EFFECTS OF pH ON REMOVING LOW-LEVEL CHROMIUM CONTAMINATION IN GROUNDWATER

J. T. Mason III and Chung-You Patrick Liau

Tennessee Technological University
Cookeville, Tennessee 38505

Abstract

Research on removal of low-level chromium contamination from samples of groundwater, along with included impurities, concentrated on effects of pH. In order to find the best pH for reducing the chromium contamination by adsorption, a series of tests varying adsorbent amount, flow rate, and pH showed that Duolite ES-392 worked best at a pH of about 5.6.

Introduction

In one of the adjacent southern states approximately 7.57×10^5 liters per day (200,000 gallons per day) of water are being pumped from an aquifer into an open stream in order to maintain a required water-free area. Appropriate state and federal environmental agencies have been informed that low levels of chromium are present which exceed the current water quality criteria under the Clean Water Act (PL 95-217). The responsible organization is attempting to eliminate these pollutants quickly in an economical manner by adsorption.

Recent studies have shown that chromium can be effectively removed by either activated charcoal or ion exchange resins, but the practical application of these techniques depends on the adsorption capacity as well as the pH values of the water and other similar characteristics. The concentraton of chromium found in the water samples from the chemical analysis available (November, 1982) is 0.1-1.2 mg/1, but the standard for chromium is 0.05 mg/1. Therefore, chromium must be reduced to 0.05 mg/l and the optimum combination of pH, activated carbon, and ion exchange resin was to be determined.

The influence of flow rate and quantity as well as a comparison between batch and single-column dynamic studies was also investigated for this water.

Materials and Procedures

Adsorbents were selected based on an original intent to investigate both chromium and phenol removal. Subsequent to initiation of the project it became necessary to study only the chromium removal. Two commercial activated carbons—CECA Carborundum GAC 30 and Witco Witcarbon 950, and an ion exchange resin, Duolite ES-392, were used. Comparison of these materials is shown in Table 1. Although the two carbons are comparable, the physical properties of the resin necessarily varies widely.

In this research the Freundlich isotherm (Freundlich 1926) was found to fit satisfactorily and is perferred because of the ease in interpreting results; its use has been described elsewhere (Fornwalt and Hutchins 1966). The equation may be expressed as

$$\frac{x}{M} = k\, C^{1/n}$$

where

x = amount of impurity adsorbed; obtained by the difference in initial concentration (C_o) and the final concentration (C_f)

M = weight of carbon or resin

C = concentration of impurity in solution

k, n = constants.

It is more convenient to express the equation in logarithmic form:

$$\log \frac{x}{M} = \log \frac{(C_o - C_f)}{M} = \log k + 1/n \log C$$

Thus, a plot of x/M versus C would be a straight line on logarithmic graph paper with $1/n$ the slope of the line and k the intercept at $C = 1$. From such plots considerable information can be deduced about the performance of an adsorbent, especially in relation to other adsorbents tested with the same liquor.

Isotherm data in Freundlich form for priority pollutants including chromium has been reported (Dobbs and Cohen 1980). The aqueous phase pH often affects the equilibrium isotherm, but the effect must be determined experimentally and this is the reason for this study.

Before experimenting, the carbon was placed into an oven and dried for three hours at 150°C. The resin was pretreated as required (Diamond Shamrock 1983). Temperature was fixed at 25°C throughout the experiments and variables were considered to be contact time, amount of adsorbent, and pH.

Contact time is very critical to the adsorption process. There must be sufficient time to allow for approach to adsorption equilibrium. A preliminary experiment was performed to determine the contact time required to produce an isotherm that reaches equilibrium at the pH of the water. It was found that the contact time required for the solution is approximately one hour at several different adsorbent/solution ratios for all adsorbents.

After determining the approximate contact time required, batch studies were conducted to get a preliminary appreciation for the combined effects of pH and contact time. In the batch studies the carbon was pulverized to provide

TABLE 1. *Property Comparison of Adsorbents (from Manufacturers)*

Typical Properties	GAC 30	Witcarb 950	Duolite ES-392
Mesh size	8 x 30	12 x 30	16 - 50
Apparent density			
(lb/ft³)	32	29 - 33	42
(gm/cm³)	0.51	0.46 - 0.53	—
Moisture content	1.0%	1.0%	42 - 47% (free-base form)
Surface area (m²/gm)	900 - 1000	1000 - 1100	—
Effective size (mm)	1.5 - 1.7	—	0.3 - 1.2
Iodine number mg/gm	950	1050	—
Physical form	dry	dry	moist beads
Material	coal	petroleum base	Styrene-DVB copolymer

more surface area pores for adsorption, however, the resins were left intact. Contact was obtained simply by stirring various amounts of adsorbent in solutions of various pHs.

Subsequent to the batch studies dynamic studies were run to develop data that more closely matches the necessary dynamic situation associated with treating 7.57×10^5 1/day.

DISCUSSION AND RESULTS

In order to obtain a meaningful isotherm from the batch studies, a wide range of adsorbent dosages—0.05, 0.10, 0.20, 0.50, 1.0, 2.0 and 5.0 grams of adsorbent per 100 grams of the test liquid—were used. The pH of each solution was adjusted to three different initial values (2.0, 7.0, 10.0) with 1 N HCl or 1 N NaOH in order to get the effective isotherm. The adsorbent particles were separated by filtration after reaching equilibrium and the residual chromium in the water was determined. An Atomic Absorption Instrument (Perkin-Elmer HGA-400) was used for analytical analysis. The results plotted in Figure 1 for Duolite ES-392 shows that the adsorption is most favorable at pH 7. All three adsorbents showed the same trend during the batch studies.
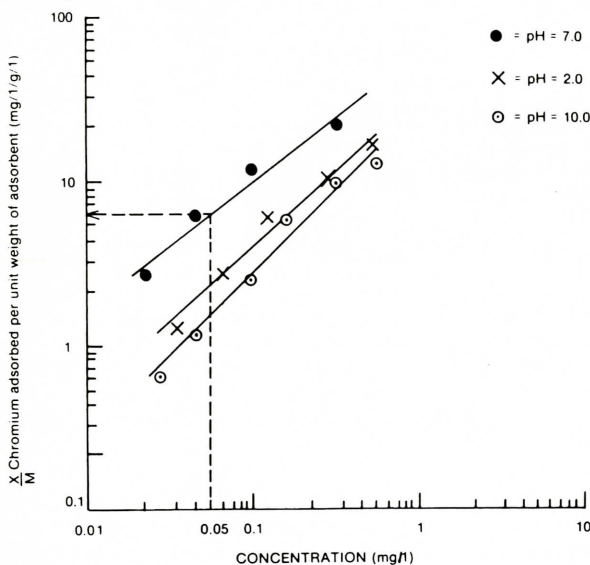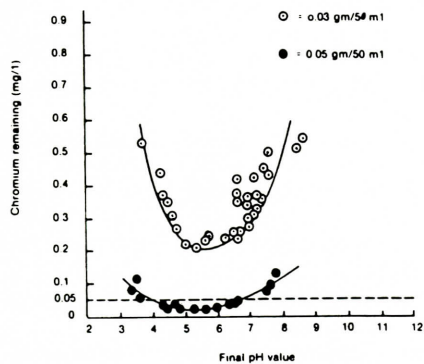

FIG. 1. *Duolite ES-392 Isotherm*

FIG. 2. *The pH Effect of Adsorption on Chromium for Duolite ES-392*
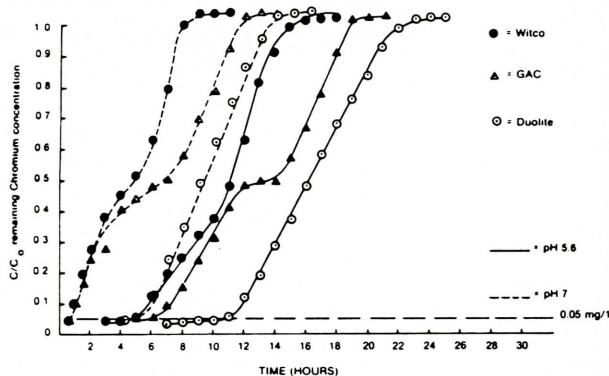

FIG. 3. *Breakthrough comparison based on pH at the same flow rate (4.076 ml/min.) and quantity (6 gm)*

Since the carbons were treated with a basic material during activation, the final pH of solution in the batch studies varied based on the amount of adsorbent used. The resin did not exhibit this phenomena. In order to establish a uniform pH measurement, the final pH was used for all batch studies.

As a second phase of the batch studies, the effect of pH on chromium reduction was investigated. This was done by placing 0.03 or 0.05 grams of carbon into 50 ml groundwater. When equilibrium was reached, the liquid was sampled for the pH change and the remaining chromium concentration. Figure 2 shows a significant effect of pH on chromium adsorbed by Duolite ES-392. The best pH for all of the adsorbents is near 5.6.

Based on the batch studies, decisions were made for conducting the dynamic studies. Initially, the parameters chosen were:

pH	- 4, 5, 5.6 and 7
adsorbent quantity	- 6, 8, and 10 grams
flow rates	- 2, 4, and 8 ml/min

After the adsorbents had been placed in columns, they were back-washed, settled, drained, and pretreated as necessary.

The results of the dynamic studies are shown in Figure 3 as normal breakthrough curves. They are drawn to show only the effects of pH for each of the adsorbents. Only two curves are shown in order to provide a comparison between the adsorbents because the curve becomes cluttered with more information. The breakthrough curves for adsorbent quantity and flow rate were very similar to the one shown with the best adsorption at lower flow rates and higher adsorbent quantity, as expected.

It is obvious from each of the figures that the resin performed better than either of the carbons every time. However, since the adsorbents for the study were originally selected based on both chromium and phenol removal other carbons might perform better.

Table 2 shows that the minimum adsorbent quantity (6 gm) and the medium flow rate (4.076 ml/min) produce satisfactory chromium removal from pH 5 to 7 with the optimum pH somewhere closer to pH 5.

CONCLUSIONS

The following conclusions have been drawn from these preliminary experimental studies. The amount of chromium adsorbed increased from lower pH to near 5.6 and

TABLE 2. *Liters of water treated to under 0.05 ppm chromium based on flow rate, pH and weight of adsorbent.*

F(ml.min.)	Variation pH	M(gm)	Witco 950 Liquor Treated (l)	GAC 30 Liquor Treated (l)	Duolite Es-392 Liquor Treated (l)
8.180	7.0	6	0	0	0.9816
4.076	7.0	6	0.1223	0.1223	1.4674
1.754	7.0	6	0.6341	0.8419	1.4750
4.076	4.0	6	0.4891	0.9783	2.0054
4.076	5.0	6	0.9782	1.5896	2.4456
4.076	5.6	6	1.2230	1.7608	2.7390
4.076	7.0	8	0.4891	1.5896	2.8858
4.076	7.0	10	1.1250	2.6902	4.3282

then decreased rapidly with increasing pH values in the groundwater. The effects of flow rate demonstrate that velocity is a significant factor in treating to under 0.05 mg/l chromium. Comparison of three different adsorbents shows that Duolite ES-392 is the most effective adsorbent.

LITERATURE CITED

Diamond Shamrock Company, Manufacturer Information, Personal Communication.

Dobb, R. A., and J. M. Cohen, "Carbon Adsorption Isotherms for Toxic Organics," U.S. Environmental EPA-600/8-80-023, 1980

Fornwalt, H. J., and R. A. Hutchins, "Purifying Liquids with Activated Carbon." Part I, *Chem. Eng.*, 73, 179 (April 11, 1966)

Freundlich, H., *Colloid and Capillary Chemistry*, (London: Methuen, 1926)

AN ANALYSIS OF THE BENTHIC MACROINVERTEBRATE COMMUNITY OF A FLUCTUATING RIVER-RESERVOIR ZONE IN MIDDLE TENNESSEE

STEVEN K. BURIAN[*]
Florida Department of Environmental Regulation
West Palm Beach, Florida 33406

ABSTRACT

Changes in the structure of a benthic macroinvertebrate community (induced by seasonal variations in reservoir stage) were studied from February - November 1981. Cluster analysis was used to study changes in benthic community structure in relation to changes in river channel morphology. Association matrices and dendrograms were construted using the Pinkham and Pearson coefficient of association. Distinctly different benthic communties were identified through cluster anlaysis and appeared to result from the alteration of micro-and macrohabitats as fluctuations in river-reservoir stage occured. In addition, cluster analysis employing the Pinkham and Pearson coefficient proved to be an effective means of providing information on the relative enviromental tolerances of the 94 taxa of benthic invertebrates identified during this study.

INTRODUCTION

Within natural lotic environments, benthic macroinvertebrate community structure varies widely. Spatial and temporal differences among communities result from natural variations in channel morphology, riparian vegetation, the type and amount of organic input to the stream, aquatic vegetation, and the natural history of benthic populations in general (Cummins et al., 1964; Cummins 1974, 1975, 1979; Hynes 1970a, 1970b). In regulated streams, however, differences in benthic community structure are usually attributed to large and frequent modifications in the morphology of the river system caused by the operation of an artificial impoundment or reservoir (Ward and Stanford 1979). In Tennessee, modifications such as these commonly result from the controlled retention and discharge from multipurpose hydroelectric impoundments. Seasonally the operation of these impoundments affects the parent river systems by altering flow rate, water level, substrate composition, water temperature, and water quality. The effects of reservoirs on stream channel morphology have been summarized by Simons (1979).

In most cases, the increased stress imparted to these systems by fluctuating environmental conditions severely depresses benthic community diversity, radically alters species abundances, and greatly changes species distribution. The purpose of this investigation was to study the effects of controlled retention on the structure of the benthic macroinvertebrate community of the Falling Water River within the headwaters zone of influence of Center Hill Reservoir in Middle Tennessee.

MATERIALS AND METHODS

The study area comprised a section of the Falling Water River, from the base of Burgess Falls to Center Hill Reservoir in White and Putnam Counties, Tennessee (Fig. 1). This section of river is approximately 1.8 kilometers in length and has been seasonally inundated each year by Center Hill Reservoir since the 1950's. Six sampling stations were established in the study area, so that all stream habitats were represented in collections.

All stations were sampled monthly (from February - November 1981) according to a stratified random sampling design. Strata were determined by flow regimes and substrate types in the low water condition. Within each stratum three random samples were collected. Sampling method varied depending upon stream depth and stratum

*- Currently at the University of Maine, Dept. of Entomology, Orono, ME 04469