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**Development of HUMASORB™, A Lignite Derived Humic Acid for
Removal of Metals and Organic Contaminants from Groundwater**

Authors:

H.G. Sanjay
K.C. Srivastava
D.S. Walia

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14100 Park Meadow Drive, Suite 210
Chantilly, Virginia 22021

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P11.13 Development of HUMASORB™, A Lignite Derived Humic Acid for Removal of Metals and Organic Contaminants from Groundwater

H.G. Sanjay (archtech@cais.com; 703-222-0280)
Kailash C. Srivastava (archtech@cais.com; 703-222-0280)
Daman S. Walia (archtech@cais.com; 703-222-0280)
ARCTECH, Inc.
14100 Park Meadow Drive, Suite 210
Chantilly, VA 22021

Introduction¹

Heavy metal and organic contamination of surface and groundwater systems is a major environmental concern. The contamination is primarily due to improperly disposed industrial wastes. The presence of toxic heavy metal ions, volatile organic compounds (VOCs) and pesticides in water is of great concern and could affect the safety of drinking water. Decontamination of surface and groundwater can be achieved using a broad spectrum of treatment options such as precipitation, ion-exchange, microbial digestion, membrane separation, activated carbon adsorption, etc. The state of the art technologies for treatment of contaminated water however, can in one pass remediate only one class of contaminants, i.e., either VOCs (activated carbon) or heavy metals (ion exchange). This would require the use of at a minimum, two different stepwise processes to remediate a site. The groundwater contamination at different Department of Energy (DOE) sites (e.g., Hanford) is due to the presence of both VOCs and heavy metals. The

two-step approach increases the cost of remediation. To overcome the sequential treatment of contaminated streams to remove both organics and metals, a novel material having properties to remove both classes of contaminants in one step is being developed as part of this project.

Objective

The objective of this project is to develop a lignite derived adsorbent, **Humasorb™**, to remove heavy metal and organic contaminants from groundwater and surface water streams in one processing step. As part of this project, **Humasorb™** will be characterized and evaluated for its ion-exchange and adsorption capabilities.

Approach

Humic acid is a natural material with many properties which can be exploited for several cost effective applications. Humic substances are complex mixtures of naturally occurring organic materials. These substances are formed from the decay of plant and animal

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residues in the environment. Humic acid constitutes a significant portion of the acid radicals found in humic substances.

Humic acid is dark brown to black in color and is considered a complex aromatic macromolecule with various linkages between the aromatic groups. The different compounds involved in linkages include, amino acids, amino sugars, peptides, aliphatic acids and other aliphatic compounds. The various functional groups in humic acid include, carboxylic groups (COOH), phenolic, aliphatic and enolic - hydroxyl and carbonyl (C=O) structures of various types. Humic acid is an association of molecules forming aggregates of elongated bundles of fibers at low pHs and open flexible structures perforated by voids at high pHs. The voids can trap and adsorb both organic and inorganic particles if the charges are complementary.

A major source of humic acid is coal - the most abundant and predominant product of plant residue coalification. All ranks of coal contain humic acid but lignite represents the most easily available and concentrated form of humic acid. Humic acid concentration of lignite varies from 30-90 % depending on location. Peat, humates and sewage sludge also contain significant quantities of humic acid.

Chelation of metals

Metals are bound to the carbon skeleton of humic substances through heteroatoms such as nitrogen, oxygen or sulfur. The most common metal binding occurs via carboxylic and phenolic oxygen, but nitrogen and sulfur also have a positive effect on metal binding. The cation exchange capacity (CEC) of humic acid derived from leonardite is 200-500 meq/100 grams, whereas the CEC of leonardite is only 50 meq/100 grams.

Musani et al. (1) studied the chelation of radionuclides such as ^{65}Zn , ^{109}Cd and ^{210}Pb by humic acid isolated from marine sediments. The chelation of metals by humic acid was observed to be significant. The binding mechanism was found to be different depending on the physical state of the humic acid. Binding was stronger with precipitated humic acid than with dissolved humic acid. The chelation effect was stronger for the metals in the absence of calcium and magnesium. The order of binding was determined to be $\text{Pb} > \text{Zn} > \text{Cd}$ (1).

Pahlman and Khalafalia (2) used humic acid to remove heavy metals from process waste streams. The efficiency of heavy metal removal by humic acids derived from lignite, a sub-bituminous coal and peat were evaluated. The effect of pH on metal removal was determined. Humic acid was very effective in removal of toxic metal ions. The pH range of 6.5 to 9.5 was determined to be the optimal range for complete removal of heavy metal ions by humic acids derived from lignite and subbituminous coal. The efficiency of heavy metal removal by humic acid was higher compared to the conventional lime treatment even at lower concentrations of metals. Humic acids were very effective in the removal of the most toxic metals such as cadmium, mercury and lead. The removal of these toxic metals by lime is incomplete, particularly at near neutral pH.

Adsorption of organics

The adsorption of organic chemicals onto humic substances such as humic acid have been studied extensively. The reported investigations on adsorption of organic compounds by humic acid include studies on:

- non-ionic organics such as benzene, halogen substituted benzene, and chlorinated

- hydrocarbons such as 1,1,1-trichloroethane (TCA),
- nitrogen compounds such as urea and anilines,
- polychlorinated biphenyls (PCB),
- fumigants such as telone and insecticides such as DDT,
- herbicides such as paraquat, diquat, triazines,
- organophosphorous compounds such as parathion.

It is believed that humic acid combines with herbicides by electro-static bonding, hydrogen bonding and ligand exchange. In addition, the high concentrations of stable free-radicals in humic acid are capable of binding herbicides that can ionize or protonate to the cation form. The mechanisms that have been postulated for the adsorption of organic compounds include (3):

- Van der Waals attractions
- hydrophobic bonding
- hydrogen bonding
- charge transfer
- ion-exchange
- ligand exchange.

The adsorption of benzene, halogen substituted benzenes, and chlorinated hydrocarbons such as TCA, and similar nonionic organic compounds on soil containing different amounts of soil organic matter has been reported by Chiou (4). The adsorption on soil organic matter of various nonionic organic compounds from water was attributed primarily to solute partitioning into the organic adsorbent. The partitioning theory was supported by experimental observations of linear adsorption isotherms up to concentrations approaching saturation. In addition, the absence of competitive effects between solutes support the partition approach. The presumed partition was

also analyzed in relation to the equilibrium properties of organic compounds in solvent-water mixtures (4).

Humic acid has been shown to adsorb considerable amounts of nitrogen compounds such as urea, anilines, etc. The stable free radicals in humic acid are believed to play a significant role in urea-humic acid interaction (5). In addition, it has been postulated that urea forms an addition complex with humic acid through the carboxyl and phenolic hydroxyl group (6). It has been further determined that the complex formed is very stable and that the decomposition of urea is inhibited in the presence of humic acid. The adsorption of aniline on soil organic matter is directly related to the concentration of the humic acid. The adsorption of aniline on humic acid has been shown to follow both the Freundlich and Langmuir relations (6).

Adsorption of PCBs from aqueous streams has been reported by Haque and Schmedding (7). The adsorption on humic acid increased with the increase in the number of chlorine atoms in the PCB. Adsorption isotherms of PCBs on humic acid followed the Freundlich equation and the constant K (measure of adsorptive capacity) increased from di- to hexa-chloro PCB. The high K value on humic acid was attributed to a combination of high surface area and the number of functional groups present in humic acid.

The brief discussion in this section and a review of the literature clearly indicate the unique properties of humic acid to chelate metals and adsorb organics. The humic acid complex however, will dissolve in water above pH 2 and in the presence of ions such as sodium and potassium. The aim of this project is to develop a humic acid polymer that will be insoluble in water under the conditions

encountered during remediation of contaminated streams. The various steps involved in the development of Humasorb™ are discussed in the following section.

Project Description

The starting material for the development of Humasorb™ is actosol^R, a humic acid based soil amendment product manufactured by ARCTECH, Inc. The various phases in the development of this unique material include:

- isolation and purification of humic acid
- construction of metal-sorption and organic adsorption isotherms
- characterize and quantify metal-sorption and adsorption capacity
- cross-link humic acid to make it insoluble at higher pH
- evaluate cross-linked humic acid polymer for metal-sorption and adsorption capacity.

Isolation and purification of humic acid

Humic acid was isolated and purified from actosol^R by acidification using concentrated hydrochloric acid (HCl) to lower the pH (below 2). The precipitated solids were purified by repeated washing with distilled water and acidification. A pressure filter (60 psig) was used to separate the precipitated humic acid from the other humic substances dissolved in water. The amount of humic acid recovered ranged from 11.79 % to 14.79 % of actosol^R by weight. Approximately 300 grams of humic acid was isolated and purified to conduct the various experimental tasks in the project.

Metal sorption

The effect of pH on the sorption of metals by actosol^R humic acid was evaluated by adjusting the pH with sodium hydroxide (NaOH, 1 N) or concentrated hydrochloric acid (HCl, 10 N). In polypropylene centrifuge bottles, actosol^R humic acid was contacted with spiked water solution containing known concentration of metals. The spiked solutions were prepared by dissolving the metal salts in water. The centrifuge bottles were shaken at 300 rpm and 25°C for the desired contact time. After the desired contact time, alum (10% solution) was added to the centrifuge bottles to coagulate humic acid. The bottles were then centrifuged at 2000 rpm for 30 minutes to separate the solid and liquid phases. The supernatant in the bottles was analyzed for the target metal.

The adsorption capacity of purified humic acid was evaluated by developing metal sorption isotherms. The spiked water solution was contacted with different amounts of humic acid in centrifuge bottles. The pH was not adjusted in these tests. The centrifuge bottles were shaken at 300 rpm and 25°C for two hours. After the desired contact time, the bottles were centrifuged at 2000 rpm for 30 minutes to separate the solid and liquid phases. The ability of humic acid to reduce toxic metals such as chromium (VI), present as anions (Cr₂O₇⁻²), to less toxic Cr(III) was also evaluated in a similar manner.

Organic adsorption

Isotherms for adsorption of chlorinated and petroleum hydrocarbons were developed using purified humic acid. Initial experiments were conducted using actosol^R humic acid. The chlorinated hydrocarbons used were trichloroethylene (TCE) and tetrachloroethylene

(PCE); benzene was the representative petroleum hydrocarbon used in this study.

Isotherms were developed by contacting spiked water samples with different amounts of humic acid in a 20 ml serum vial. Humic acid was ground to less than 350 mesh for use in the experiments. The spiked water solution and the humic acid were contacted in the crimp-sealed vials at 350 rpm and 25°C for the desired time. The vials were centrifuged at 2000 rpm for 30 minutes after the contact time to separate the liquid and solid phases. The liquid phase was analyzed by using purge and trap GC-MS.

Results

Metal sorption

The effect of pH on uranium removal using **actosol**^R humic acid is shown in Figure 1. Clearly, the results indicate that humic acid is very effective in removing uranium from water under acidic conditions. Uranium is soluble in water under acidic conditions and increasing the pH to 4 using NaOH results in only 6 % removal of uranium. Uranium is completely removed from the solution at pHs greater than 6. However, at pH 4, the addition of humic acid removed all the uranium from solution and was recovered as a solid bound to humic acid. The recovery of uranium decreased at higher pH in the presence of humic acid. The observed decrease in uranium recovery at higher pH in the presence of humic acid is expected as humic acid dissolves in water at higher pH levels. The comparison of uranium recovery both in the absence and presence of humic acid indicates that uranium is bound to humic acid over the pH range 2-12 and remains in solution under basic conditions in the presence of humic acid. The addition of a coagulant such as alum did not have a significant effect at higher pH. However, at near neutral pH (6-8), the addition of alum

increased the amount of uranium recovery from water. The effect of pH on the removal of different metals using **actosol**^R humic acid is shown in Figure 2.

The sorption of copper and nickel by purified humic acid was represented well by both the Freundlich and Langmuir models (Figures 3 & 4). The Langmuir model for nickel however, gave negative values for the constants. However, the sorption of cadmium did not follow either the Freundlich or the Langmuir model indicating a complex multilayer sorption.

The metal sorption data was also analyzed using the method developed by Scatchard (8). The presence of more than one inflection point on a plot based on Scatchard analysis usually indicates the presence of more than one type of binding site. The Scatchard plot for the sorption of different metals by humic acid is shown in Figure 5. The plot clearly indicates the presence of more than one type of binding site for copper and nickel sorption. The plot was however, linear for cadmium indicating that possibly only one type of binding site was active for cadmium sorption.

Humic acid can act as a reducing agent and influence oxidation-reduction of metal species. An unchelatable toxic oxo-anion such as chromium present as dichromate ($\text{Cr}_2\text{O}_7^{2-}$), is reduced to relatively non-toxic Cr(III). The reduced chromium is then stabilized through chelation by humic acid. The reduction of different metal species such as mercury, vanadium, iron and plutonium by humic acid has been reported by a number of investigators (9-12). The purified humic acid used in this study was able to reduce Cr(VI) completely as shown in Figure 6.

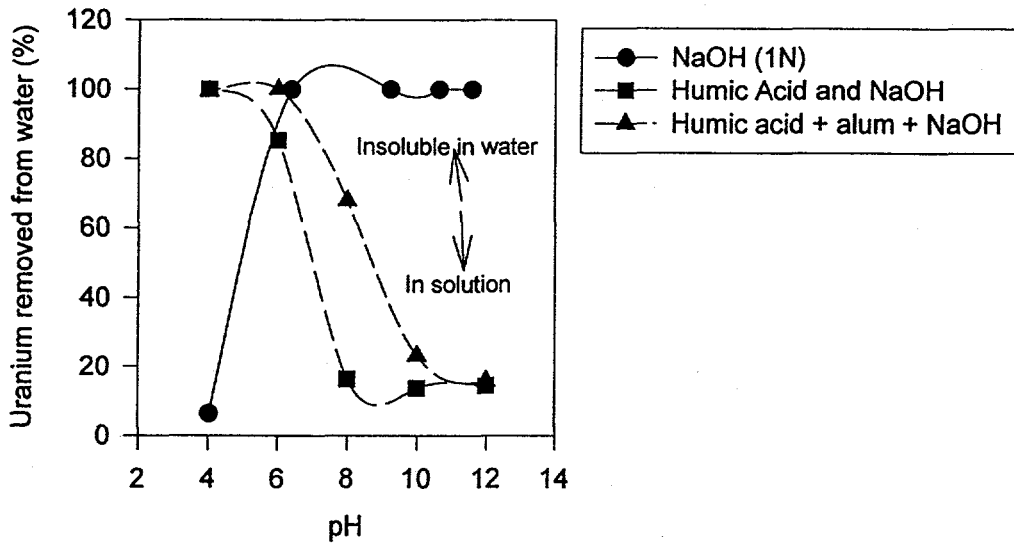


Figure 1. Effect of pH on Uranium Removal Using actosol® Humic Acid

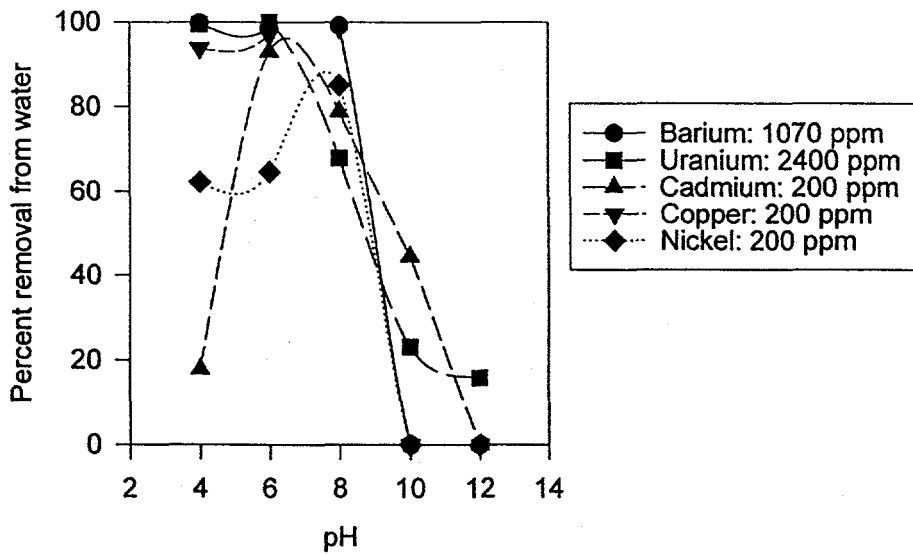
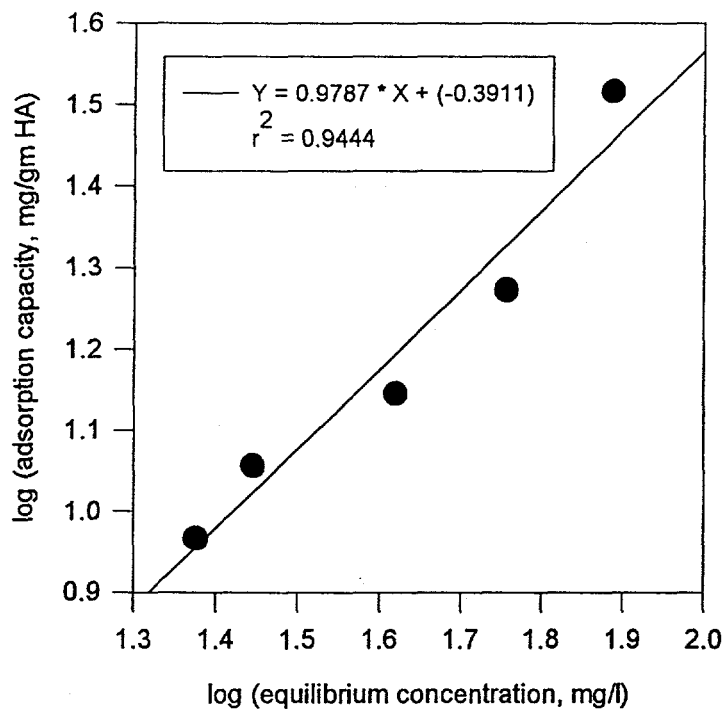
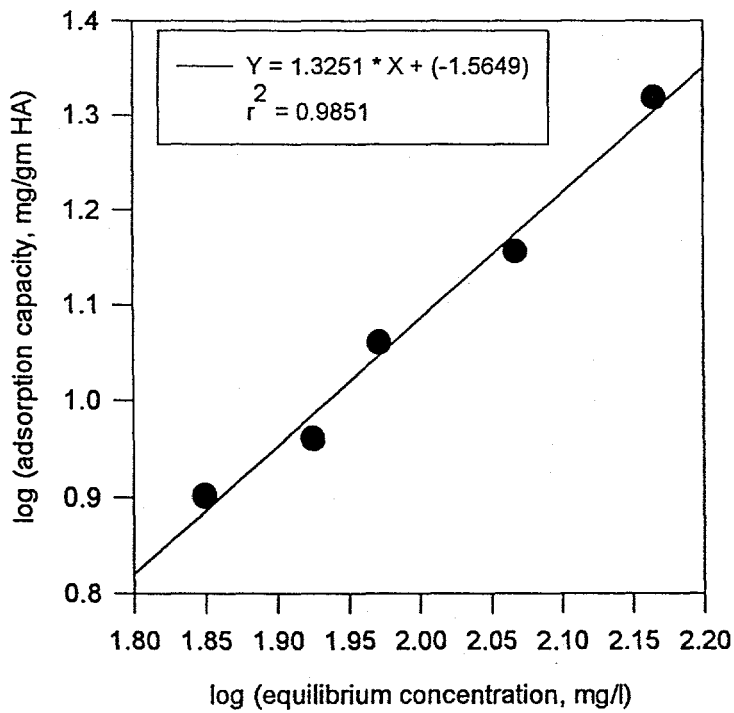


Figure 2. Effect of pH on Metal Removal Using actosol® Humic Acid

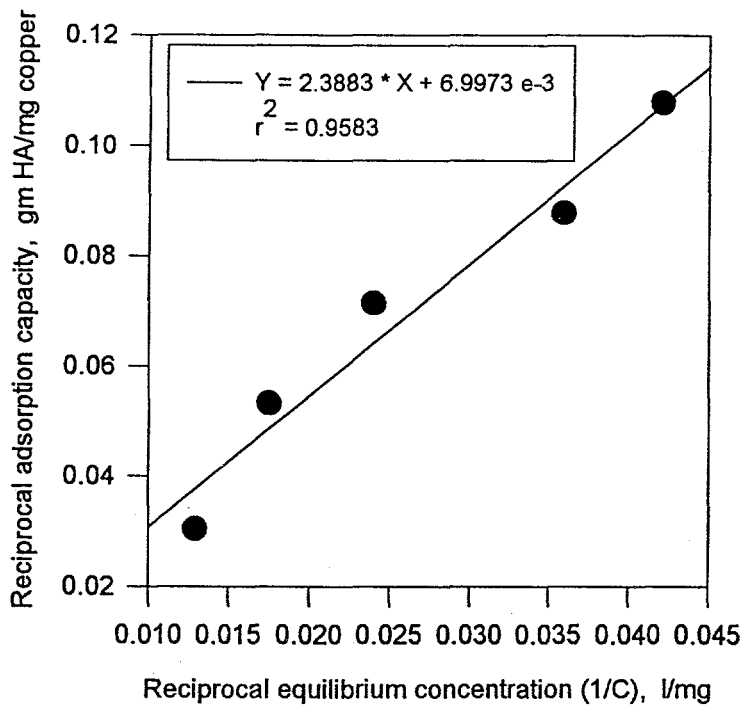


(A) Copper

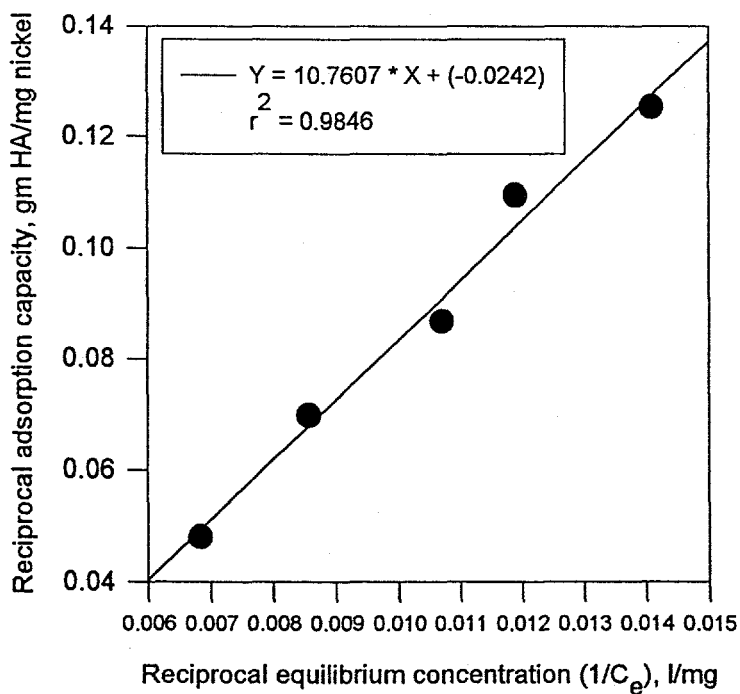


(B) Nickel

Figure 3. Freundlich Plot for Metal Sorption by Humic Acid



(A) Copper



(B) Nickel

Figure 4. Langmuir Plot for Metal Sorption by Humic Acid

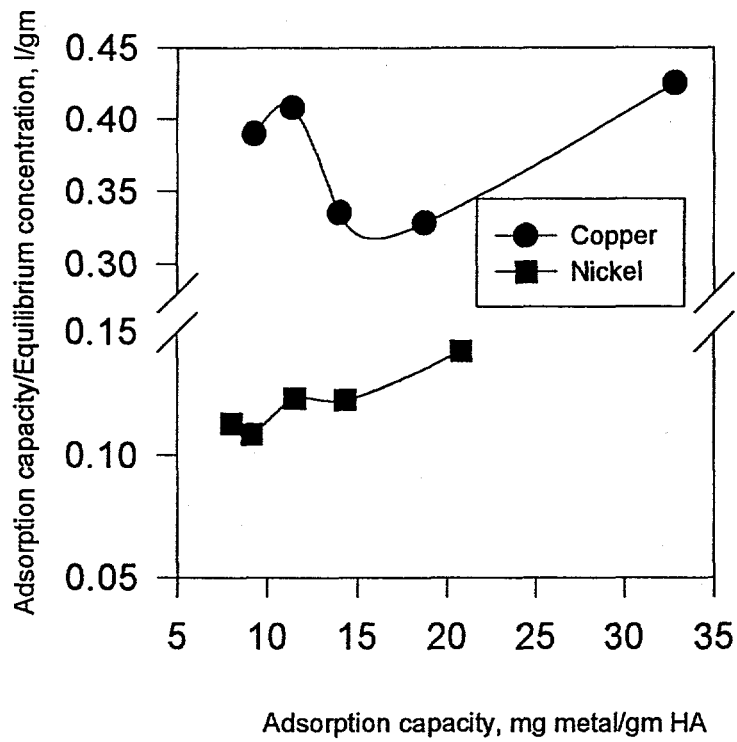


Figure 5. Scatchard Plot for Metal Sorption on Humic Acid (HA)

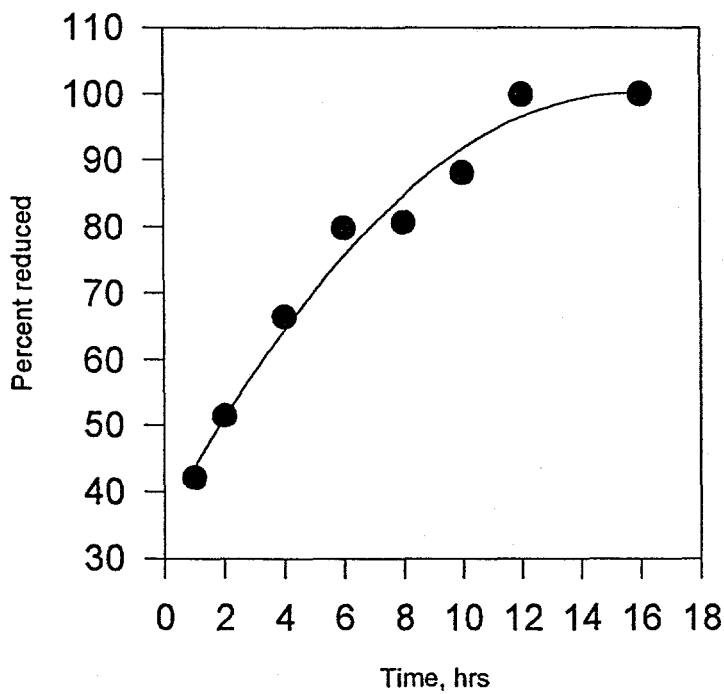


Figure 6. Reduction of Chromium (VI) by Humic Acid

Organic adsorption

Freundlich and Langmuir adsorption models were used to represent the data obtained for organic adsorption. The data for TCE adsorption was not represented by either model (Figure 7). The isotherms show two distinctive phases with adsorption capacity increasing only slightly with concentrations up to 210 ppm and increasing rapidly above 210 ppm. The shape of the isotherm indicates the possibility of multi-layer adsorption, with adsorption capacity increasing rapidly at higher concentration.

The adsorption of PCE on humic acid was also represented well by both Freundlich and Langmuir models as shown in Figure 8. However, the Langmuir model gave negative values for the constants. The Freundlich and Langmuir model parameters determined from the isotherms for some of the contaminants evaluated in this study are shown in Table 1.

Benzene adsorption on humic acid was represented very well by both the models at the relatively higher equilibrium concentrations obtained in this study. The removal of PCE from spiked water was higher compared to the removal of both TCE and benzene under the conditions used for the development of the adsorption isotherms. However, the removal of both TCE and benzene increased significantly with the increase in the amount of humic acid as shown in Figure 9.

Future work

The purified humic acid isolated in this project, though insoluble in water, can dissolve at higher pH in the presence of certain metal ions such as sodium and potassium. The purified humic acid will be rendered insoluble in water by cross-linking and forming a water-insoluble polymer in a number of screening

trials. The cross-linked humic acid polymer will be further evaluated for its contaminant removal capabilities. Initial cross-linking studies in our lab have been successful in producing a material that is only sparingly water-soluble at near neutral pH even in the presence of ions such as sodium. Efforts are underway at present to characterize the cross-linked material. The future work in this project includes the following tasks:

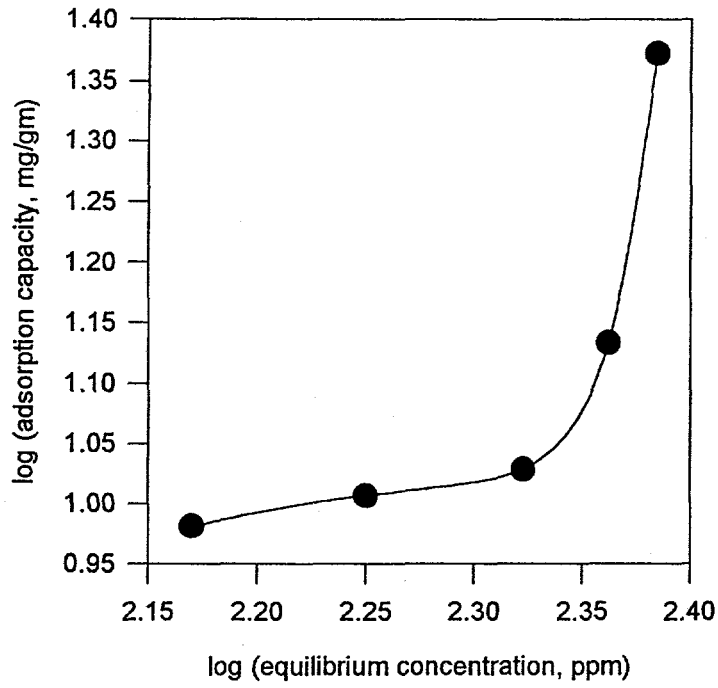
- cross-link the purified humic acid to form a water-insoluble polymer,
- evaluate of cation exchange and organic adsorption capacity of cross-linked humic acid polymer,
- bench scale column studies with **Humasorb™**
- conceptual design and economic analysis.

Applications

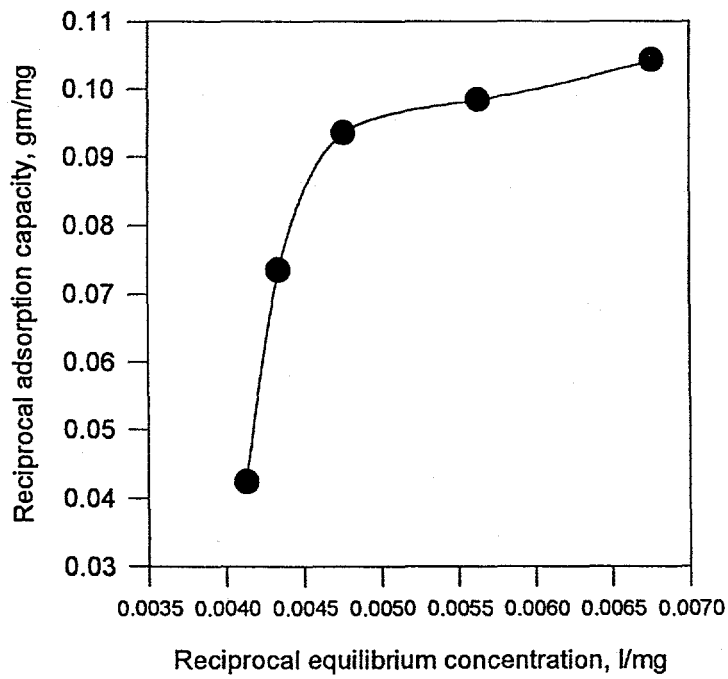
The remediation of contaminated streams and groundwater has been traditionally approached with at least a two-step process including some combination of activated carbon and ion-exchange process.

The removal of heavy metals from contaminated water has been accomplished by techniques such as the addition of a precipitating agent, ion-exchange or reverse osmosis. These techniques require considerable capital investment and in addition would require pretreatment in some cases to remove oil and suspended solids.

The removal of organic compounds by activated carbon, though very effective, is associated with high capital and operating costs,

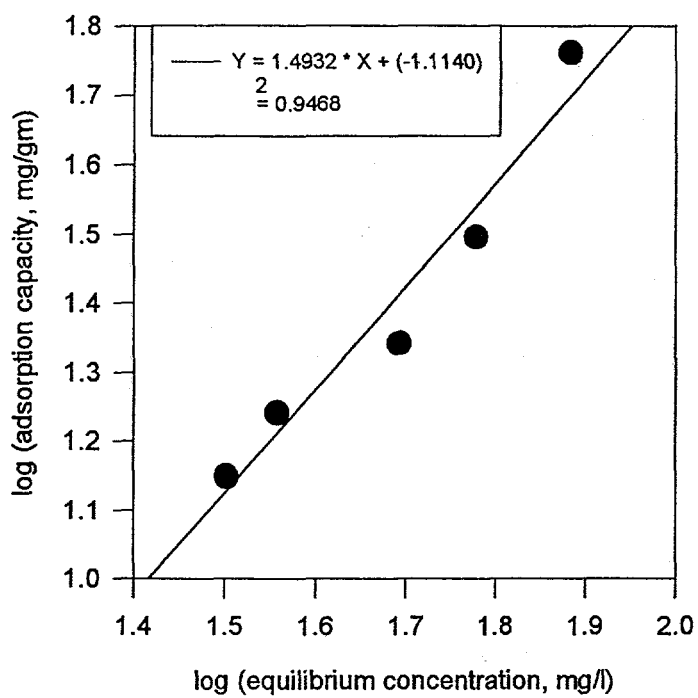


(A) Freundlich

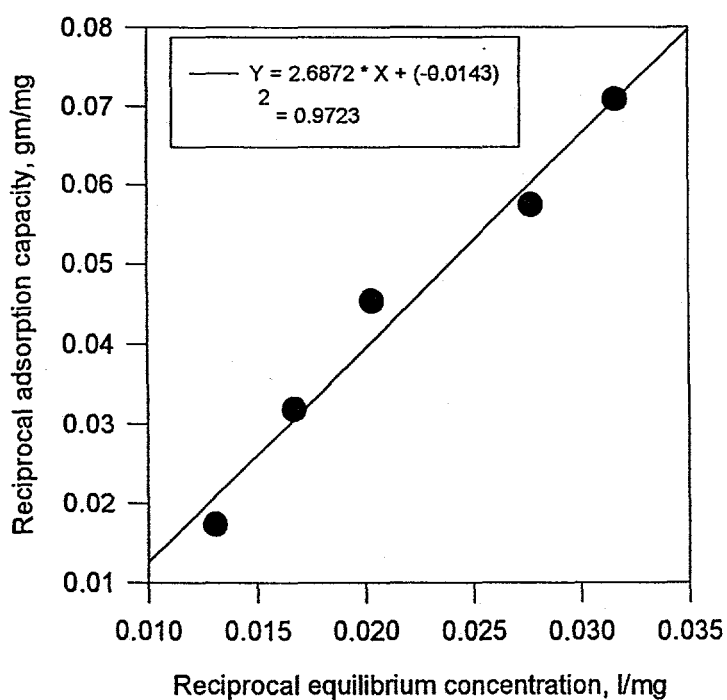


(B) Langmuir

Figure 7. Isotherm for TCE Adsorption on Humic Acid



(A) Freundlich



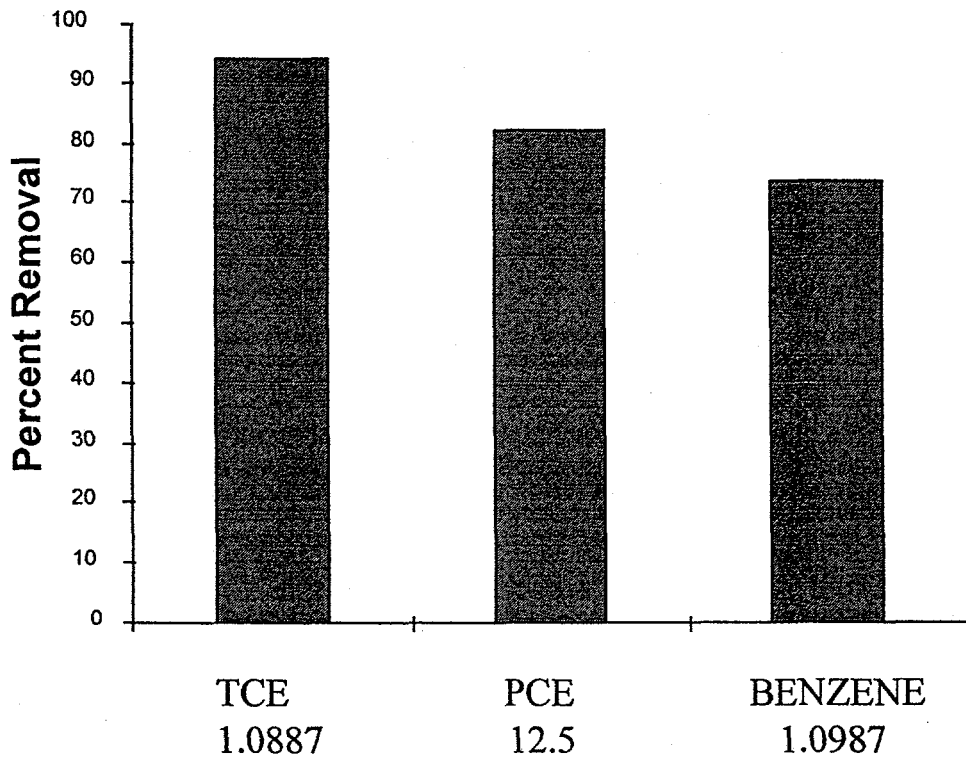
(B) Langmuir

Figure 8. Isotherm for PCE Adsorption on Humic Acid

Table 1.

Freundlich and Langmuir Model Parameters

Contaminant	Freundlich	Langmuir
Copper	K = 0.4064 mg/gm n = 1.0218	K = 142.91 mg/gm b = 0.0029 l/mg
Nickel	K = 0.0300 mg/gm n = 0.7500	Negative values
PCE	K = 0.07691 mg/gm n = 0.6697	Negative values



Initial ratio of organic contaminant to humic acid

Figure 9. Organic Contaminant Removal using Humic Acid

especially when regeneration is carried out by the most effective process-thermal reactivation. Also, this technique is very sensitive to the presence of suspended solids, oil and grease requiring pretreatment for effective performance.

Humasorb™, derived from a naturally occurring material has the potential to alleviate some of these limitations by combining remediation efforts into a single step process. **Humasorb™** can be used for groundwater cleanup both in the *in-situ* mode and in a pump and treat process. The examples of potential applications for the remediation of DOE contaminated sites include the following:

- Hanford: chromium, uranium and chlorinated compounds
- Fernald: uranium and chlorinated compounds
- Oakridge: mercury and chlorinated compounds.

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