alternative extractants for remediation of a soil that is contaminated with both a metal cation and an organic compound.

**Theory**

**Binding Reactions**

The binding reactions of pollutants to the porous matrix may be classified, at least in part, by where and how the binding reaction takes place. The term “adsorption” is used for reactions that take place at the interface between the solid and the solution. All other factors being equal, solids with a greater specific surface area (ex. units: m²/gram) will adsorb greater amounts of a dissolved solute. In adsorption reactions, the surface is referred to as an “adsorbent” and the solute as an “adsorbate”. Some adsorption reactions are driven by electrostatic attraction between the surface and the solute. “Ion exchange” is the term used for this type of reaction. All other factors being equal, surfaces with a greater number of charged sites per unit surface area will be able to bind greater quantities of dissolved ions. The concentration of surface exchange sites is commonly quantified as an “ion exchange capacity”. Surfaces with a high density of negatively charged sites (cation exchangers) will selectively bind positively charged ions while those with a high density of positively charged sites will be selective for anions.

“Absorption” is a process in which a solute penetrates within the solid matrix. “Partitioning” is a term that is synonymous with absorption. As an example, we would carry out a partitioning process if we were to add a pollutant to a separatory funnel containing water and an organic liquid such as octanol and then observe the resulting distribution of the contaminant between the aqueous and octanol liquid phases. The distributed contaminant would exist as a dissolved solute in each phase. As is noted below, the phase distribution behavior of nonionic organic pollutants in soils and aquifer media displays many characteristics of absorption reactions. The absorption of nonionic organics appears to be primarily into the organic matter content of the porous medium. This reaction is driven by the water loving nature of the solute, or lack thereof (i.e., pollutant “hydrophobicity”). All other factors being equal, porous media with higher organic carbon contents would have greater uptake of nonionic organic pollutants.

The term “sorption” is somewhat loosely used when the exact mechanistic nature of the pollutant’s distribution between the solution and the porous medium is not
understood, or when both adsorption and absorption reactions may contribute to the contaminant’s phase distribution.

Contaminant sorption reactions result from a reaction between a material that is dissolved in an aqueous solution with a solid phase. The physical/chemical properties of the contaminant, the solution and the sorbent all influence the resulting contaminant phase distribution. These influences are discussed below.

**Sorbent Surface Charge**

As noted above, if the sorbate is an ion, then electrostatic attraction to the surface can play an important role in contaminant adsorption. Virtually all soil surfaces are charged.

**Oxide Minerals**

Surface charge can result from the ionization of surface functional groups in response to the hydrogen ion concentration of the aqueous phase. Oxide minerals are often modeled as diprotic acids (Westall and Hohl, 1980). Accordingly the surface may donate two hydrogen ions as indicated by the following reactions:

\[
\text{SOH}_2^+ \xrightarrow{K_1} \text{SOH} + H^+ \quad 7.1
\]

\[
\text{SOH} \xrightarrow{K_2} \text{SO}^- + H^+ \quad 7.2
\]

where \(\text{SO}\) represents the oxide surface that may exchange two hydrogen ions, and \(K_1\) and \(K_2\) are equilibrium constants for the first and second acid dissociation reactions.

Note, each dissociation constant can be thought of as a expression of the relationship between the concentration of protonated and deprotonated surface sites and the solution hydrogen ion concentration. Accordingly:

\[
K_1 = \frac{[\text{SOH}][H^+]}{[\text{SOH}_2^+]} \quad 7.3
\]

\[
K_2 = \frac{[\text{SO}^-][H^+]}{[\text{SOH}]} \quad 7.4
\]

\(K_1\) therefore represents the solution hydrogen ion concentration at which the concentration of positively charged, diprotic, surface sites \([\text{SOH}_2^+]\) is equal to that of surface sites containing a single proton\([\text{SOH}]\). Similarly, when \([H^+]\) equals \(K_2\) then \([\text{SO}^-] = [\text{SOH}]\).

Although other models of the acid base behavior of oxide surface are conceivable, the above model is helpful in that it predicts that the surfaces can have both positively and negatively charged sites. With this model, \(H^+\) release from the surface will occur
in response to a decrease in the solution H⁺ concentration (i.e., an increase in pH, where pH is defined as \(-\log[H^+]\)). Accordingly, we would expect increasingly higher solution pH conditions to favor formation of negatively charged surfaces, and this is observed. Different surfaces would have different acidity constants (K₁ and K₂) and would be expected to have different surface charges at the same solution pH. Each surface, at one unique pH, would have an equal concentration of \(\text{SOH}_2^+\) and \(\text{SO}^-\) sites and would have no net charge. This is also observed and is referred to as the pH point of zero charge (PZC). SiO₂, a common oxide in porous media (the main component of sand), has a low PZC (≈ pH 2 to 3) while iron and aluminum oxides (that commonly occur as surface coatings) have considerably higher PZCs (≈ pH 7 to 8) (Parks and DeBruyn, 1962).

**Soil Organic Matter**

Another pH-dependent origin of surface charge is the ionization of the acidic functional groups in soil organic matter. The carboxyl groups of humic-type organic matter typically have acidity constants \(\leq 10^{-5}\) (pK ≤ 5) and are therefore highly ionized at circumneutral pH.

**Isomorphic Substitution**

A final source of charge in soil is isomorphic substitution in the crystalline lattice of some clay minerals. Substitution of Al⁺³ for Si⁺⁴ and Mg⁺² for Al⁺³ will result in a net negative charge for the clay mineral phase.

The combined effects of isomorphic substitution, ionization of organic functional groups and the low PZC of silicon oxide minerals make it likely that many porous media will have a net negative charge. Consequently, stronger binding of cationic contaminants is generally anticipated.

**Sorbent Ion Exchange Reactions**

Ion exchange reactions involve the exchange of ions of the same charge at an oppositely charge site on the solid surface. Exchange reactions are often characterized by “selectivity coefficients” that may be thought of as equilibrium constants for the exchange reaction. For example, in the exchange of two monovalent cations, the exchange reaction may be depicted as:

\[
\text{SO}^- - x^+ + y^+ \xrightarrow{K'_x} \text{SO}^- - y^+ + x^+
\]

where:

\[
K'_x = \frac{[\text{SO}^- - y^+] \cdot [x^+]}{[\text{SO}^- - x^+] \cdot [y^+]}
\]

The magnitude of the selectivity coefficient, \(K'_x\), reflects the extent to which ion \(x^+\) vs. \(y^+\) will accumulated at the surface. Ions with high selectivity coefficients can displace more weakly held ions from an exchange site.
In a negatively charged soil, anionic compounds (ex. ionized organic acids, $\text{NO}_3^-$, $\text{Cr}_2\text{O}_7^{2-}$, etc.) will be repelled from the surface and therefore may be highly mobile. Cationic species (ex. quaternary ammonium organic compounds, divalent transition metals, etc.) will be attracted to the surface and have restricted mobility. In principle, exchangeable pollutant cations may be mobilized by introduction of high concentrations of an innocuous cation. The practicality of such an approach would be dictated by the extent to which other exchangeable cations (that are not of environmental concern) are also exchanged. Since cations such as $\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$ $\text{Mg}^{2+}$ are abundant in porous media, the amount of a cation added for exchange of a trace pollutant would have to be in great excess of the pollutant cation. As a result, release of contaminant cations by an ion exchange mechanism does not appear to be economically feasible.

**Sorbent Hydrophobic Interactions**

The mechanisms responsible for the adsorption of charged species differ considerably from those for nonionic compounds. Adsorption of charged ions may, in some cases, involve more than the simple electrostatic attraction of ions to a surface of opposite charge. Transition metal cations, for example, will often adsorb to oxide surfaces even under solution conditions that confer a positive charge on the surface (see additional discussion below under the topic of solution characteristics).

The sorption of nonionic organic pollutants behaves as if it is a partitioning process into the organic matter that is present as part of the soil matrix. Some of the general characteristics that lead to this conclusion are the observance of linear sorption isotherms at high solution concentrations (that can approach the solubility limit of solute compounds). [Note, an “isotherm” is simply the relationship between the quantity of pollutant that is bound (per unit mass or unit surface area of the sorbent) and the concentration of contaminant in solution.] In contrast, adsorption reactions are limited by the availability of surface sites and adsorption isotherms are typically non-linear at high solute concentrations. Partition reactions are also relatively free from competition (i.e., the presence of a second solute does not affect the sorptive uptake of the first) while competition for surface sites is an expected characteristic in an adsorption process. The extent of sorption of a given nonionic organic onto a variety of sorbents is highly correlated with their organic content as expressed by the weight fraction of organic carbon, $f_{oc}$ (Karickhoff, 1984). For the same sorbent, the sorption of different nonionic solutes is highly correlated with their octanol-water partition coefficients ($K_{ow}$) (Karickhoff, 1984). Collectively, these observations lead to the conclusion that the sorption of nonionic organic pollutants is primarily driven by hydrophobic interactions between the solute and the organic matter in the sorbent.

**Solution pH**

Solution conditions can have dramatic effects on the adsorption of cationic contaminants. For example the adsorption of cationic transition metals to oxide surfaces typically increases markedly over a narrow range of 1 to 2 pH units referred to as the “adsorption edge”. The pH dependence of metal ion adsorption can be explicitly accounted for by writing the adsorption reaction as:
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\[
\text{SOH}_x + Me^{z+} \xrightleftharpoons[K_d]{[a]} \text{SOMe}^{z-x} + xH^+ \tag{7.7}
\]

where \( K_d \) is the pH-dependent metal distribution coefficient, and according to Honeyman and Santschi (1988)

\[
K_d = \frac{[\text{SOMe}^{z-x}][H^+]^x}{[\text{SOH}_x][Me^{z+}]} \tag{7.8}
\]

A plot of \( \log \left( \frac{[\text{SOMe}^{z-x}]}{[\text{SOH}_x][Me^{z+}]} \right) \) versus pH, is referred to as a “Kurbatov plot” (after Kurbatov et. al., 1951), and may be used to reveal the magnitude of the exponent, \( x \) for \([H^+]\) in the distribution coefficient. The ratio \( \frac{[\text{SOMe}^{z-x}]}{[\text{SOH}_x]} \) is the quantity of adsorbed metal per unit surface. Since the above reaction and its equilibrium constant, \( K_d \), are an over simplification of the actual adsorption mechanism, measured values of \( x \) are rarely integers. Nevertheless, \( x \) values ranging from 1 to 2 are common for adsorption of metal cations on oxide surfaces and demonstrate the strong dependence of the adsorption processes on pH. For example, if \( x = 2 \), an increase of 1 pH unit would result in a 100 fold increase in the amount of bound metal per unit surface (at the same solution concentration of metal ion). In general, adsorbed metal cations will be released as a consequence of a decrease in solution pH. Since the surfaces in the porous medium also have acid/base properties, and because many porous media contain acid-reactive components (such as carbonate minerals) a very large acid dose may be required to effectively alter the pH of the pore water. For this reason, acid extraction of adsorbed metals may not always be feasible.

**Metal-Ligand Complexes**

Another influence of solution conditions on metal adsorption is through the reactions of metals with ligands to form complexes. In some cases, metal-ligand complexes adsorb weakly or not at all (ex. Cl⁻ complexes of Cd and Hg), in other cases metal-ligand complexes may adsorb with a binding strength greater than that of the free metal (ex. organic complexes of Cu) (Benjamin and Leckie, 1982). Judicious selection of a ligand for introduction into a porous medium may, therefore, be used to accomplish the release of adsorbed cations. Added ligands may, in some cases, undergo exchange reactions with the porous media or react to form complexes with cations that are not of environmental concern. For this reason the dose of a ligand needed to effectively release adsorbed metals will vary with the composition of the porous media and ligand addition may not prove feasible in some cases.

**Oxidants and Reductants**

Changing solution composition by the introduction of oxidizing or reducing agents may accomplish the release of adsorbed metals. Iron oxides are strong metal binding
agents and may be solubilized by reduction from ferric (Fe III) to ferrous (Fe II) iron. Many transition metals (e.g. Cd, Co, Cu, Ni, Pb, Zn) will remain as divalent cations during such a shift in redox status, and may therefore simply re-absorb to another surface. In some cases, alteration of the media redox conditions may directly influence metal mobility. For example reducing conditions would favor the presence of a cationic form of chrome (Cr$^{3+}$) over the more mobile anionic form (Cr$_2$O$_7^{2-}$). Addition of oxidants may therefore help to mobilize chrome, however the organic matter in soils and ferrous minerals will also react with added oxidants.

In a manner similar to the role of iron oxides, the organic matter in porous media can be responsible for the binding of metal cations. The reaction of an added oxidant with humic-type organic matter may therefore accomplish solubilization of some metals (Lion et al., 1982). Strong oxidants will also act to break down organic contaminants.

**Hydroxyl Radicals**

One application that has been used for remediation of organic contaminated soils is the introduction of Fenton’s reagent. Fenton’s reagent is a mixture of hydrogen peroxide and ferrous iron (Fe$^{2+}$). These chemicals react to produce hydroxyl radicals\(^3\) (OH•) according to the following reaction:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}•
\]

The hydroxyl radicals produced by Fenton’s reagent are highly reactive and can effectively degrade recalcitrant aromatic compounds by ring substitution followed by ring cleavage (Sedlak and Andren, 1991).

**Surfactants**

Additions of surfactants may aid in the release of sorbed nonionic organic pollutants. In the case of sorption reactions that are driven by hydrophobic interactions, surfactant additions can have two beneficial effects: 1) a decrease in the aqueous activity coefficient for the dissolved nonionic organic compound and 2) formation of micelles in the aqueous phase.

The effect of the aqueous activity coefficient can be illustrated by examination of the sorption isotherm for the organic pollutant. If the isotherm is linear, then we may write:

\[
\Gamma = K_L^S \gamma C_L
\]

where \(\Gamma\) is the mass of solute sorbed per mass of solid, \(K_L^S\) is the sorptive distribution coefficient, \(C_L\) is the aqueous concentration of the sorbate, and \(\gamma\) is the activity coefficient of the dissolved sorbate.

Surfactants may act to decrease the activity coefficient, \(\gamma\), for a nonionic molecule increasing the concentration in the aqueous phase in equilibrium with a given adsorbed amount, \(\Gamma\). Surfactants increase the solubility of nonionic molecules

\(^3\) Radicals contain an odd number of electrons.
because the hydrophobic-nonionic molecules adsorb to the long hydrocarbon group while the ionic sulfonic group provides high solubility (Figure 7-1).

However, since surfactants are surface-active, they may also sorb to the porous medium, increase its organic content, and consequently increase the sorption of a nonionic organic contaminant. High concentrations of water-soluble cosolvents such as methanol and acetone can also act to decrease the activity coefficient, \( \gamma \), and act to solubilize sorbed nonionic organic compounds (Schwarzenbach et al., 1993).

Surfactant molecules can aggregate into micelles in which their polar functional groups are oriented towards the aqueous solvent and their non-polar tails are oriented inward toward each other. The space within the micelles therefore provides a hydrophobic refuge for nonionic contaminants (Edwards et al., 1991). Surfactants will form micelles at aqueous concentrations greater than their “critical micelle concentration” (CMC). Since, as noted above, surfactants will sorb at the surface of the porous media, a high dose of surfactant may be required in order to maintain an aqueous concentration greater than the CMC.

**Bacterial Polymers**

Many of the solution modifications discussed above involve the addition of synthetic agents to contaminated soil to accomplish the release of sorbed contaminants. Natural constituents that occur in soils and aquifers may also enhance contaminant transport (McCarthy and Zachara, 1989). Bacterial polymers naturally occur in soil solution and have well-documented metal binding properties. The presence of bacterial polymers may therefore act as a natural process by which metal mobility is enhanced (Chen et al., 1995). The extracellular polymers produced by bacteria are hetero-polysaccharides and have high molecular weight. Interestingly, these large molecules have also been show to be effective at binding nonionic organic pollutants and at enhancing their transport in aquifer materials (Dohse and Lion, 1994). In principle, bacterial polymers with suitable binding properties could be produced in engineered reactor systems and be applied to contaminated waste sites to enhance the mobility of metal and nonionic organic contaminant mixtures. The efficacy of this type of remediation process has yet to be determined.

**Apparatus**

Students will apply a range of extractant types (or mixtures of different types) to remove contaminants (Zn and methylene blue) from a porous medium. Laboratory extractions will mimic an engineered soil washing system in which the contaminated soil is actively mixed with the extractant and then separated. A rotator will be used to provide agitation of samples of the medium with extractants, and a centrifuge will be used to provide phase separation. A UV/visible spectrophotometer with a diode array detector will be used to measure the concentration of the extracted organic pollutant.

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**Figure 7-1.** Molecular structure of detergent. The hydrocarbon chain (R group) of the detergent used in this lab is C\(_{12}\)H\(_{25}\).
Extracted metal concentrations will be measured with an atomic absorption (AA) spectrophotometer.

**Experimental Procedures**

Each group will develop their own hypothesis and experimental protocol. Different concentrations of extractants, different organic contaminants, and different washing techniques could be the investigation subjects. Alternate organic contaminants should be cleared with the instructor prior to the lab period. Each group should limit the investigation to approximately 10 samples and should include appropriate controls and replicates.

The following protocol assumes that a common sand is employed to represent the porous medium. It is desirable, but not essential, to characterize each medium to be used (prior to the laboratory exercise) with respect to its carbon content [the “Walkley Black” method is one common procedure (Allison, 1965)], cation exchange capacity, and specific surface area [by sorption of ethylene glycol monoethyl ether (EGME) (Cihacek and Bremmer, 1979)].

I. Creation of a Contaminated Porous Medium

A stock solution containing the soil contaminants will be provided [50 mg/L Zn and 100 mg/L methylene blue]. For each extractant used in part II below, 2 samples of contaminated sand and one sample of clean sand will be used. The following procedure is based on the assumption that each student group will evaluate 3 extractants or 3 concentrations of an extractant.

1) Weigh out 9 aliquots of sand, 2.5±0.05 g each, and pour into 10 mL plastic centrifuge tube.
2) Record the mass of the centrifuge tube with the sand (see Table 7-1).
3) Add 5 mL of the contaminant stock solution to 6 of the samples.
4) Add 5 mL distilled water to 3 of the samples (clean controls).
5) Place all of the samples on a rotator to mix the sand and the contaminant/clean solutions. Agitate for 15 minutes.
6) Centrifuge the suspensions at 3000 x g for 5 minutes.
7) Pour the supernatant from the 6 contaminated sand samples into a 125 mL bottle.
8) Pour the supernatant from the 3 clean sand samples into a separate 125 mL bottle.
9) Weigh the centrifuge tubes with the sand and pore water. Calculate the volume of pore water by subtracting the centrifuge tube and sand masses.

II. Determination of the Amount of Contaminant Sorbed by the Sand

*Methylene blue - UV/Vis Spectroscopy*

Nitrate absorbs ultraviolet light and is present in the contaminated samples from the addition of Zn(NO₃)₂·6H₂O. We could account for this either by preparing a nitrate standard and using it as a component in spectral analysis or by eliminating the ultraviolet part of the spectrum from the analysis. We will eliminate the nitrate interference by using a wavelength of 660 nm when measuring methylene blue. See
http://ceeserver.cee.cornell.edu/mw24/Software/Spectrophotometer.htm for instructions on using the UV/Vis Spectrophotometer.

1) Measure the absorbance of 1, 5, and 10 mg/L methylene blue solutions as “Standards.” Save the file as \Enviro\enviro\Courses\453\soilwash\netid_MBstd.

2) Measure the absorbance of the combined supernatant from the 3 clean sand samples, the combined supernatant from the 6 contaminated sand samples, and the contaminating solution (diluted by a factor of 10) as “Samples.” Save the file as \Enviro\enviro\Courses\453\soilwash\netid_contamsuper.

3) Record the concentration of methylene blue in the clean supernatant and contaminated supernatant (see Table 7-2). You can drag the blue cursor on the "standard graph" to the wavelength of choice and read the exact absorbance (and wavelength) in the digital display to the left of the graph and concentration in the digital display at the bottom of the Spectrophotometer window. If the clean supernatant has significant absorbance at 660 nm then alternate analytical techniques may need to be used.

4) The difference between the methylene blue concentration in the contaminant solution and the concentration in the supernatant may be used to determine the sorbed contaminant concentration as:

\[
\Gamma = \frac{(C_{\text{initial}} - C_{\text{final}}) \text{(solution volume)}}{\text{mass of sand}} \tag{7.12}
\]

where \( C_{\text{initial}} \) is the contaminant solution concentration and \( C_{\text{final}} \) is the concentration of the supernatant. Solution volume is the volume of contaminant added initially.

**Zinc - Atomic Absorption Spectroscopy**

1) Calibrate the AA using the zinc standards (1, 2, and 6 mg/L).

2) Dilute all of the following samples by a factor of 10 to ensure sufficient sample volume for the analysis and to ensure that the results are in the calibrated range.

3) Measure and record the zinc concentration of the combined supernatant from the 3 clean sand samples.

4) Measure and record the zinc concentration of the combined supernatant from the 6 contaminated sand samples (see Table 7-3).

5) Measure and record the zinc concentration in the contaminating solution (the zinc concentration should be close to 50 mg/L).

6) The difference between the zinc concentration in the contaminant stock and the concentration in the supernatant may be used to determine the sorbed contaminant concentration using equation 7.12.

**III. Soil Washing Solutions**

Students may wish to experiment with extractant mixtures. Some combinations of extractant solutions may react violently! All proposed mixtures of extractants should
be cleared with the course instructor prior to their use. The following combinations should be avoided: mixtures of oxidants with reductants, mixtures of acids with bases, and mixtures of oxidants with organic extractants including: surfactants, chelating agents or cosolvents. The following extractant solutions will be available for testing. At least one group should measure the extractant capabilities of distilled water because it is by far the cheapest!

1) Distilled water.
2) Acid: $\approx 1$ M solution of HCl prepared by diluting 27.4 mL of the concentrated acid to 1 L with distilled water.
3) Cosolvent: 1:1 (v/v) mixture of acetone and distilled water.
4) Non-ionic surfactant: 10% (v/v) solution of Triton X-100 prepared by diluting 100 mL to 1 L with distilled water. Note: Triton X-100 is a non-ionic surfactant with a CMC of $2 \times 10^{-5}$ M (Edwards et al., 1991). The chemical formula for Triton X-100 is:

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \text{-C-CH}_2 \text{-C} \\
\text{CH}_3 \text{-C-CH}_2 \text{-C} \\
\text{CH}_3 \text{-C-CH}_2 \text{-C}
\end{array}
\]

\[
(\text{OCH}_2\text{CH}_2)_x\text{OH}
\]

where: $x = 9$ to 10, giving the surfactant a molecular weight of $\approx 607$ g/mole.
5) Anionic surfactant: 100 mM solution of dodecyl sulfate, sodium salt ($\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ with MW of 288.4 so 28.84 g/L). This extractant works very well at full strength; lower concentrations could be investigated.
6) Chelating agent: $\approx 0.1$ M solution of ethylenediamine-tetraacetate (EDTA) prepared by dissolving 37.22 g of the disodium salt in distilled water and diluting to 1 L.
7) Base: $\approx 1$ M NaOH solution prepared by dissolving 40 g of NaOH distilled water and diluting to 1 L.
8) Oxidant: 1:1 (v/v) mixture of 30% $\text{H}_2\text{O}_2$ and distilled water.
9) Reductant: $\approx 1$ M solution of $\text{Na}_2\text{S}_2\text{O}_3\cdot5\text{H}_2\text{O}$ prepared by dissolving 248 g in distilled water and diluting to 1 L.

**IV. Soil Washing Protocol**

The ability of each extractant to remove the zinc and methylene blue from the contaminated soil will be measured by exposing the contaminated soil to the extractant and then measuring the concentration of the zinc and methylene blue in the extractant.

1) Add 5 mL of each extractant to be tested to 2 contaminated sand samples and 1 clean sand sample.
2) Place the sand extractant mixtures on a rotator to mix for 15 minutes.
3) Centrifuge the suspensions at 3000 x g for 5 minutes.
4) Decant the supernatant from each centrifuge tube into labeled 15 mL bottles. A small air line can be used to help force the supernatant from the centrifuge tubes.
V. Analysis of Extracted Metal and Organic Pollutants

**Methylene blue - UV/Vis Spectroscopy**

Note that it is unnecessary to measure the methylene blue concentration in samples that do not appear to have any blue. Samples that are visually free of methylene blue can be recorded as 0 mg/L methylene blue.

1) Measure the absorbance of each of the clean sand extracts as “Samples.” All of the clean extracts can be analyzed together if desired. Save as `\Enviro\enviro\Courses\453\soilwash\netid_cleanext`.

2) Measure concentration of methylene blue in each of the clean extracts based on the absorbance at 660 nm (see Table 7-2).

3) Measure the absorbance of each of the extracts of the contaminated sand as “unknowns.” There will be 2 replicates for each extract. All of the contaminated extracts can be analyzed as a group so that their results are saved in a single file. Save as `\Enviro\enviro\Courses\453\soilwash\netid_contamext`.

4) Measure concentration of methylene blue in each of the contaminated extracts based on the absorbance at 660 nm (see Table 7-2). Note that it may be necessary to choose a different analytical wavelength or to dilute the sample if the absorbance exceeds \(\approx 2.5\) at 660 nm.

5) Calculate the mass extracted per mass of sand as:

\[
\Delta \Gamma = \left( \frac{C_{\text{extracted}}}{\text{mass of sand}} \right) \times (\text{solution volume})
\]

where solution volume is the sum of residual pore water volume after decanting the contaminant plus the extractant volume.

**Zinc - Atomic Absorption Spectroscopy**

1) Dilute all samples by a factor of 10 prior to analysis.

2) Measure and record the absorbance of the supernatant from the 3 clean sand samples (see Table 7-3).

3) Measure and record the absorbance of the supernatant from the 6 contaminated sand samples. Dilute the supernatant with distilled water if the absorbance is not less than the absorbance of the 6-mg/L standard.

4) Calculate the concentration of zinc in each of the sand extracts.

5) Calculate the mass of Zn removed per mass of sand using equation 7.13.

The results for any extractant must justify the cost of its use. The results obtained by extraction of contaminated soil using distilled water serve as a basis for comparison to which results obtained with extractants should be compared. Results from all extractants or extractant combinations evaluated should be compared to provide an inter-comparison of their relative effects of the removal of metal and organic pollutants.
Prelab Questions

1) The point of zero charge for SiO₂ is approximately at pH = 2.5. Is the charge of SiO₂ positive or negative at a pH of 7?

2) Do cations or anions generally bind most strongly to soil?

3) Develop a hypothesis concerning soil washing, and write an experiment protocol to test your hypothesis that you can do in a lab period. Include detail of concentrations of extractants and contaminants for each vial. You may want to work with your lab partner(s) because this will be your experiment! Design your experiment to use no more than 9 vials.

Data Analysis

1) Report the contaminated sand concentration (grams of contaminant/gram of sand) for zinc and methylene blue.

2) Calculate the fractional removal of zinc and methylene blue for each extractant or extractant concentration. The fractional removal based on the amount of contaminant initially sorbed is \( f = \frac{\Delta \Gamma}{\Gamma} \) where \( \Gamma \) is defined in equation 7.12 and \( \Delta \Gamma \) is defined in equation 7.13. Present this using an appropriate graph.

3) Discuss which extractant performed best at removal of the zinc. Which was best at removing the test organic? Which extractant worked best at removing both contaminants? Discuss these results in terms of the chemical change that the extractant was designed to accomplish. (Note that these questions may need to be modified based on the samples you analyzed.)

4) Discuss any difficulties in evaluating extractant effectiveness and propose improved analytical techniques.

5) Discuss your results and their implications for the hypothesis that you developed.

6) Analyze your results including the reproducibility of replicate analyses in terms of possible sources of error.

7) Suggest options for additional research.

References


Table 7-1. Data table.

<table>
<thead>
<tr>
<th>bottle #</th>
<th>contaminated or clean</th>
<th>mass sand (g)</th>
<th>mass bottle + sand (g)</th>
<th>mass bottle + sand + pore water (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>clean</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>cont.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>cont.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>clean</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>cont.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>clean</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>cont.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7-2. Methylene blue data table.

<table>
<thead>
<tr>
<th>concentration</th>
<th>clean sand supernatant</th>
<th>contaminated sand supernatant</th>
<th>extractant 1 clean sand</th>
<th>extractant 1 cont. sand rep 1</th>
<th>extractant 1 cont. sand rep 2</th>
<th>extractant 2 clean sand</th>
<th>extractant 2 cont. sand rep 1</th>
<th>extractant 2 cont. sand rep 2</th>
<th>extractant 3 clean sand</th>
<th>extractant 3 cont. sand rep 1</th>
<th>extractant 3 cont. sand rep 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>dilution</td>
<td>clean sand supernatant</td>
<td>contaminated sand supernatant</td>
<td>extractant 1 clean sand</td>
<td>extractant 1 cont. sand rep 1</td>
<td>extractant 1 cont. sand rep 2</td>
<td>extractant 2 clean sand</td>
<td>extractant 2 cont. sand rep 1</td>
<td>extractant 2 cont. sand rep 2</td>
<td>extractant 3 clean sand</td>
<td>extractant 3 cont. sand rep 1</td>
<td>extractant 3 cont. sand rep 2</td>
</tr>
</tbody>
</table>

Table 7-3. Zinc concentration measurements data table.

<table>
<thead>
<tr>
<th>dilution</th>
<th>concentration</th>
<th>clean sand supernatant</th>
<th>contaminated sand supernatant</th>
<th>extractant 1 clean sand</th>
<th>extractant 1 cont. sand rep 1</th>
<th>extractant 1 cont. sand rep 2</th>
<th>extractant 2 clean sand</th>
<th>extractant 2 cont. sand rep 1</th>
<th>extractant 2 cont. sand rep 2</th>
<th>extractant 3 clean sand</th>
<th>extractant 3 cont. sand rep 1</th>
<th>extractant 3 cont. sand rep 2</th>
</tr>
</thead>
</table>
Table 7-4. Reagent list.

<table>
<thead>
<tr>
<th>Description</th>
<th>Supplier</th>
<th>Catalog number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(NO₃)₂·6H₂O</td>
<td>Fisher Scientific</td>
<td>M291-25</td>
</tr>
<tr>
<td>Methylene Blue HCl</td>
<td>Fisher Scientific</td>
<td>M291-25</td>
</tr>
<tr>
<td>NaOH</td>
<td>Fisher Scientific</td>
<td>S318-500</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>Fisher Scientific</td>
<td>H325-500</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>Fisher Scientific</td>
<td>S445-500</td>
</tr>
<tr>
<td>nitrilotriacetic acid</td>
<td>Aldrich</td>
<td>N840-7</td>
</tr>
<tr>
<td>Triton X-100 acetone</td>
<td>Aldrich</td>
<td>23,472-9</td>
</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>Aldrich</td>
<td>A929-1</td>
</tr>
<tr>
<td>alginic acid, sodium salt</td>
<td>Aldrich</td>
<td>31,007-7</td>
</tr>
<tr>
<td>Fe(NO₃)₃·9H₂O</td>
<td>Aldrich</td>
<td>21,682-8</td>
</tr>
<tr>
<td>Humic acid</td>
<td>Aldrich</td>
<td>H1,675-2</td>
</tr>
<tr>
<td>Nitric Acid 6 N</td>
<td>Fisher Scientific</td>
<td>LC17-70-2</td>
</tr>
<tr>
<td>Dodecyl sulfate, sodium salt (C₁₂H₂₅SO₄Na)</td>
<td>Aldrich</td>
<td>85,192-2</td>
</tr>
<tr>
<td>Zinc reference solution</td>
<td>Fisher Scientific</td>
<td>SZ13-100</td>
</tr>
</tbody>
</table>

Table 7-5. Stock Solutions (100 mL each).

<table>
<thead>
<tr>
<th>Description</th>
<th>MW (g/M)</th>
<th>conc. (g/L)</th>
<th>100 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₆H₁₈N₃SCl</td>
<td>319.87</td>
<td>10</td>
<td>1 g</td>
</tr>
<tr>
<td>Zn(NO₃)₂·6H₂O</td>
<td>297.4</td>
<td>227.4048</td>
<td>22.74 g</td>
</tr>
</tbody>
</table>

Table 7-6. Contaminating Solution (1 L)

<table>
<thead>
<tr>
<th>Description</th>
<th>MW (g/M)</th>
<th>conc. (mg/L)</th>
<th>1 L</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₆H₁₈N₃SCl</td>
<td>319.87</td>
<td>100</td>
<td>10 mL stock</td>
</tr>
<tr>
<td>Zn(NO₃)₂·6H₂O</td>
<td>297.48</td>
<td>50 (as Zn)</td>
<td>10 mL stock</td>
</tr>
</tbody>
</table>
Table 7-7. Equipment list

<table>
<thead>
<tr>
<th>Description</th>
<th>Supplier</th>
<th>Catalog number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refrigerated centrifuge MP4R</td>
<td>Fisher Scientific</td>
<td>05-006-4</td>
</tr>
<tr>
<td>4-place rotor 4B</td>
<td>Fisher Scientific</td>
<td>05-006-9</td>
</tr>
<tr>
<td>Diode array spectrophotometer rototorque rotator</td>
<td>Cole Parmer</td>
<td>H-07637-00</td>
</tr>
<tr>
<td>10 mL centrifuge vials</td>
<td>Fisher Scientific</td>
<td>05-529-1A</td>
</tr>
<tr>
<td>Repipet II Dispensor</td>
<td>Fisher Scientific</td>
<td>13-687-62B</td>
</tr>
<tr>
<td>PP bottles 15 mL</td>
<td>Fisher Scientific</td>
<td>02-923-8G</td>
</tr>
</tbody>
</table>

Zinc Disposal Guidelines

The amount of zinc that can be disposed to the sanitary sewer is limited. The wastewater treatment plant has a limit on the concentration of zinc that can be in the sludge. The Zinc stock solution should not be disposed to the sanitary sewer. Zinc that is sorbed to the sand can be dried and sent to the landfill in the trash.

Setup

1) Use repipet dispensers for contaminating solution, distilled water and possibly for additives.
2) Prepare calibration standards for the AA and for the UV-Vis spectrophotometers.
3) Each group needs 9 centrifuge vials, 20 15-mL bottles, and 2 125-mL bottles.
4) Connect a very fine tube to an air line at each island to be used to help empty the supernatant from the centrifuge vials.
5) Devise technique to filter samples prior to AA analysis!

Class Plan

1) Demonstrate use of AA when samples contain particulate matter. (Keep sipper tube off of the bottom of the vial!)
2) EDTA works well for Zn at 0.1 M
3) Dodecyl sulfate works well for MB at 0.01 M