

EFFECTS OF pH ON CHROMIUM ADSORPTION IN GROUNDWATER

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ABSTRACT

Samples of groundwater contaminated with chromium were passed through adsorption columns to determine the effects of pH on adsorption rate. The water, with contaminants other than chromium, was used to determine the most effective adsorbent to use as part of an overall abatement process. In this study, material from three separate adsorbent manufacturers were compared and it was found that a wide variation in capabilities exists.

Equilibrium studies eliminated one of the four adsorbents initially under investigation and indicated the pH values for additional study. Dynamic studies at a pH varying from 3 to 8 were performed as part of a matrix with flow rate and adsorbent dosage.

It was found that only two of the remaining adsorbents would reduce the chromium concentration lower than the EPA standard of 0.05 mg/l during dynamic studies. Although both adsorbents reduced the chromium to the desired level, one, a new fibrous material containing an anion exchange resin, performed best at the neutral pH of the water. The other material, activated carbon, also performed well but required a pH of approximately 6.4.

1. INTRODUCTION

It has been proven that disposing of industrial and other wastes in air, soil, and water is damaging the environment. Until recently, however, the removal of dissolved minerals from wastewater has been given relatively little attention, because minerals have been considered to be less of a pollution hazard than other constituents, such as organic matter and suspended solids. Chromium is one of the heavy metals which is considered to be highly toxic, and the purpose of this study was to investigate the effect of pH on the removal of low concentrations of chromium from a contaminated aquifer.

Chromium occurs in aqueous systems as the divalent (Cr^{+2}), trivalent (Cr^{+3}), or hexavalent (Cr^{+6}) ion. Hexavalent chromium is the ion of concern and is present in industrial wastes primarily in the form of chromate (CrO_4^-) and dichromate (Cr_2O_7^-). Although the largest potential sources of chromium pollution in water streams are the metallurgical and metal finishing industries, chromium is commonly used in a wide variety of industrial processes such as: pigment manufactures, leather tanneries, textile industries, and as a corrosion inhibitor in cooling towers and boilers.

At one location in Alabama, local groundwater was contaminated by the

discharge of various organic materials and dissolved chromium from an unknown source. The Clean Water Act (PL 95-217), passed by the United States Congress in 1976, discusses the standards for contamination levels of various organic and inorganic materials in waste streams being discharged into the environment [1]. The Environmental Protection Agency (EPA) has been charged with implementing this law and has published maximum contaminant levels that are allowable.

An analysis of the groundwater used in this study [2] showing the major contaminants and the current EPA Standards for these contaminants are given in Table 1. Since the groundwater contained levels of contaminants that exceed the established standards, the water required treatment to reduce the levels of contaminants. Preliminary studies by the organization responsible for the cleanup of the groundwater indicated that the volatile organics may be reduced to acceptable levels by air stripping but chromium remained as a contaminant of major concern.

Table 1. Analysis of Alabama groundwater and current EPA Standards

Contaminant	Concentration mg/l	EPA Standard [1] mg/l
CIS & trans 1,2 Dichloroethane	0.053	0.0094
Trichloroethylene	0.240	0.027
2 Methyl Phenol	0.070	*
Total Chromium	0.770	*
Hexavalent Chromium	0.750	0.05

* None established at this time.

2. OBJECTIVE OF RESEARCH

There are several techniques now available for the removal of chromium from wastewater. Reduction of hexavalent chromium to trivalent chromium and subsequent hydroxide precipitation of the trivalent chromium ion is the most common method of hexavalent chromium removal [3]. The use of ion exchange resins to adsorb metals such as chromium has been well established, and to meet current EPA Standards some industries have adopted ion exchange techniques to treat chromium ions in wastestreams [4]. ANDO, Inc. has developed an electrochemical treatment for the reduction of hexavalent chromium to the trivalent form [5]. In recent years many studies have been conducted in the area of activated carbon material as a possible adsorbent for chromium [6,7,8,9,10,11,12,13,14,15,16]. In most of the above processes the effect of pH has been determined to have a significant effect on the removal of chromium ions from wastewater.

In addition to pH, the adsorption of a contaminant from the liquid phase is also influenced by surface functional groups and polarity of the contaminant. Functional groups on the surface of activated carbons and ion exchange resins allow cation or anion exchange with ions in the liquid depending upon the nature of the groups. Hydrogen and hydroxide ions are removed quite readily by adsorbents and may hinder or enhance the adsorption of other ions from solution [17]. When the solvent for the contaminant is

water, increased polarity of the contaminant usually inhibits adsorption. Generally adsorption increases as pH decreases. The pH of the solution also influences the solubility of ions. Shinsky has shown that chromium ions may precipitate due to pH changes in solution [18]. In light of the above information it is evident that the effect of pH on adsorption must be considered in the removal of chromium from groundwater. The objective of this research was to study the experimental effects of pH on adsorption of chromium by both carbon and ion exchange materials.

3. EXPERIMENTS

Adsorption studies are normally conducted in two phases. Phase one, the equilibrium study, is done to determine the maximum capability of the adsorbent in the specific contaminant/solution system. Phase two, the dynamic study, establishes factors to determine the rate at which the adsorbent is saturated in a flowing system.

Experiments were conducted with four different adsorbents as shown in Table 2. These were chosen to represent a variety of adsorbents and do not necessarily constitute the ultimate in chromium removal capabilities. The main purpose of the experiments being to determine the preliminary effects of pH on removal, it was considered important to see where each type would fail.

Table 2. Adsorbents used for chromium removal from groundwater

Adsorbent	Manufacturer	Type
Filtrisorb 300	Calgon	Activated Carbon
Ecosorb C	Graver Water Company	Carbon Based Adsorbent
Duolite ES-765	Diamond Shamrock	Carbon Based Adsorbent
Ecosorb R	Graver Water Company	Fibrous Material Containing Anion Exchange Resin

3.1. Equilibrium Studies

Equilibrium studies are usually accomplished by putting a known amount of adsorbent into a given volume of liquid that has a known initial concentration of contaminant. The system is allowed to come to equilibrium at a selected temperature and the final contaminant concentration in the liquid phase is measured. The concentration change is then used to calculate the amount of contaminant adsorbed. From this, an isotherm is produced which relates concentration change per unit weight of adsorbent.

Most equilibrium data follow one of three commonly used models for the isotherm: the Brunauer, Emmett, and Teller (BET) isotherm; [19] the Langmuir isotherm [20] or the Freundlich isotherm [21]. The Freundlich model is the most common isotherm and was found to be appropriate for this study.

The Freundlich isotherm is an exponential model and can be represented by the linear expression:

$$\log_{10} \frac{x}{m} = \log_{10} K + \frac{1}{n} \log_{10} c \quad (1)$$

where:

- x = amount of contaminant adsorbed (mg/l)
- m = mass of adsorbent (grams)
- c = equilibrium concentration of contaminant in solution (mg/l)
- n = constant (reciprocal of the slope)
- K = Freundlich adsorption coefficient (intercept at c = 1)

In Equation 1, the constants are indicative of the adsorbent ability to remove a contaminant from solution. High K and high n values indicate high adsorption throughout the concentration range studied. A low K and high n indicates a low adsorption throughout the concentration range studied. A low n value, or steep slope, indicates high adsorption at strong solute concentrations and low adsorption at dilute concentrations.

Based on the initial concentration a value for $(x/m)_{CO}$ can be obtained which represents the ultimate adsorptive capacity at the CO conditions tested. From the $(x/m)_{CO}$ value the total quantity of liquid that can be treated is calculated using CO the formula:

$$W_{CO} = \frac{(x/m)_{CO} (W)}{CO} \quad (2)$$

where:

- W_{CO} = theoretical weight of liquid that can be treated per unit weight of adsorbent
- $(x/m)_{CO}$ = theoretical amount of contaminant that can be removed per unit weight of adsorbent based on the initial concentration of contaminant
- W = weight of liquid used in the equilibrium study
- CO = initial concentration of contaminant

Equation 2 is used to identify suitable adsorbents and determine appropriate flow rates in the dynamic studies.

3.2. Dynamic Studies

Dynamic studies are conducted with a steady flow of contaminated solution through a column packed with adsorbent. The adsorbent becomes saturated with the contaminant in layers somewhat similar to a chromatograph column. As the contaminated solution continues to flow the saturated layer moves preceded by a mass transfer zone, until the entire column is saturated. This is displayed graphically on a breakthrough curve which relates volume of solution to the ratio of final concentration over initial concentration.

Most breakthrough curves are shaped like an s with the concentration ratio increasing rapidly once the leading edge of the mass transfer zone reaches the end of the column. This is the break point.

A number of factors determine the shape of the breakthrough curve and the thickness of the mass transfer zone: flow rate of the feed, composition and

concentration of the contaminants in the feed, temperature, and pH. An increase in flowrate increases the thickness and rate of movement of the mass transfer zone. Initial breakthrough tends to occur faster and the mass transfer zone moves down the column faster as the initial concentration of the contaminants increases. In wastewater treatment the effect of temperature on adsorption is usually small but adsorption generally increases as temperature increases. The temperature was held constant at 25°C for this study. Finally, a decrease in the feed pH usually increases adsorption as was discussed earlier.

Comparison of data from dynamic studies generally indicates higher loading capacities for continuous-flow studies than equilibrium studies. This discrepancy is explained by realizing that the top of the mass transfer zone is always in contact with full-strength feed, while in equilibrium studies the concentration gradient decreases with time. Data obtained from properly performed laboratory studies should indicate both the feasibility of adsorbents for the removal of contaminants and provide data which may be used for design purposes.

3.3. Materials and Equipment

The principal analytical equipment consisted of an Atomic Absorption (AA) spectrophotometer, a pH meter, a chart recorder, and an analytical balance. A Perkin-Elmer Model 403 AA coupled with a Model 400 Heated Graphite Atomizer (HGA-400) temperature programmer for the graphite furnace was used for the determination of chromium concentration.

The solution pH was determined using a Fisher Accument Model 230 pH/Ion Meter. Sample weights were determined using a Cahn Model TA4100 analytical balance.

Equilibrium studies were conducted in 250 ml beakers. To insure the samples were well mixed a Thermolyne Model SL-7225 magnetic stirrer and teflon-coated stirring bar was used. Dynamic studies were conducted in standard 50 ml glass burettes packed with glass beads in the bottom. The contaminated water was gravity fed through the adsorption column.

4. RESULTS

Initial equilibrium studies were performed using the four different adsorbents shown in Table 2 at varying pH. The adsorbents which removed chromium below the .05 mg/l standard were then used to study the effect of pH on adsorption in further equilibrium studies.

After completion of the equilibrium experiments, dynamic studies were performed to investigate the adsorbents in a non-equilibrium situation. Parameters investigated in the dynamic tests included pH, flowrate, and adsorbent dosage.

4.1. Equilibrium Studies

Data for plotting isotherms were obtained by treating fixed quantities of contaminated groundwater with a range of adsorbent dosages. It was experimentally determined that one hour of contact time was sufficient to attain equilibrium for all adsorbents tested.

After the adsorbent and water were mixed for one hour the adsorbent was removed by filtration. The chromium remaining in the water was then measured using the graphite furnace atomic absorption spectrophotometer.

To investigate the influence of pH on the removal of chromium from the contaminated water, isotherms were conducted at initial pH values of 3.1, 7.4, and 9.2. It was noted that after contact with the carbon based adsorbents the pH of the solution changed. Singer suggests this phenomena is due to surface functional groups and the conditions of activation [15]. There was no pH change noticed during the Ecosorb R equilibrium studies.

Isotherm data denoting the influence of pH and the adsorptive capacity of Ecosorb R are shown in Figure 1. Similar plots for Ecosorb C and Filtrasorb 300 were obtained. Duolite ES-765 (a developmental product) was not an effective adsorbent for chromium in preliminary contact studies at any pH and it was not studied further. The adsorption constants for the Freundlich model are given in Table 3.

These constants were determined using a least-squares fit of the isotherm data. Based on calculations from Equation 2 and literature citations, dynamic studies were continued at pH value of 3.1, 6.3, and 7.4 (the original pH of the water).

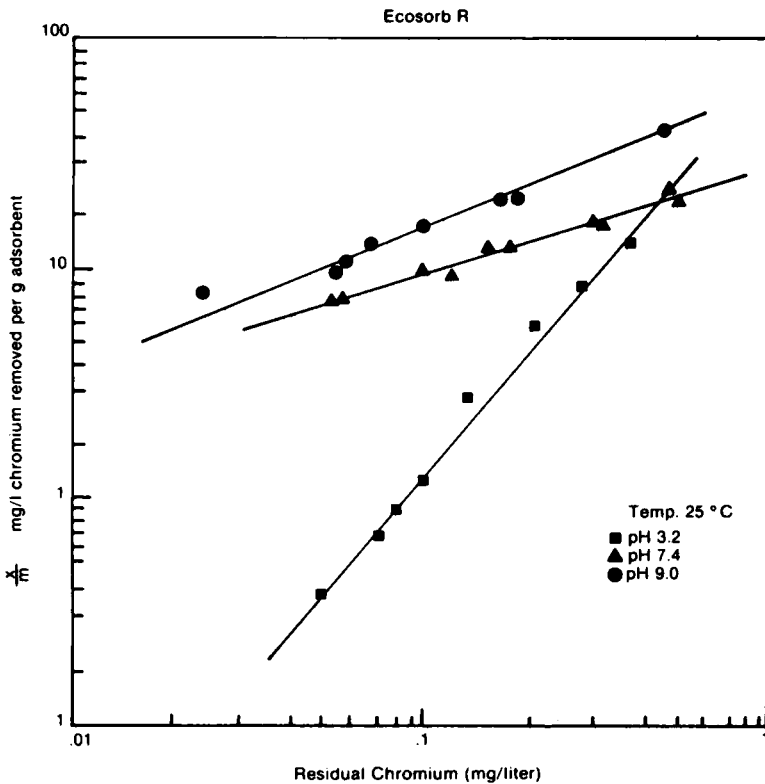


Figure 1. Isotherm for Ecosorb R

Table 3. Adsorption constants for isotherms

Adsorbent	pH	K	n
Filtrisorb 300	3.2	1.93	18.01
	7.4	13.40	0.97
	9.4	0.76	2.30
Ecosorb C	3.2	37.04	0.63
	7.4	4.12	1.46
	9.1	7.05	1.16
Ecosorb R	3.2	80.67	0.55
	7.4	25.35	2.12
	9.0	57.57	1.61

4.2. Dynamic Studies

Parameters of interest for the dynamic studies were adsorbent dosage, pH, and flowrate. The effect of flowrate on the removal of chromium from the contaminated water was investigated by holding inlet pH and dosage constant while breakthrough curves were obtained at two different flowrates. The effects of pH and adsorbent dosage were studied in similar fashion. Since pH changed during the equilibrium studies, the pH of the effluent stream was monitored during the dynamic studies.

Dynamic studies using Ecosorb C did not remove the chromium from the groundwater below the EPA Standards of .05 mg/l. Studies with Filtrisorb 300 and Ecosorb R did provide satisfactory results.

Breakthrough curves showing the influence of flowrate and adsorbent dosage for Ecosorb R are given in Figure 2. The curve for Filtrisorb 300 was similar, however, it was found that the concentration from the column was initially high because of the contact pH effects mentioned previously. The pH of the solution was raised by the adsorbent to a level such that removal of the contaminant was reduced until the adsorbent surface pH was lowered. Huang and Bowers (14) found this same characteristic.

The curves for both Filtrisorb 300 and Ecosorb R in Figure 3 show comparable conditions based on the isotherm data even though the weights are different and the flowrates are not exactly the same. From this it can be seen that, although initial breakthrough occurs first for the Filtrisorb 300, it appears to remain effective for a longer time.

5. DISCUSSION

The results obtained generally follow those expected, however, the pH was found to have more effect for this water than anticipated.

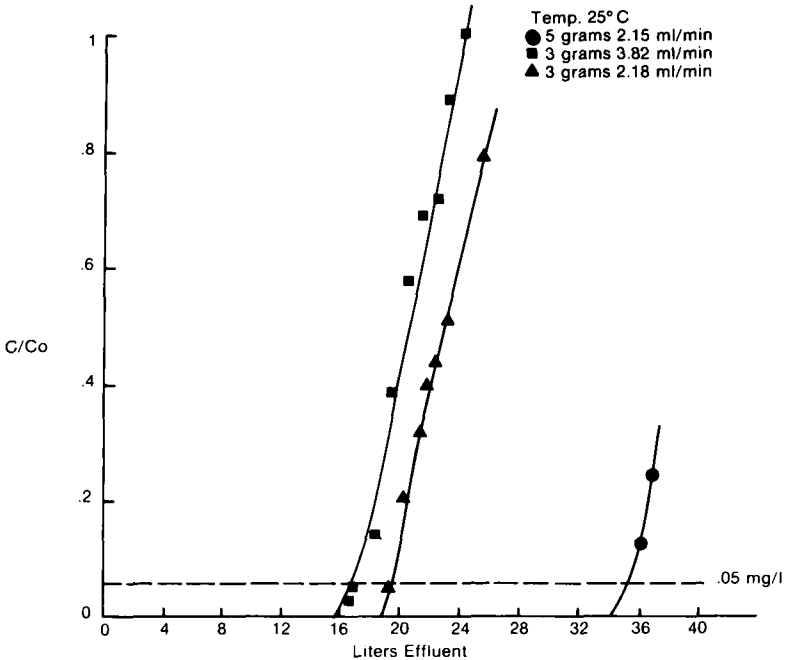


Figure 2. Breakthrough curves for Ecosorb R with inlet pH of 7.7

5.1. Equilibrium Studies

Table 3 shows the variation discovered in the effective adsorbents. It is immediately apparent that Ecosorb R has the requisite characteristics for good adsorption throughout the concentration range at all pH's. The high K value and high n show that maximum adsorption could exist on either side of pH 7.4, however, Figure 1 shows that it should be close to 7.4. The Ecosorb C follows the same trends, only at lower values, and it would appear that this would also be an effective adsorbent. The variations in Filtrasorb 300 make analysis somewhat more difficult. Taken together, the data predicts the best adsorption somewhat below pH 7.4 for low concentrations of contaminant.

Based on these observations it was decided that the most profitable area to continue into the dynamic studies was at a pH ranging between 3 and 8.

5.2. Dynamic Studies

The dynamic studies, conducted with three parameters varying, were done in glass burettes instead of 1 inch columns normally recommended because of the limited of groundwater available directly from the source. Based on this, the preliminary data obtained should not be used to scale up directly to full size adsorption columns, however, the overall parametric effects are valid for further study.

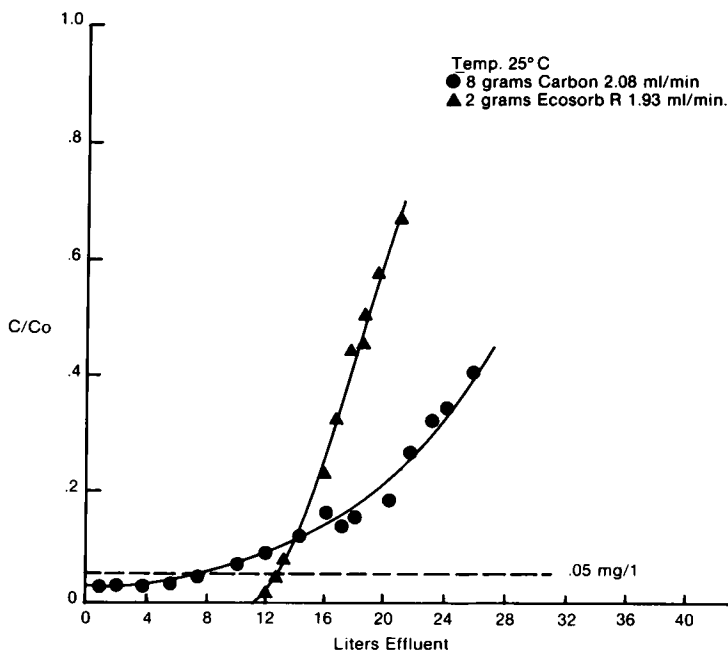


Figure 3. Breakthrough curves for Filtrasorb 300 and Ecosorb R with inlet pH of 6.4

It again became obvious that the Ecosorb R was the better adsorbent of those which were still effective. Looking for the pH which would remove the chromium below the EPA Standard of 0.05 mg/liter with the maximum flow rate or volume treated and a minimum amount of adsorbent was the objective. Using Ecosorb C the concentration was never brought down to 0.05 mg/l so the results are not shown. Table 4 summarizes the results of the studies with the flow rates and adsorbent amount grouped into broad values.

From this it can be seen that the lower flow rate and higher adsorbent amount produced results for all pH values using Filtrasorb 300. Any modification can only produce less desirable results. It should also be noted that the volume treated was better at an interior pH around 6 as opposed to the extremes. At higher flow rates the pH 7 failed to reduce the effluent below the standard even at the higher adsorbent amount.

In contrast to this the Ecosorb R performed even at the higher flow rate and lower adsorbent amount. Although most data was collected at the lower flow rate, the results at pH 7 for both higher flow rate and also more adsorbent amount indicate that this adsorbent is very effective to remove chromium.

It appeared that raising the pH even higher than 7 would prove more effective for Ecosorb R but this was not evaluated during this preliminary study because of the decision made at the conclusion of the equilibrium studies. Also, with the source of water being at a pH varying from 7.4 to 7.7, the possibility of removing the chromium without pretreatment made

Table 4. Volume treated at breakthrough (liters)

Flowrate (ml/min)	Adsorbent	Adsorbent Weight (gr)					
		1-4			5-10		
		pH3	pH6	pH7	pH3	pH6	pH7
1 - 2.3	Filtrisorb 300	-	-	-	0.5	8.0	3.5
	Ecosorb R	1.0	13.0	19.0	-	-	35.0
2.4 - 5	Filtrisorb 300	-	-	No	0.5	-	No
	Ecosorb R	-	-	17.0	-	-	-

success in this pH range a desirable end point. The effectiveness of Filtrisorb 300 at a pH near 6 follows the expected results more closely and would give an option for adsorption with pH adjustment in an economic analysis.

An additional observation which can be made as a result of Figure 3 concerns the distribution of the adsorbent. The figure shows that, at the same pH and flow rate, Ecosorb R provides better initial breakthrough characteristics even with only 25% as much adsorbent in use. However, the slope of the Filtrisorb 300 curve indicates that multiple columns could provide better adsorption. Although the Filtrisorb 300 would never reach the capacity of the Ecosorb R, its capabilities could be improved.

6. CONCLUSIONS AND RECOMMENDATIONS

As a result of this preliminary study, the following conclusions and recommendations for additional research are significant for the system studied.

6.1. Conclusions

1. Ecosorb R and Filtrisorb 300 are effective adsorbents for chromium.
2. No pH adjustment is necessary for Ecosorb R to remove chromium below .05 mg/l at all conditions examined.
3. A pH of 6.4 enhances the adsorption of chromium by Filtrisorb 300.
4. The breakthrough curve for Filtrisorb 300 suggests multiple columns in series would be required to utilize the carbon efficiently.
5. The breakthrough curve for Ecosorb R suggests a single column adsorber may be effective in treating the contaminated groundwater.

6.2. Recommendations for Future Work

Future study of this project should include dynamic studies investigating column sizes, pH values ranging from 4 to 8 or higher, and regeneration of adsorbents. Larger column diameters and multiple columns should be investigated to gain a better understanding of adsorbent usage rate. An

economic analysis should also be performed to evaluate the feasibility of each adsorbent.

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