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Project Summary

Removal of DBCP from Groundwater Volume 2 Field Pilot Plant Operation

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Freundlich adsorption isotherm determinations were performed on groundwaters containing different pesticide contaminants:1,2-dibromo-3-chloropropane (DBCP), ethylenedibromide (EDB), and 1,2-dichloropropane (DCP). The bottle-point Freundlich adsorption isotherm constants for the groundwater were considerably lower than the constants for the same pesticide in deionized reagent water indicating the natural matrix in the groundwater occupied or otherwise made unavailable to the pesticide a large number of the adsorption sites.

When performing the static Freundlich adsorption isotherm test, the GAC was not exposed to the water for any appreciable time before being exposed to the pesticide thereby minimizing the occurrence of preadsorption. Likewise, when performing the dynamic isotherm test, the pesticide broke through the GAC bed immediately due to its relatively high concentration and the small amount of GAC in the micro-columns. In this manner the Freundlich adsorption isotherm tests departed from practice where a significant part of a GAC bed may not be in contact with the natural organic matrix in the water being applied for days and even weeks before being in contact with the pesticide, thereby promoting preadsorption and significantly decreasing the adsorption capacity of the GAC bed.

No decrease in the DBCP concentration or change in carbon use could be attributed to bacterial organisms as determined by the heterotrophic plate count test. It should be noted that the extracellular metabolic products of these organisms could be a source of material adsorbing onto the GAC.

This Project Summary was developed by EPA's Risk Reduction Engineering 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

Two basic solutions exist for the problem of providing safe drinking water from wells that obtain groundwater from aquifers contaminated with synthetic organic chemicals. One solution is to drill deeper wells to tap aquifers containing water which meets water quality standards. The second solution is to continue to use existing wells while removing the contaminants by use of a treatment process. Granular activated carbon (GAC) has long been recognized as a substance capable of adsorbing organic contaminants from water. Competitive adsorption of target synthetic organic contaminants and naturally occuring dissolved organic substances is a major factor responsible for GAC unit performance variability. The primary emphasis in this report is the evaluation of the field use of GAC for the removal of DBCP and other pesticides from groundwater containing natural dissolved organic substances and experiencing natural variabilities in water quality.

Background

Large areas of California's irrigated farmlands were treated with the soil fumigant, 1,2-dibromo-3-chloropropane (DBCP), for the control of nematodes. The DBCP has migrated through the soil, contaminated aquifers, and has been the cause for the closure of thousands of wells used for drinking water. California's San Joaquin Valley now contains the nation's heaviest and most widespread DBCP pollution. The use of DBCP was suspended in California in 1977 after it was identified as a testicular toxin and potential carcinogen to humans. Other pesticides used in the past as soil fumigants and now found in groundwater, though not as extensively as DBCP, are ethylenedibromide (EDB) and 1,2-dichloropropane (1,2-DCP).

The natural organic matrix in a groundwater is poorly adsorbed by the GAC bed of an adsorption unit, and when the unit is put into operation, the natural organic matrix is almost immediately in intimate contact with the total contents of the carbon bed. On the contrary, the organic compound for which the water is being treated may require days, weeks, or even months before it permeates the total GAC bed. Throughout this time period, often lengthy, the natural organic matrix has been adsorbing to the carbon. This adsorption by the natural organic material is poorly reversible.

Extensive research during the 1960s on the use of GAC in treating waters with a very high organic content revealed several attributes of GAC which remain applicable today: pilot columns can model the performance of full-scale beds; specific synthetic organic contaminants can be removed by GAC adsorption; and the removal of compounds producing taste and odor is more effective than the removal of certain specific compounds. Technical difficulties with the use of GAC for water treatment include the potential growth of microorganisms on GAC surfaces and the possible subsequent creation of harmful substances such as endotoxins and nitrosamines. Adverse chemical effects include the leaching of metals and other inorganic metal elements from GAC. The major disadvantages of GAC adsorption can be minimized by proper operation and monitoring.

Results and Discussion

A mini-pilot plant was constructed with three columns having a 1.3 cm ID and having 60x80 mesh GAC beds with depths of 3, 6, and 9 cm. A fourth column with a 5.1 cm ID had a 16x40 mesh GAC bed with a depth of 9 cm. The hydraulic loading rate generally varied within the range of 10 to 14 m/hr.

The organic matrix in the groundwater was characterized by its concentration of total organic carbon (TOC) which was present at concentrations generally about three orders of magnitude greater than the pesticide. The mini-pilot plant was operated under ambient conditions in the field treating groundwaters containing dissolved organic substances and experiencing natural variabilities in water quality including a large variance in temperature during its lengthy period of operation (DBCP field site data collection began during July 1987 and concluded during February 1988). This temperature variation is a real world phenomenon particularly impacting Point-of-Entry/Point-of-Use systems treating groundwater since these systems treat small flows. The dynamic isotherm and carbon use data collected from such a real world system can differ from data obtained from temperature-controlled bench studies conducted in the laboratory.

Conventional bottle-point and dynamic adsorption isotherm determinations were conducted in the laboratory. A micro-pilot plant having 3 mm ID columns packed with 80x100 mesh GAC to a bed depth of 1 cm was used for the dynamic isotherm determinations. The higher pesticide concentrations used for these determinations were within an order of magnitude of the concentration of the TOC. Lower pesticide concentrations approaching concentrations found in the environment were also used when conducting the bottle-point Freundlich adsorption isotherm test. When performing this test, the GAC was not exposed to the water for any appreciable time before being exposed to the pesticide, thereby minimizing the time for preadsorption. Likewise, when performing the dynamic isotherm test, the pesticide broke through the GAC bed immediately due to the relatively high pesticide concentration (106 to 298 µg/L) and the small amount of GAC in the micro-columns. In this manner, the adsorption isotherm tests departed from practice where a significant part of a GAC bed may be in contact with the natural organic matrix in the water being applied for days and even weeks before being in contact with the pesticide. This might promote significant preadsorption and possibly decrease the adsorption capacity of the GAC bed for the pesticide.

Figure 1 shows bottle-point, mini-plant, and micro-plant Freundlich isotherm data determined using DBCP field site water. The regression line and the 95% confidence limit lines were derived using only bottle-point isotherm data. With the exception of one datum, all the values fall within the 95% confidence limits.

Heterotrophic bacteria plate counts were determined for a $5^1/_2$ month field run, starting in July 1987 and ending in February 1988 on a groundwater containing DBCP. The bacterial counts in the product water were significantly greater than those in the feed water during the warmer months. These bacterial levels decreased to approximately feed water levels during the colder months.

Conclusions

GAC contactors operating in the field including point-of-entry/point-of-use units can experience large variabilities in water quality including water temperature. These large variabilities in water quality can affect the operational efficiency of the GAC contactors.

The determination of adsorption isotherm data in the laboratory may use pesticide concentrations up to several orders of magnitude greater than the concentrations of the pesticide normally found in drinking water. The data collected under these conditions do not represent "real-world" conditions.

It appears that any of the three systems (i.e., bottle-point, mini-plant, micro-plant) are capable of determining carbon use data for GAC at exhaustion. This is particularly interesting considering the temperature variability experienced by the mini-plant and the lack of preadsorption in both the bottle-point and micro-plant tests. These findings indicate that preadsorption was not a significant factor. This finding is significant since static isotherm data are easier and less costly to develop.

No decrease in the DBCP concentration could be attributed to bacteria as determined by the heterotrophic plate count test. The extracellular metabolic products of these organisms could be one source of material adsorbing onto the GAC.

Recommendations

The significance of TOC preadsorbing onto the active adsorption sites in a GAC bed should be established for a range of "typical" surface waters and groundwaters.

The effect on adsorption of microorganisms colonizing the GAC bed of an adsorber should be determined including the effect of extracellular metabolic products of the microorganisms.

Additional pilot-plant field work should be carried out to determine the effect of natural variations in temperature on the adsorption dynamics of GAC.

The full report was submitted in partial fulfillment of Cooperative Agreement CR-812227-01-3 by the California State University, Fresno under the sponsorship of the U.S. Environmental Protection Agency.

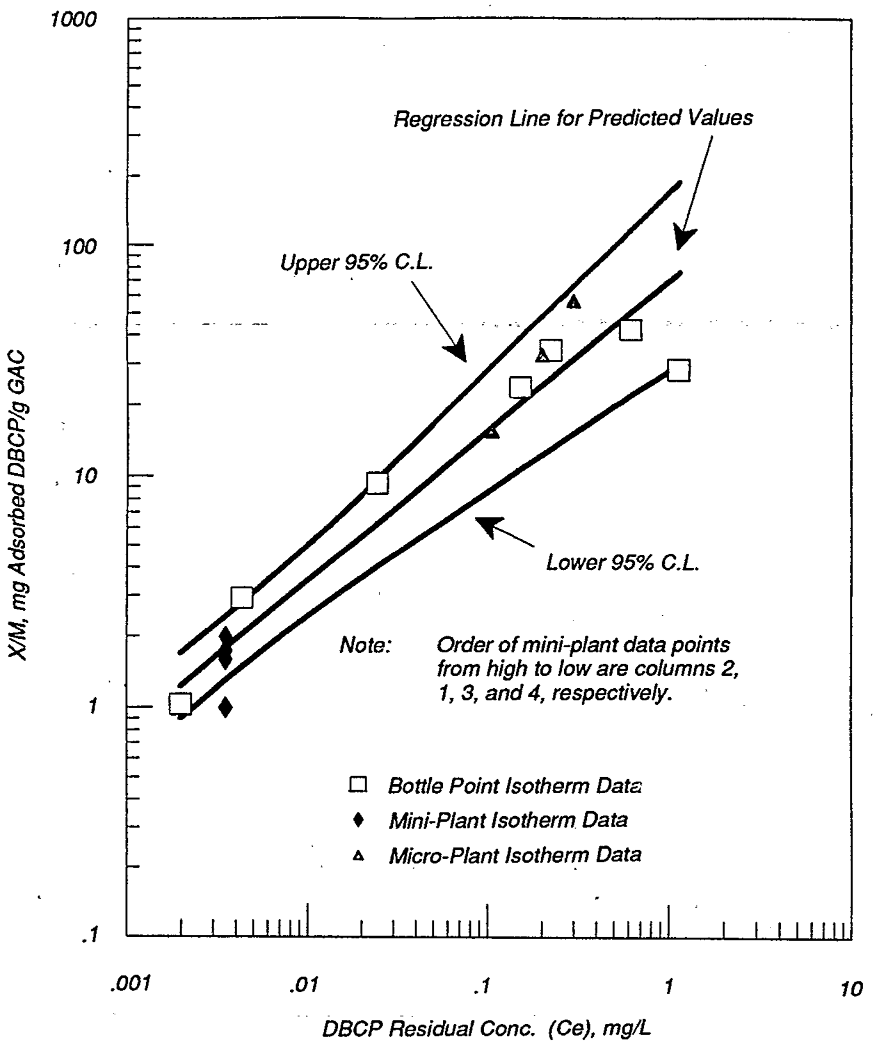

Figure 1. *Bottle-point, mini-pilot plant and micro-pilot plant isotherm data with DBCP field site water.*

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The complete report, entitled "Removal of DBCP from Groundwater; Volume 2, Field Pilot Plant Operation," (Order No. PB91-234 609/AS; Cost: $26.00; subject to change) will be available only from:
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