United States
Environmental Protection
Agency

Hazardous Waste Engineering
Research Laboratory
Cincinnati, OH 45268

Research and Development

EPA/600/S2-86/029 Aug. 1986

EPA

Project Summary

Groundwater and Leachate Treatability Studies at Four Superfund Sites

Alan J. Shuckrow, Andrew P. Pajak, and C. J. Touhill

Bench-scale evaluations of wastewater treatment processes were performed using contaminated groundwaters and leachates from four hazardous waste problem sites: (1) Ott/Story Site, Muskegon, Michigan; (2) Gratiot County Landfill, Gratiot County, Michigan; (3) Marshall Landfill, Boulder, Colorado; and (4) Olean Wellfield, Olean, New York.

Processes were selected on the basis of a previous literature review and desktop analysis of 18 candidate processes. Treatment processes reported on include adsorption (granular and powdered carbons, and carbonaceous and polymeric resins), biological treatment (activated sludge, and upflow anaerobic filter), coagulation and precipitation, filtration (gravity and multimedia), ozonation, sedimentation, and stripping (diffused aeration, packed-tower air stripping, and packed-tower steam stripping). Processes were used singularly and in various process train configurations.

Process performance was measured under a range of operating conditions. Total organic carbon (TOC) was generally used as a surrogate for routine process monitoring, and specific compounds were examined at selected times.

Methods and process performance results are detailed. Because site-specific conditions greatly influence process performance, site-specific studies must usually be conducted to select a viable, cost-effective approach for a particular problem site.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Groundwater resources are being threatened by a rising incidence of poor hazardous waste disposal practices. At many sites, the need exists to prevent further contaminant migration and to meet user demands for water. One way to accomplish these goals may be to treat contaminated groundwater.

Though numerous unit processes have been demonstrated for water and wastewater treatment, the applications do not accurately duplicate conditions associated with contaminated groundwater treatment. In this research, studies were conducted using contaminated groundwaters from four hazardous waste disposal sites to investigate process performance under various wastewater conditions. The research will aid future efforts to formulate viable, cost-effective solutions to groundwater contamination problems.

The following unit processes have been identified as broadly applicable to concentrating aqueous hazardous wastes: biological treatment, carbon adsorption, chemical coagulation, membrane processes, resin adsorption, and stripping. Chemical oxidation (e.g., ozonation) was also judged as potentially applicable because of its ability to enhance the treatability of numerous organic compounds. All of these processes must

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Five process trains were assembled as being broadly applicable to most types of known contamination: (1) Biological treatment and carbon sorption, (2) carbon sorption and biological treatment, (3) biophysical treatment, (4) membrane and biological treatment, and (5) stripping and carbon sorption.

Because hazardous waste contamination problems differ substantially, treatability studies are usually required to select the optimum treatment approach. Using the unit processes and the process trains listed earlier, such studies were conducted for contaminated groundwater or leachates from four Superfund sites:

- Ott/Story Site, Muskegon, Michigan
- Gratiot County Landfill, Michigan
- Marshall Landfill, Boulder County, Colorado
- Olean Wellfield, Olean, New York

The report describes the methods used at each site to screen treatment methods, and it discusses the advantages and disadvantages of the unit processes in various situations. Potential approaches for other applications are also recommended.

Procedures

Bench-scale studies were used instead of pilot-plant studies because the objective was to assess process performance under various conditions, not to create an optimum process for treating a particular waste stream. Evaluations most often began with batch tests of individual unit processes. For selected processes or process combinations, continuous flow or sequential batch studies were undertaken.

Monitoring influent and effluent chemical characteristics was potentially complex and costly. To develop specific compound data in a cost-and-time-effective manner, measurements of routine indicators or surrogate parameters were supplemented with specific compound analyses at critical times. Total organic carbon (TOC) was used as a surrogate when the wastewater was predominantly organic; heavy metals or organic priority pollutants were analyzed when removal of specific compounds was of interest.

Experimental procedures generally used to evaluate each technology are summarized below.

Adsorption

Granular activated carbon (GAC) adsorption studies generally began with batch isotherm testing followed by continuous-flow, small-diameter-column studies. Data were used to develop Freundlich adsorption isotherms. Continuous-flow studies were undertaken to examine the effects of hydraulic and solute loading rates, and contact times, as well as to develop solute breakthrough curves.

Studies of powdered activated carbon (PAC) also used batch isotherm tests. Continuous-flow studies involved addition of PAC to activated sludge reactors for concurrent adsorption and biological treatment.

Batch isotherm and continuous-flow studies were also conducted using polymeric and carbonaceous resins.

Biological Treatment

Biological treatment processes investigated were activated sludge, trickling filter, and upflow anaerobic filter (UAF). Activated-sludge processes included conventional activated sludge, conventional activated sludge with the addition of PAC to the aeration chamber, and activated sludge seeded with a commercial mutant bacteria product. All systems were operated on a continuous-flow basis using raw or pretreated wastewater. Before process performance was assessed, attempts were made to acclimate the systems to the wastewater being investigated.

Filtration

When wastewaters contained suspended solids that were expected to interfere with the primary treatment process (e.g., by plugging the GAC adsorption column), granular media filtration was used for pretreatment.

Ozonation

Evaluation of ozonation was conducted on a batch basis. Ozonation was investigated as a primary treatment process and as a pretreatment technology.

Stripping

Air stripping techniques included diffused aeration as well as stripping under mechanical mixing and quiescent conditions. Air stripping was generally investigated whenever stripping was judged to be one of several contaminant-removal options for a particular treatment technology, for example, during diffused aeration, activated-sludge treatment or ozonation.

A packed-column, continuous-flow apparatus was used to evaluate steam stripping. The primary operation parameters investigated were feed flow rate and overhead flow rate. Maintenance of steady-state conditions proved difficult, and the apparatus was not capable of operating in the desired range of overhead-to-feed flow ratio (0.02 to 0.05).

Ott/Story Site

At the Ott/Story site, groundwater has been severely contaminated by numerous organic compounds because of disposal and poorly controlled storage of chemical production wastes. Because of the complex nature of the problem and the willingness of the current site owner to cooperate with the U.S. Environmental Protection Agency (EPA), extensive treatability studies were conducted onsite for an 18-month period.

Preliminary investigations focused on (1) pretreatment by neutralization, chemical coagulation, and precipitation, (2) methods of solids and liquids separation, and (3) volatility concerns. Batch studies of individual unit processes were then undertaken. These included air and steam stripping, activated carbon and resin adsorption, aerobic and anaerobic biological treatment, and chemical oxidation. The process train that performed best was GAC adsorption followed by activated-sludge treatment.

Air and Steam Stripping

Since most of the priority pollutants at the site were associated with the volatile fraction, it was concluded that (1) air stripping would be the simplest approach to removing bulk hazardous constituents, and (2) steam stripping with reflux would remove volatile halogenated hydrocarbons to a greater degree and would also allow such materials to be recovered and concentrated in the condensed overhead stream, thus abating potential air pollution problems.

In air stripping experiments, all volatile priority pollutants were reduced to nondetectable levels. Activated carbon treatment of the air-sparged effluent resulted in virtually complete removal of the remaining basic, neutral, and acid fractions of the priority pollutants. A significant TOC residual remained after air stripping and air stripping/carbon sorption batch treatment sequences.

Though air sparging resulted in about 11% volatilization of TOC from the bulk flow with removal of virtually all volatile priority pollutants, steam stripping removed about 34% of TOC and recovered these organics in a more concentrated overhead product. Air stripping appears to be an acceptable pretreatment technique if air emissions are judged insignificant.

Aerated groundwater may require further treatment for oxygen demand, trace organics, and heavy metal removal before discharge.

Adsorption

Isotherm studies were performed using raw groundwater and groundwater pretreated by aeration, ozonation, biological treatment, and various sorbents.

Batch contact study data using raw composite groundwater showed that sorption alone cannot achieve high degrees of TOC removal from raw groundwater. Similar studies were conducted using composite groundwater pretreated by aeration, ozonation and activated sludge, and anaerobic treatment by upflow filter. Except for the ozonation and activated sludge pretreatment, sorption characteristics were not affected, even though initial TOC concentrations varied considerably as a result of pretreatment.

The following batch sequences were also examined: (1) air stripping followed by carbon sorption, (2) carbon sorption followed by air stripping, and (3) carbon sorption followed by resin sorption. Wastewater TOC concentration following these treatments remained high.

The isotherm and sequential batch studies indicated that adsorption is applicable to the situation at the Ott/Story Site. Carbon adsorption alone and resin sorption to a smaller extent could achieve high degrees of removal for organic priority pollutants. However, the adsorption process alone could not reduce groundwater TOC concentrations to levels typically acceptable for direct discharge to surface waters.

In continuous-flow studies, adsorption was used as the primary treatment process for both pretreatment and post-treatment. Data indicate the following:

1. Operating at empty bed contact times of 10 to 226 min had no consistent effect on the adsorption of TOC.
2. Adsorption capacity of the resin was lower than that of GAC under similar study conditions.
3. Adsorption capacity of GAC and typical TOC breakthrough characteristics were not affected by pretreating the wastewater with ozone.
4. Though carbon adsorption capacity was improved by pretreating with ozonation followed by activated sludge, improvement in capacity was only slightly better than demonstrated by activated-sludge pretreatment alone.

Despite the inability to maintain high levels of TOC removal, GAC adsorption demonstrated substantial removals of organic priority pollutants. At a loading of 233 mg TOC/g carbon, the only priority pollutants detected in the GAC effluent were methylene chloride, 1, 2-dichloroethane, and toluene.

Biological Treatment of Activated Sludge

A total of 46 activated-sludge treatability studies were conducted. Investigations included the use of a biomass acclimated to raw contaminated groundwater, sludge seeded with Phenobac® , the addition of PAC to the activated-sludge aeration chamber, and pretreatment of groundwater by carbon adsorption or ozonation.

Attempts to develop an acclimated culture were minimally successful. Once the systems were acclimated to the extent possible, TOC removal ranged from about 35% to 60%. Though effluent TOC concentrations ranged from 174 to 472 mg/L, subsequent studies indicated that the stripping effect of diffused aeration could account for about two thirds of the removal.

Phenobac® , a commercially available bacterial culture adapted for hydrocarbon degradation, achieved an average TOC reduction of about 48%, with a range of 37% to 58%.

Adsorption Pretreatment and Biological Treatment

Additional activated-sludge studies were conducted using groundwater pretreated by (1) sorption using GAC, (2) organic resin, (3) GAC and upflow anaerobic filter processing, (4) chemical oxidation by means of ozone, (5) GAC and ozone, and (6) the addition of PAC to the aeration chamber.

GAC pretreatment of raw groundwater permitted development of a culture of aerobic organisms capable of further treating GAC effluent. More than 95% TOC removal was achieved by this process train during the period when the GAC process accounted for at least 30% of the TOC removal. Nearly all organic priority pollutants detected in raw groundwater were removed consistently to below the level of detection (0.01 mg/L) by the process train. The activated-sludge process completely removed the few organic priority pollutants leaking through the GAC system, even though overall TOC removal declined. The continued removal of organic priority pollutants may be due to stripping, biological degradation, or adsorption to sludge floc. Greater than 99% total phenol removal was observed.

When the pretreatment process was converted from GAC to resin, activated-sludge units following resin pretreatment were not able to produce effluents containing less than 100 mg/L TOC.

Anaerobic biological treatment was selected as a candidate treatment process because the organic content of the groundwater was high and because volatile priority pollutant stripping in the activated-sludge process could be avoided. Overall, the GAC/upflow anaerobic filter process train, with an upper TOC removal limit of about 81%, did not perform as well as the GAC/activated-sludge system.

A process train consisting of GAC, an upflow anaerobic filter, and activated sludge indicated that performance of the activated-sludge process in the train is inversely proportional to GAC performance. That is, as leakage from the GAC column increased, so did the amount of overall removal attributable to the activated-sludge process. Data indicate that this result may largely be due to stripping in the aerobic system. Performance of the system was not as good as the GAC/activated-sludge process train.

Studies made to determine whether ozonation enhanced adsorption or biological treatment indicated that preozonation did not improve activated sludge performance, and it did not improve performance or extend TOC breakthrough characteristics of the GAC process.

To provide a preliminary assessment of GAC as a polishing process, an isotherm study was conducted with effluent from the O_3, activated sludge train using PAC. Though batch data suggest that much lower effluent TOC concentrations can be produced by the train of O_3, activated-sludge, and GAC, continuous-flow operation of this train showed no advantage to GAC polishing.

Gratiot County Landfill

The problem at the Gratiot County landfill in Bethany Township, Michigan, involved contamination of groundwater by polybrominated biphenyls (PBB). Because this chemical is relatively insoluble, PBB contamination was found to be associated primarily with the sediment of the water samples taken in this study. Thus it was concluded that physical separation processes should effect significant levels of PBB removal. The technologies judged to be suitable candidates were GAC adsorption, coagulation and precipitation, sedimentation, filtration, ion exchange, and reverse osmosis.

The monitoring well selected for sampling was the one that had previously yielded the most highly contaminated samples in volumes sufficient for experimental studies. Freezing was judged to be the most suitable preservation method. Before freezing, a representative sample was withdrawn and analyzed for PBB and total and dissolved metals, including most priority pollutant metals.

Analysis indicated that metals were predominantly in the insoluble form. By analyzing metals that exceeded interim primary drinking water standards or water quality criteria, the study concluded that granular media filtration and gravity sedimentation could effectively remove metals associated with silt in the sample. Because PBB appears to be associated with the silt, these processes should also achieve significant levels of PBB removal.

Marshall Landfill

Marshall Landfill in Boulder County, Colorado, is a predominantly municipal solid waste landfill that accepted some industrial wastes from surrounding light manufacturing and fabricating industries. In 1979, seepage was observed to be draining from the fill into a small surface waterway linked to the drinking water supply for a nearby municipality. Analysis of the seepage indicated presence of numerous priority and nonpriority organic compounds at concentrations up to 6 mg/L.

Seepage collected in an impoundment was selected for use in laboratory evaluations. Though limited composition data were available, the TOC was significant (168 mg/L). An adequate volume of sample for use in treatability studies could be collected easily and dependably — an advantage that did not exist for other locations.

Treatment techniques evaluated included (1) batch adsorption isotherm tests with both activated carbon and resins as sorbents, (2) aerobic biological treatment using activated sludge, (3) continuous-flow GAC, (4) activated-sludge treatment of GAC pretreated seepage, and (5) air stripping.

In the adsorption isotherm studies, the activated carbons effected better TOC removal than did the resins.

Though nutrient levels, pH, dissolved oxygen concentration, and heavy metal concentrations were within acceptable ranges for aerobic biological treatment, attempts at activated sludge acclimation to raw groundwater were unsuccessful as measured by TOC removal and biological solids growth. Influent and effluent TOC averaged 93 mg/L; attempts at maintaining sludge solids by frequent reseeding were unsuccessful.

Continuous-flow GAC systems were evaluated. Influent TOC during these studies ranged from 126 to 182 mg/L. For the two-column system, 91% TOC removal was achieved initially; but after some 50 bed volumes were processed, removal decreased to 70%. Effluent TOC was about 40 mg/L. Data from the three-column system indicate slightly better performance at increased contact time.

To evaluate removal of organic priority pollutants, samples of raw seepage and effluent from the three-column system were obtained at points corresponding to TOC breakthroughs of about 5%, 10%, and 22%. The following priority pollutants were detected in the raw seepage but not in the carbon column effluents: Benzene, 1,2-dichloropropane, ethylbenzene, tetrachloroethylene, toluene, and diethyl phthalate. No trend of increasing priority pollutant breakthrough with increased TOC breakthrough was apparent.

A process train consisting of GAC adsorption followed by activated-sludge treatment reduced TOC levels to 20 mg/L. The GAC column alone reduced the TOC to 23 mg/L, showing that the activated-sludge process did not contribute appreciably to TOC removal.

Air stripping achieved minimal TOC removal, as expected, since Marshall Landfill leachate did not contain high concentrations of volatile priority pollutants. Instead, it contained phenolics, aromatics, and heavier priority pollutants with low vapor pressures.

Olean Wellfield

In late 1981, three wells providing most of the drinking water for Olean, New York, were found to contain 120 to 250 μg/L of trichloroethylene (TCE). Because of the nationwide prevalence of TCE contamination of drinking water supplies, groundwater from the Olean Wellfield was selected to evaluate treatment technologies.

Samples from one well indicated that the groundwater had a COD of 4.8 mg/L and a TCE concentration of 46 μg/L — well below the anticipated concentration of 200 to 250 μg/L. Batch air stripping tests and adsorption isotherm studies were conducted with these samples.

A second set of samples was obtained from the combined flow of two city wells. They were found to contain 90 and 95 μg/L of TCE. Based on this analysis and results of the air stripping and adsorption isotherms studies, it was determined that approximately 960 liters (250 gal) of groundwater would be required to develop a GAC breakthrough curve for TCE using a bench-scale system. Isotherm studies were repeated with this batch of sample. Continuous-flow GAC column studies then were conducted. A pilot test of air stripping was conducted at Olean by the U.S. EPA Office of Drinking Water during the course of this study.

Adsorption isotherms were prepared for several carbons and a carbonaceous resin. Powdered carbon exhibited somewhat poorer TCE adsorption characteristics. Resin sorption data did not show a clear trend.

Continuous-flow GAC column studies were conducted using two columns in series. The system was operated until the supply of contaminated water was exhausted. No TCE breakthrough was detected at that time, even though theoretical TCE breakthrough calculated on the basis of Freundlich isotherm parameters suggests that some breakthrough should have been detected.

Total plate counts were made of carbon effluent to investigate the possibility of biological growth in the GAC columns and subsequent contamination of the treated water. Data indicate elevated plate counts following GAC treatment, which may partially explain the nondetectable TCE levels in the carbon effluent. Further study in this area may be warranted when carbon adsorption systems are planned for the treatment of residential or small-scale water supplies.

Field evaluation of TCE removal by packed-column air stripping was carried out by the EPA Office of Drinking Water, Technical Support Division. Their results show that more than 99% TCE can be removed economically by air stripping.

The full report was submitted in fulfillment of Contract No. 68-03-2766 by Michael Baker, Jr., Inc., under the sponsorship of the U.S. Environmental Protection Agency.