



Emerging Technology Bulletin

Metals Treatment at Superfund Sites by Adsorptive Filtration

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Technology Description: This project evaluated an innovative approach for removing inorganic contaminants from the liquid phase at Superfund sites. In the process, called adsorptive filtration, metals are collected by attachment to a thin layer of ferrihydrite (iron oxide) that has been immobilized on the surface of sand grains. Some relevant features of the plain sand and the two batches of coated sand used in the project are presented in Table 1. The modification of the sand surface allows the grains to simultaneously adsorb soluble heavy metals and remove particulate metals by filtration in a column packed with the media.

Table 1. Characteristics of Plain Ottawa Sand and Iron Oxide Coated Sand Used in Adsorptive Filtration Study. All Sands Were 20-30 Mesh Size.

	Plain Sand	Media I	Media II
Fe salt used for coating	none	Fe(NO ₃) ₃	FeCl ₃
% iron by weight	0	2.1	3.2
surface area by BET, m ² /g	0.04	2.4	9.1
pH of the PZC	0.7	9.2	9.8

Model influent solutions contained 0.5 or 5.0 mg/L of three metals (Cu, Cd, and Pb), sometimes individually and sometimes in combination. The pH of the test solutions ranged from 7.0 to 9.5, with most tests conducted at pH 9.0. Test solutions also contained 0.01 M NaNO₃. Also, several tests were conducted in which an additional substance was added to the influent solution, in order to assess its effect on metal behavior in the column. The substances tested in this way included ammonia (as a complexing agent), EDTA (as a chelating agent), sodium dodecyl sulfonate (a surfactant), motor oil, and antifreeze. In addition, some tests were conducted using a column containing biogrowth. Finally, a few tests were run with a synthetic influent containing As and Se, and with a solution collected from a Superfund site where conventional treatment is currently being applied.

Waste Applicability: The process was shown to be applicable for removing Zn from the effluent of a conventional precipitation/coagulation process at a Superfund site. This test gave an indication of the incremental metal removal that could be obtained by using adsorptive filtration as a polishing step after a conventional treatment process. The total and soluble Zn concentrations in the samples collected were in the ranges 0.6 to 4.0 and 0.3 to 0.6 mg/L, respectively. The corresponding Zn concentrations in the effluent were around 0.2 and <0.1 mg/L, respectively.

The solutions investigated contained one to three heavy metals, at total heavy metal concentrations ranging from 0.5 to 15 mg/L. These solutions were treated successfully at empty bed contact times (EBCTs) of 1 to 4 min, with the only significant effect of EBCT being that headloss develops more rapidly at the higher throughput rate. Additionally, a reasonable data base has been developed that identifies acceptable regeneration conditions. Though the optimum treatment and regeneration conditions may depend on the specific water being treated, the results presented here provide a good baseline from which to start such an evaluation.

Most types of organic contaminants that are likely to co-exist with metals at Superfund sites do not interfere significantly with the adsorptive filtration process. Mild complexing agents such as ammonia do not prevent sorption of the metals, and this is a significant advantage of adsorptive filtration over conventional precipitation. Strong complexing agents such as EDTA do prevent adsorption. The process might be affected slightly, but appears not to be affected dramatically, by the presence of surfactants, oily substances, and nutrients that allow a biofilm to grow on the media.

The long-term stability of the adsorbent appears adequate, although additional tests that last even longer than those described here would be useful to quantify the effective lifetime of the media.

Test Results: Runs were conducted using a packed bed containing 250 mL (bulk volume) of the coated sand. Once a predetermined criterion was met (related to either the duration of the run or the headloss), the bed was cleaned by backwashing and/or acid regeneration, and the 'cleaning' solutions were analyzed. Regeneration was generally accomplished using a solution adjusted to and maintained at pH near 2.0.

In general, adsorptive filtration proved to be an efficient and effective treatment process. Soluble and particulate forms of all the metals tested could be removed from the water stream at both concentrations tested. The contact time required for treatment was minimal (<5 min), and treatment was successful at moderate pH values (near 9). Removal efficiencies ranged from about 70 to >99%, depending on treatment conditions. For instance, when influent solutions contained 0.5 mg/L each of Cu, Cd, and Pb, the effluent concentrations gradually increased from near zero to about 0.1 mg/L each of Cu and Cd and 0.2 mg/L Pb during treatment of 7000 and 13000 bed volumes of influent.



In the runs with 5 mg/L of each metal in the influent, most of the metal load was particulate; soluble influent concentrations were typically around 1.5 mg Cd/L, 0.8 mg Pb/L, and 0.2 mg Cu/L. Under these conditions, for the process to be successful, filtration must be at least as significant a mechanism of metal removal in the columns as adsorption.

The total concentrations of all the metals in the effluent were well below 0.1 mg/L until a few hundred bed volumes had been treated (a 6- to 12-hour period), at which point particulate metals began breaking through the column. Backwashing of the media allowed additional influent to be treated effectively. Removal of soluble metal was substantial throughout these runs. Typical removal efficiencies for soluble metals in the influent were 80% for Cu, 90% for Pb, and 98% for Cd, and typical overall removal efficiencies (comparing total effluent and total influent) were 99% or greater for all three metals.

Regeneration was also fairly rapid and efficient. The metal concentration in the recirculation fluid increased rapidly at first and then only slowly thereafter. A recirculating period as short as 10 minutes released a large fraction of the available metal. Metal concentrations in the first and second regenerant solutions were as high as 3000 and 500 mg/L after the 5 mg/L runs. The overall recovery efficiencies (backwash plus regeneration) were almost always greater than 80% and were often 100% \pm 10%. During the course of these runs, the media was backwashed over 20 times and regenerated about 10 times over a period of a few months, with no apparent deterioration in performance.

In tests with ammonia-complexed metal in the influent, about 1500 mg of each metal sorbed per liter of media before the effluent concentration exceeded a few tenths of a mg/L, and about 4000 mg of each metal sorbed per liter of bed before the effluent concentration reached 4 mg/L. Regeneration of this column at pH 2.0 recovered 93% of the sorbed Cd and 100% of the

Cu. Similarly, the presence of 0, 15, or 30 mg/L of the surfactant sodium lauryl sulfonate had no noticeable effect on metal sorption. When the metals were complexed with EDTA, however, they broke through the column almost immediately.

The presence of a biofilm on the media reduced the capacity of media for the metals by about 50%. It is expected that this interference could be partially reversed by exposing the column to a high pH solution, which would probably solubilize a substantial amount of the biofilm.

In runs evaluating the removal of As and Se by the coated sand, the influent was adjusted to pH 3.5, but conditions were otherwise similar to those for removal of cationic metals. Significant amounts of Se or As began appearing in the effluent after about 200 to 300 bed volumes of solution had been treated. The removal pattern was remarkably consistent, regardless of the metal (As or Se) being treated and its oxidation state (+3 or +5 for As; +4 or +6 for Se). The latter result was particularly surprising, since selenate (SeO₄²⁻) is generally much more difficult to remove from solution than is selenite (SeO₃²⁻).

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