PESTICIDES REMOVAL USING SORPTION TO IRON OXIDE COATED SAND

BY

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Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
May, 1993

OKLAHOMA STATE UNIVERSITY

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ACKNOWLEDGMENTS

I would like to dedicate this thesis to my husband, Farhad, and to my parents, Mr. and Mrs. Razavi. Without their continual love, understanding, and encouragement, this thesis would not have been possible.

I wish to extent my sincere appreciation to Dr. John Veenstra, my principal advisor, for the professional inspiration which he has given to me during my graduate studies at Oklahoma State University. He has been a constant source of assistance, guidance, and understanding during my endeavors.

I also wish to thank Dr. Greg Wilber for his concern and his valuable instruction.

Suthan, Sirikant, Stuart, and the other graduate students in the environmental engineering program deserve special thanks for their assistance and continual friendship.

I also wish to thank Mr. Don Spoonemore for his assistance in the laboratory.

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CHAPTER I

INTRODUCTION

In recent years there has been a rapidly growing public concern about the widespread contamination of potable water supplies by organic pesticides originating from agricultural run off. The reasons for such concerns may be attributed to a number of factors: high mammalian toxicity levels of these pesticides, insidious health effects, and their persistence in the environment. These concerns have therefore provided sufficient cause for the U.S. Environmental Protection Agency (EPA) to regulate the use of these pesticides. Pesticide removal processes having efficiencies in the range of 50% to 75% would be adequate to put most supplies into compliance because pesticide concentrations are generally in the range of 2 to 5 μg/l, although higher levels have been reported (Ritter 1990). A number of conventional treatment technologies have been considered for purification of ground and surface waters contaminated with pesticides in general, and organochlorine pesticides in particular. Among them, the fixed bed granular activated carbon (GAC) adsorber system has been identified as the best available technology (Adams et al. 1989). But for many smaller cities adoption of this process would be very costly.

It has long been recognized that preformed hydrous oxides of manganese or iron are capable of uptaking metals, phenol, and radium. This work studied sorption of pesticide from aqueous solution using sand coated with iron hydroxide and analyzed by chromatographic techniques over a moderate to high concentration range.

This work presents the sorption data for two pesticides (bromacil, alachlor) in three phases; batch, column, and desorption/regeneration studies. In the batch experiments, the effects of different parameters; for example, pH, time, hydrogen peroxide dosage, different size of sands, and amount of sand on the extent of pesticide removal were investigated. Of the above parameters, only one was varied at a time to observe its effect on removal efficiency. In the column studies, the performance of fixed-bed coated sand columns fed pesticide-spiked tap water was studied. In the third phase, to make the sorption process more economically attractive, regeneration of spent sand was studied.

The specific objectives of this study were: 1) to conduct a preliminary feasibility study on using Fe-coated sands as a pesticide removal technology, and 2) to examine the potential of regenerating and the Fe-coated sands.

CHAPTER II

LITERATURE REVIEW

Introduction

The current investigations on the coated sand filtration process normally describe it as a purifying media which sorbs contaminants from drinking water. In spite of the fact that the fundamentals of sorption reactions on the surfaces of hydrous oxides are well understood, their use in water treatment has been limited largely to the control of trace elements. The literature reviewed in this chapter includes not only the results of different approaches to coat the sand, but also application and development of coated sands for different types of contaminants. The purpose of this chapter is to present literature which will be beneficial in the analysis of the coated sand filtration processes for removing pesticides (alachlor and bromacil) from drinking water.

Review of Different Approaches for Using Using Oxides and its Coating on Sand

Aluminum oxides are available commercially in several particle sizes and surface areas, in contrast to most other hydrous oxides, which are available only as a fine powders or are generated in aqueous suspension as a hydroxide floc or gel. In such forms, these oxides and hydroxides retain their desirable sorptive properties but are limited to system configurations that incorporate large sedimentation basins or filtration for removal. Under such conditions, the separation and regeneration of the oxide can be difficult. These disadvantages can be overcome if the oxide is available in granular form, thereby permitting its use in packed-bed designs.

Dixon (1985) studied the interaction of alkaline earth metal ions with magnetite. He suggested the use of naturally granular magnetite particles for water treatment, with separation, if desirable being achieved magnetically. A different approach has been to coat relatively inert quartz grains with iron oxide. Wangen et al. (1982) were able to achieve this through rotary evaporation of a sand-ferric chloride mixture. However, the physical integrity of the oxide coating could not be sustained during normal use.

Theis et al. (1992) studied removing lead from drinking water, using granular iron oxide which was generated by cementation of iron oxide particles together using a proprietary binding material. The specific oxide used was goethite (α-FeOOH) obtained commercially as a powder consisting of 1 to 2 μm diameter particles. The adsorbent was supplied as 1 mm extrudates, which were then ground and sieved to a uniform size of 0.5 to 1.0 mm granular particles.

Edwards and Benjamin (1989) studied the adsorption of metal-bearing wastes using Fe-coated sand. They were able to use ferric nitrate as the source of iron, resulting in a final product that contained 1% to 2% iron and that could be used and regenerated in a packed-bed design. The sand which they used in all experiments was nearly spherical grains of 20 to 30 mesh Ottawa sand. Ferrihydrite coating (Fe-coating) was applied to the sand either through precipitation or heating. The final surface concentrations of iron were $7(\pm 3)\times 10^{-4}$ grams Fe/gr sand for coatings produced through alkaline precipitation and $1(\pm 0.2)\times 10^{-2}$ grams Fe/gr sand for coatings produced through heating. The coating produced through heating was more durable than that produced through precipitation. More than 97% of the iron initially present was retained by the sand, for both coatings, during 100-minute experiments.

Use of Coated Sand Filtration

Several researchers have used iron or manganese oxides alone or attached to filter sand to remove different types of contaminants from drinking water.

Macbride and Kung (1991) studied the ability of Fe oxides to adsorb phenol and various substituted phenols from dilute aqueous solution. They concluded that certain phenols (i.e. nitrophenol, aminophenol, methoxyphenol and hydroxybenzaldehyde) can be adsorbed to a sufficient degree by oxides in soils and sediments to have a significant effect on their leaching and diffusion properties.

Theis et al. (1992) in a study of granular iron oxide for removing lead from drinking water indicated that the granular iron oxide created with a binding material can remove lead in the slightly acidic to neutral pH range, with the total capacity for lead of being 4.3±0.6 mg/gr.

Valentine et al. (1987) studied the use of a novel sand filtration process that exploits the natural capacity of filter sand to sorb radium through the use of a periodic dilute acid rinse to maintain its sorptive capacity. They observed that when using a partially softened ground water the process was capable of reducing radium concentration by 80% to 90% in the presence of iron flocs.

Valentine et al. (1990) demonstrated that the addition of preformed hydrous manganese oxides appears to be a feasible approach for removing radium from drinking water. Overall radium removal was consistently in the range of 75% to 80%. They suggested that no irreversible effects are expected if the hydrous manganese oxides are under or overdosed other than possibly inadequate radium removal or shortened filter runs. The major advantage of their study is the reliance on existing treatment facilities and simplicity of operation.

Edwards and Benjamin (1989) investigated the use of ferrihydrites metal oxides or hydroxides as metal removal systems. They studied the feasibility of separating the metal contaminants from the adsorbent and then reusing the adsorbent to treat subsequent batches of waste. Their work demonstrated that the ferrihydrite could be regenerated by exposure to a pH=3 solution and reused at least 50 times without a noticeable loss in treatment efficiency. They showed that although the ferrihydrite could be satisfactorily separated from solution, solids capture remained a limiting factor in overall process efficiency.

In late 1989, Edwards and Benjamin continued to investigate the ferrihydrite coating onto the surface of sand, creating an adsorbent with greater flexibility of application than the free ferrihydrite. They observed that sand coated with iron hydroxide out performed uncoated sand in removing particulate metals, as well as both uncomplexed and ammonia-complexed soluble metals. The removed metals were recovered and the adsorptive capacity of media was regenerated by exposure to a pH=3 solution. The oxide coating was stable when exposed to acidic solutions or moderate abrasion. Their findings offer a promising means of obtaining high-level treatment of metal-bearing wastes.

Effectiveness of Available Technologies for Pesticide Removal

This section of the literature review will be devoted to the presentation of published literature pertaining to the pesticide removal processes. Pesticide usage in the United States totaled $300\text{x}10^6$ Kg of active ingredient in 1982, with herbicides being the largest use category 54% (Shirmohammahi et al.,1986). Alachlor is an anilide herbicide. Based on literature values, 90% of it will dissipate in the field in 40 to 70 days (Stewart et al., 1975). Alachlor has a water solubility of 242 ppm and a 2.2×10^{-5} torr vapor pressure (Herbicide Handbook, 1983). The Henry's law constant is approximately 3.2×10^{-8} atm m^3/mol. Hallberg (1985) reported alachlor concentrations as high as 16.6 μg/l in the Big Spring ground water of northeast Iowa. The other pesticide used for this study is bromacil. Bromacil is a brominated uracil herbicide with a water solubility of 815 mg/l and vapor pressure of 8×10^{-4} mm Hg at 100°C (Pesticide Manual, 1977). Hebb and Wheeler (1978) applied bromacil at a rate of 22 kg/ha to a Lakeland sand in Florida with a ground water table at a depth of 4.5 to 6 m. They found bromacil residues in the ground water one year after application as high as 100 μg/l and after two years bromacil concentrations were below 1 μg/l. The Maximum Contaminant Level (MCL) for alachlor is 2 to 5 μg/l and for bromacil will be issue on July 1993.

It should be noted that pesticides pass through clarification, filtration, softening, recarbonation, and chlorination processes largely unaffected (Miltner et al. 1989). The small percent removal is attributed to analytic precision at microgram or nanogram-per-liter concentration.

Richard et al. (1974) discussed the passage of atrazine through conventional treatment processes when comparing Des Moines tap water to its surface supply. They noted that exceptions to these compounds passing through conventional treatment processes are the loss of carbofaran at high pH and the chlorination of metribuzin.

Saleh et al. (1982) conducted a series of experiments to evaluate the effectiveness of chemical and physical advanced wastewater treatment processes in removing selected organic pesticides from domestic wastewater. Biologically treated domestic wastewater was subjected to chemical coagulation, multimedia filtration, and activated carbon adsorption. They concluded that chemical coagulation with alum-lime or lime-ferric chloride had only a slight effect on the reduction of the pesticide residues. They found that multimedia filters had no discernible effect in removing pesticide residues from biologically and chemically treated wastewater. Only activated carbon columns were found to be an effective means for removing the refractory organic residues detected.

Miltner et al. (1990) investigated the control of eight pesticides, including alachlor, by conventional water treatment processes such as alum coagulation, clarification, softening recarbonation, and chlorination. They applied the t-test (Remington et al. 1970) to the pairs of data representing concentrations before and after the sampled processes for the five to nine sample pairs for each period of runoff. No sampled processes exhibited changes in concentration that were significant at the 95% confidence level. These researchers observed that the removal of eight pesticides were insignificant, emphasizing the need for a more effective treatment technology. They suggested that powdered activated carbon applied at the dosages used for taste and odor control can be sufficient to meet water quality goals where removal requirements do not exceed 80%. They concluded that depending on the influent concentration and the established Maximum Contaminant Level, powdered activated carbon may be a better choice than granular activated carbon for control of pesticides in surface waters because it can be brought on-line only during those times of the year when pesticides are present in run off.

Pirbazari et al. (1989) studied removal of alachlor and heptachlor from drinking water by granular activated carbon. They observed significant reduction in adsorber performance in the presence of humic acid due to competitive interaction. One of the objectives of their study was cost estimation for the removal of alachlor and heptachlor. Cost for removal of alachlor was $0.113/1,000 gal treated in a 10-mgd plant with an influent concentration of 100 μg/l and treatment objective of 2 μg/l. The cost for removal of heptachlor was 30% higher than for alachlor. They gave a priori appraisal of the economic viability of the granular activated carbon technology which can be viewed as an indicator as to whether it is worthwhile conducting expensive pilot-scale experiments in the first place.

While the most effective means for removal has been activated carbon, very little attention has been given to biological removal of these pesticides from water. In 1983 Mac Rae conducted a series of experiments on removing pesticides from water by microbial cells adsorbed to magnetite. He showed that microbial cells adsorbed to magnetite can remove significant amount of lindane, 2,4-D and 2,4,5-T from water. During a mixing period of 1 hour he removed 81%, 2,4-D; 21.4% lindane and 12.6% of the 2,4,5-T added to water samples. He concluded that this processes was less effective than the removals of greater than 90% (Robeck et al., 1965) and 100% (Van Rensburg et al. 1980) obtained using activated carbon, but more effective than those of chlorine and ozone (Robeck et al., 1965). He suggested that the ease of settling and regeneration of magnetite and adsorbed bacteria compared with regeneration of activated carbon, plus the relatively short mixing times required for sorption are features that may lead to a more effective and economical attractive multi-stage biological process.

Robeck et al. (1965) suggested that powerful oxidant, ozone, was able to reduce the concentrations of several pesticides up to 90%. An ozone concentration of 1 to 2 ppm, commonly used in Europe, would probably oxidize pesticides to other by-products. They showed that at relatively large and impractical concentrations such as 10 to 38 ppm, ozone did reduced chlorinated hydrocarbons somewhat, but again by-products formed and their toxicity is unknown.

Daver and Wightman (1981) studied the interaction of pesticides with chitosan. Significant uptake was realized only for the acidic pesticides 2,4-D, 2,4,5-T, Decamba, MCPA (4-chloro-2-methylphenoxy acetic acid) and MH (6-hydroxy-3-(2H)-pyrid-azinone) on chitosan.

Camazano et al. (1987) studied the adsorption and mechanism of interaction of vermiculite with the organophosphorous pesticides dichlorvos, phosdrin, sumithion and dimethoate. They indicated that dichlorvos and phosdrin are adsorbed at a solution concentration of 0.3 M in 1,2-dichloroethane forming a defined interlayer complex. The nature of the interlayer cation of the vermiculite and the polarity and molecular size of the pesticide are factors which influence the formation of this complex. They stated that sumithion and dimethoate do not form defined complex.

CHAPTER III

MATERIALS AND METHODS

Experimental Approach

The focus of this research project was on evaluating iron coated sands as an effective method for removing pesticides from water. A Series of batch experiments were used in this investigation. In the batch studies, apart from sorption kinetics and isotherms, the effects of different operational parameters such as pH, hydrogen peroxide, and sand size on the extent of pesticide removal were investigated. Of the above parameters only one was varied at a time to observe its effect on removal efficiency of coated sand. The findings from batch studies were used in designing the column study and regeneration processes.

Adsorbent Preparation

Three different sizes of Ottawa sand (quartz) were obtained from U.S Silica (Ottawa, IL). These sands consist of nearly spherical grains in the 20/30, 30/40, and 60/80 mesh sizes. Before use the sand particles were acid washed (pH=1.0, 24 hr), and then rinsed with deionized water. Ferrihydrite $Fe(NO_3)_3.9H_2O$ was obtained from Fisher

Scientific (Fair lawn, N.J) in crystal form and was applied to the sand through an evaporating process (Edwards et al., 1989). In this process, 200 grams dried sand, 20 grams $Fe(NO_3)_3.9H_2O$, and 50 ml of water, to cover the sand, were placed in a 1-L glass flask. After 2 minutes of gentle agitation on a magnetic stirring plate the $Fe(NO_3)_3$ dissolved. The uncovered flask was then placed in a $110^\circ \pm 10^\circ C$ drying oven for 20 hours, and all visible water was driven off. The coated media was then washed with deionized water until the rinsed water was clear.

Analytical Techniques

Alachlor, which is an anilide herbicide, was obtained from Supelco,Inc (Bellefonte, PA); the bromacil, which is a brominated uracil herbicide was obtained from the University of Oklahoma Department of Botany and Microbiology (Norman, OK). The C18 cartridges which are extraction columns and contained 360 mg of 40 μm C18 bonded silica were obtained from Fisher Scientific.

Alachlor, and bromacil were analyzed using an HP 5890 Gas Chromatograph (GC) (Hewlett-Packard Company) equipped with a 63Ni electron capture detector (ECD). The chromatographic column was a fused silica capillary column 30 m long and 0.25 mm in diameter containing a DB-5 stationary phase (J & W Scientific, Folosm, Ca). The injector, column, and detector temperature were $200^\circ C$, $180^\circ C$, and $250^\circ C$, respectively. Helium gas at a flow rate of 45 ml/min was employed as the carrier gas. The column temperature was held at 175°C for 5 minutes and programmed to 185°C at 5°C/min and held 18 minutes, with an injector temperature of 200°C.

Extraction Procedures

The C18 cartridges were prepared by sequentially washing with 3 ml of methanol, 3 ml of ethyl acetate, 3 ml of methanol, and 2 ml of distilled water. Both the methanol and ethyl acetate (Fisher Scientific) were pesticide grade solvents. Ethyl acetate eluted blanks of the C18 cartridges were analyzed by GC to determine retention time of interfering peaks. Since the GC response differs slightly with every usage, a series of standards were analyzed and a calibration curve was developed before any samples were injected. Standards as well as samples (100 ml) from the batch and column studies were processed through the C18 cartridges housed in Millipore workstation (Fisher Scientific). The cartridges were eluted first with air to remove residual water and then eluted with 2 ml of ethyl acetate. GC analysis of the eluantes were performed to allow capillary column separation of the bromacil and alachlor peaks.

Batch Studies

All batch studies were carried out at room temperature using distilled water and a magnetic stirring agitation system, which was employed to keep the sand in suspension. The total volume of each reaction mixture was 100 ml and it was placed in a 250 ml glass beaker that contained a 1 inch or 2 inches teflon stirring bar. Apart from the sorption isotherm, the effect of different parameters such as pH, time, hydrogen peroxide dosages, sand particle size, and amount of sand on the extent of pesticide removal were investigated. Detailed methodologies of these experiments are explained below.

Effect of PH

Each test solution (100 ml), containing a 50 μg/l concentration of both pesticides and 2 grams of 20/30 Ottawa sand was placed in a 250 ml beaker and adjusted to desired pH (ranged from 4-9) with either 0.1 N nitric acid or 0.1 N sodium hydroxide. The pH was measured with a gel filled electode coupled to an Accumet 900 pH meter (Fisher Scientific). After two hours of contact time during which the solution was gently stirred, the adsorbent was separated by gravity settling. The supernatant was filtered through 0.45 μm filters (Whatman) and analyzed by GC for pesticides remaining in the water. Because all batch studies were carried out using distilled water, which does not have any buffering capacity, 1.0 gram of sodium bicarbonate was added to each mixture in order to keep the pH at the adjusted value.

Effect of Time

The effect of contact time was investigated using a series of 100 ml samples of distilled water spiked with 50 μg/l of both pesticides and 2.0 grams of 20/30 Ottawa sand at pH=7. The beakers were withdrawn from the agitation system after 15 minutes, 1 hour, 2 hours, 10 hours, and 22 hours of contact. Each sample was then gravity settled and filtered before being analyzed with the GC.

Effect of Sand Size

The effect of Ottawa sand size was investigated using 2.0 grams of three different sand sizes 20/30 (0.5 mm), 30/40 (0.25 mm), 60/80 (0.1 mm). After 2 hours of contact the adsorbents were filtered out and the liquid analyzed by GC to observed the overall removal capacity of the different sand sizes.

Effect of Amount of Sand

The sorption was also studied by increasing the amount of the sand from 2 to 5, 10, and 15 grams. The contact time used was 2 hours and the pH was adjusted at 7. The pesticides concentration was 50 μg/l of each in 100 ml of water. The mixture was then filtered and analyzed by GC for pesticide concentration.

Effect of Hydrogen Peroxide

The effect of hydrogen peroxide was studied by varying the dosages from 1 to 100 mg/l in 100 ml of water containing 50 μg/l of both alachlor and bromacil and 2.0 grams (20/30) of coated sand. The contact time was 2 hours and pH was adjusted to 7. The mixtures was analyzed by GC for any changes in pesticide concentration from that originally present in the mixture.

Sorption Isotherm

The sorption isotherm experiment was conducted with different initial alachlor and bromacil concentrations. In each experiment 2.0 gram of 20/30 coated sand and 100 ml of water containing both pesticides with different concentrations ranging from 5.0 to 100 μg/l were used. The pH was adjusted to 7.

Batch Desorption and Regeneration

A 100 ml solution containing 2 grams (20/30) of coated sand, was agitated in a 250 ml beaker in the presence of 50 μg/l of both pesticides at pH=7. After a 2 hours equilibrium contact time, the supernatant was analyzed for alachlor and bromacil. From the difference between the initial and final pesticides concentration, the amount of pesticides sorbed by the coated sand was determined. The sorbent was then washed with 100 ml of distilled water that was adjusted to pH=1.5 for 20 minutes. The wash water was collected, filtered and analyzed by GC for any pesticide present in the wash water. The same procedure was followed for three more cycles (sorption/desorption). The pH was varied from 1.5 to 2.5, 3.5, and 4.5 for the following wash cycles. A reaction time of 2 hours and regeneration time of 20 minutes were maintained in all of these studies. After each cycle the mixture was separated by filtration and analyzed by GC for any pesticide remaining.

Column Studies Using Fe-Coated Sand

These experiments assessed the potential advantages and disadvantages of using a column packed with Fe-coated sand for pesticide removal. A conventional sand-packed column was run using pesticide- spiked tap water. A 1 inch ID glass column was filled with coated sand (100 grams of 20/30 mesh size) to a depth of 6.0 inches. The diameter of column was chosen to prevent wall effects in the bed. Wall effects are dependent on the column- to- particle size ratio (Pirbazari et al., 1991) and according to Conway and Ross (1980) to prevent wall effect from influencing test results, this ratio should be greater than 25. In this experiment, the ratio of column diameter to particle diameter was 50. Glass wool was used in the bottom of the column to support the sorbent. The feed containing an concentration of both pesticides of 50 $\mu g/l$ was pumped through the column in a downflow mode. The column studies were performed at two different empty bed contact times (EBCTs); of 4 and 16 minutes. The experiments were performed at two different flow rates of 20 ml/min and 5 ml/min. The pH was maintained throughout the column studies at 7.0 to 7.2. The media depth was 6.0 inches and the porosity was 0.32. The samples (100 ml) from the influent and effluent were periodically collected, extracted and analyzed for adsorbate concentrations. Following completion of the run the column was then backwashed to remove accumulated pesticides capture in the column. One hundred and ten milliliters of tap water (pH=7.0) was pumped through the column at a rate of 30 ml/min. Backwash fluid was collected and analyzed for pesticide presence in the water. Next the column was regenerated by exposure to 110 ml of water adjusted to pH of 3.0 with nitric acid. The regenerant solution was circulated through the column at flow rate of 30 ml/min in a closed loop for 10 minutes. A fresh regenerant solution was used for each run.

A separate column study was performed using previously regenerated sand in order to investigate any effects of hydrogen peroxide may have on column operations. The concentration of hydrogen peroxide used 5 mg/l. Other experimental conditions were maintained at the same level as in the previous column studies. Influent and effluent samples (100 ml) were periodically collected, extracted and analyzed for adsorbate concentrations.

CHAPTER IV

RESULTS AND DISCUSSION

Batch Studies

Effect of Time

The uptake of pesticides over time at pH=7.0 for initial pesticide concentrations of 50 $\mu g/l$ is shown in Figures 1 and 2. It can be observed that for bromacil, sorption rates are initially rapid and increase marginally over a period of 22 hours. For alachlor, adsorption rates are rapid and increase significantly over 22 hours of contact time. The major jump is between 10 and 22 hours. The point at 22 hours could erroneously be high. Therefore two hours of contact time was chosen as equilibrium for the batch experiments. Several workers (Inskeep and Baham, 1983, Arringhieri et al., 1985, and Ghanem and Mikkelsen, 1988) have mentioned that when the adsorbent materials are in suspension the adsorption tends to be rapid, taking place within a few minutes or hours.

Effect of Sand Size

The results also indicated that the overall capacity is greater for smaller particle sizes (Figure 3). This can be

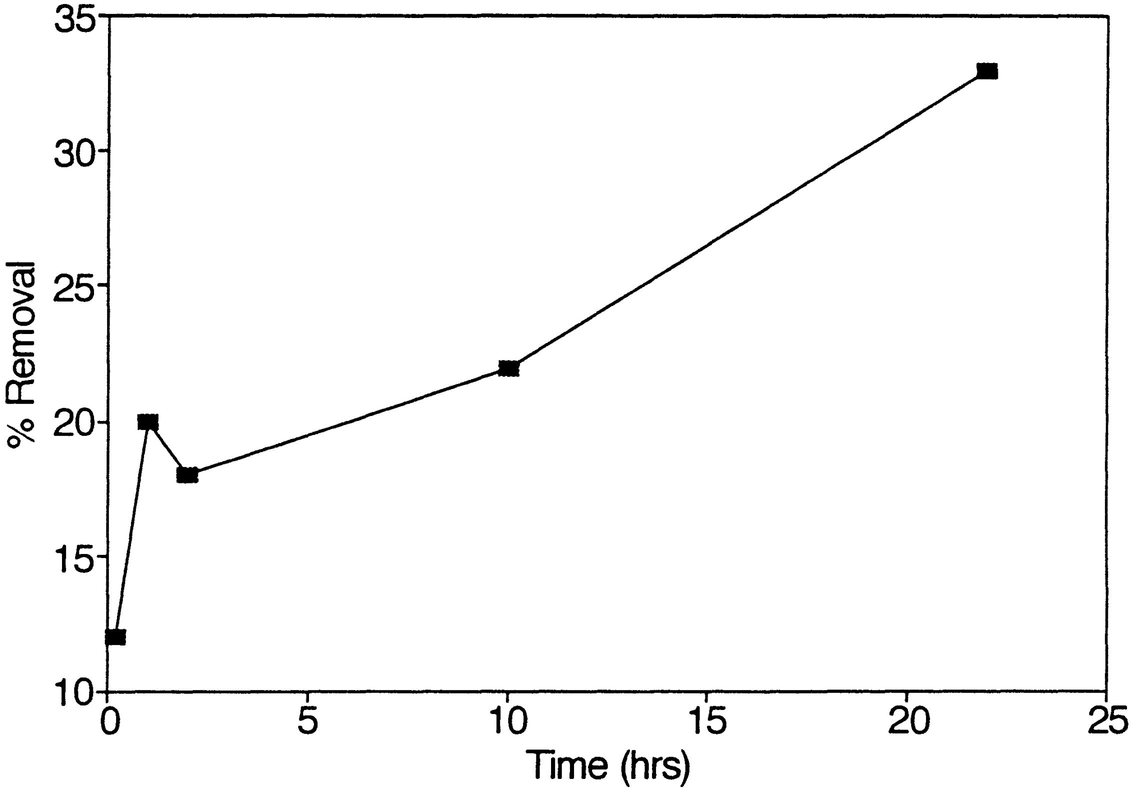

Figure 1. Effect of Time on % Removal for Alachlor

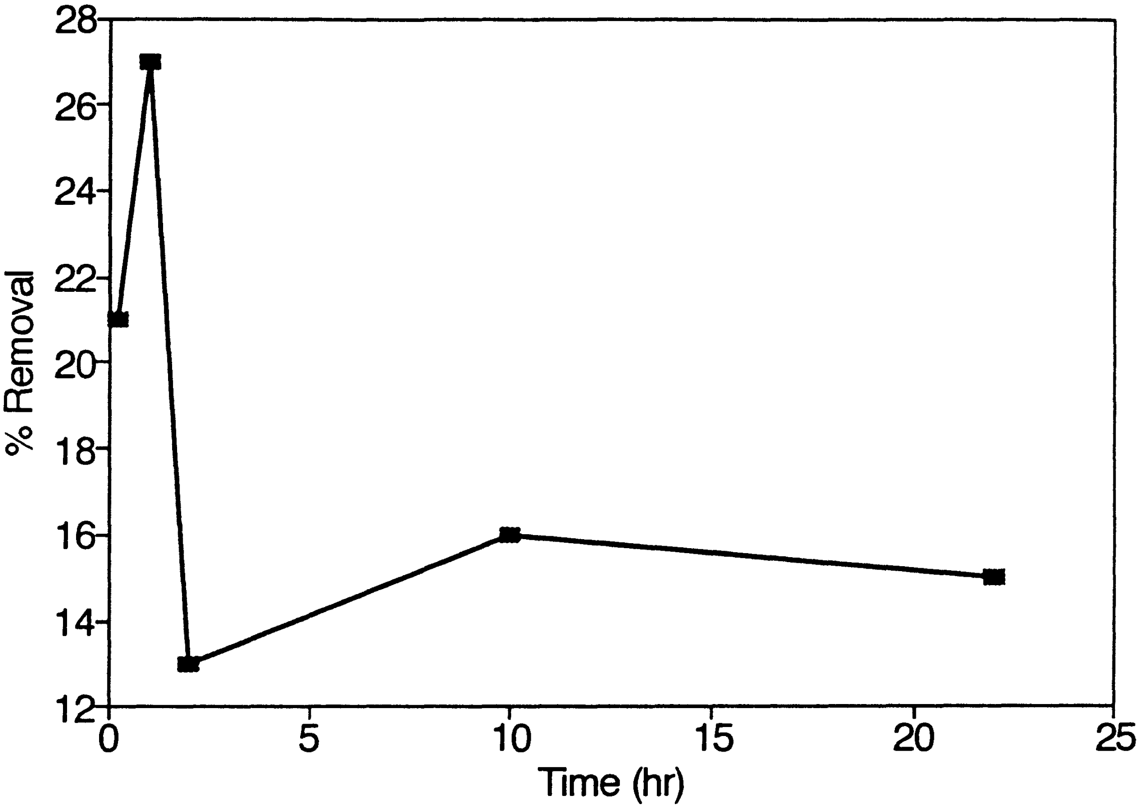

Figure 2. Effect of Time Versus % Removal for Bromacil

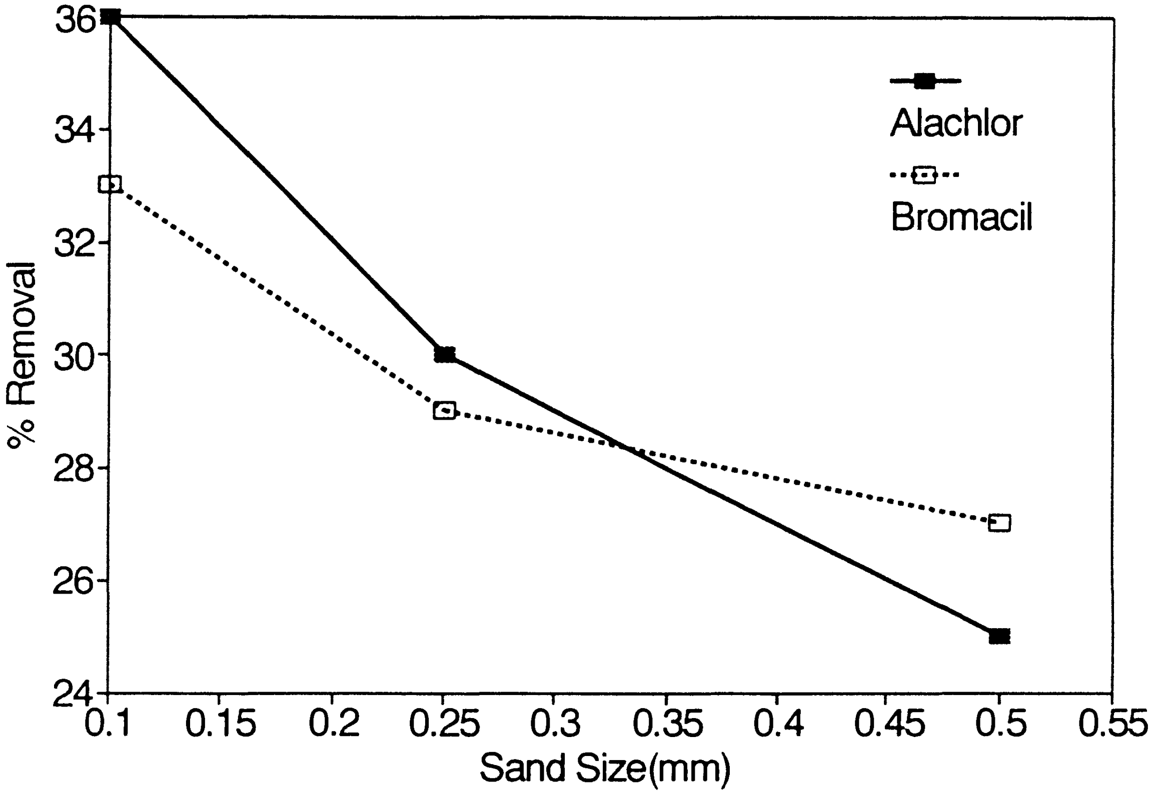

Figure 3. Effect of Sand Size on Removal of Alachlor and Bromacil by Coated Sand

explained by the fact that greater surface area is available for the pesticides. From a practical point of view the smallest size (60/80) is very fine and could potentially clog much faster than the large size particles when used in a column mode. Because of this all other experiments were performed using the 20/30 mesh size sand.

Sorption Isotherm

The sorption isotherm for bromacil and alachlor on iron coated sand system are shown in Figures 4 and 5, respectively. These experiments with initial pesticide concentrations 5.0, 25.0, 50.0, 75.0 and 100 μg/L were run for 24 hours. Experimental data for bromacil were fitted to a linearized Freundlich equation in the form of:

$$\mathrm{Log}(q) = \mathrm{Log}\ K + 1/n\ \mathrm{Log}\ C \qquad (1)$$

$$q = X/M$$

Where

X/M= quantity of pesticides adsorbed per unit weight of Fe-coated sand, mg/g

C= equilibrium concentration of pesticides remaining in solution, mg/l

K= measure of sorption capacity

1/n= sorption intensity

The slope of the linear regression line yields a value for 1/n of 1.12 and K, which is the antilog of the intercept, of 0.0075. This line yields a value of 0.98 for

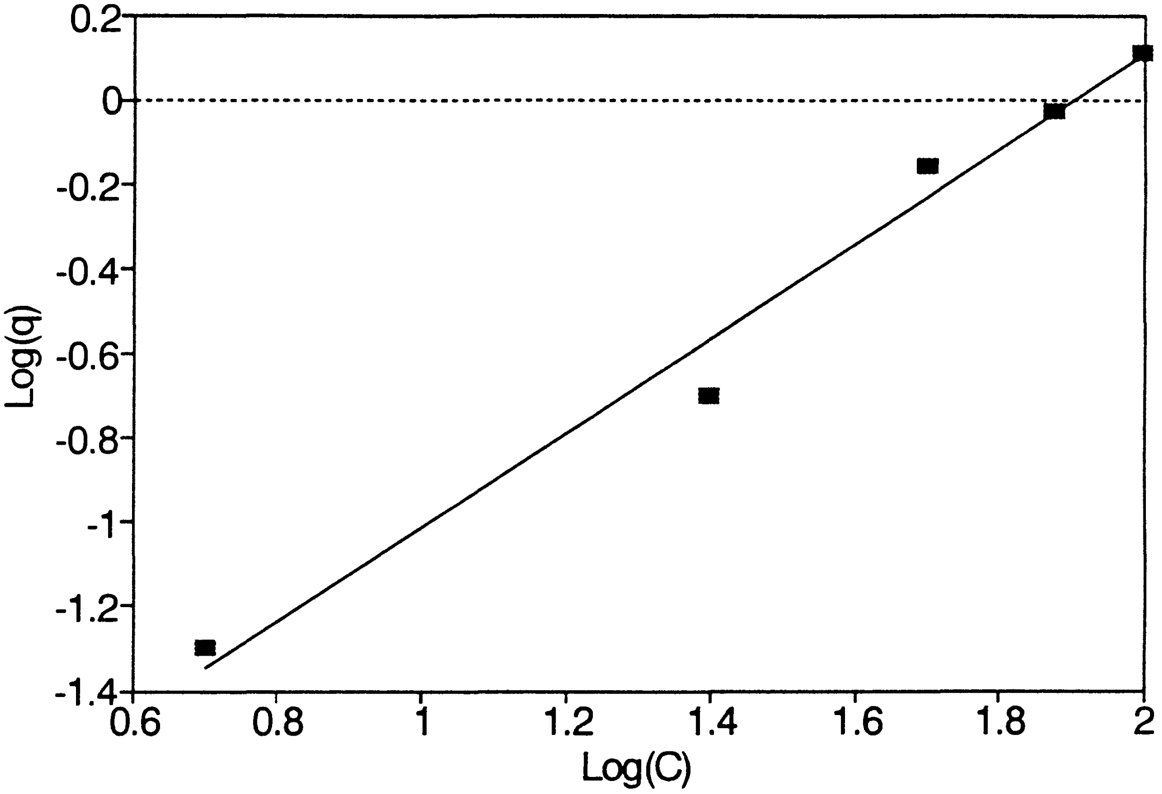

Figure 4. Linearized Freundlich Isotherm for Sorption of Bromacil onto Fe-Coated Sand

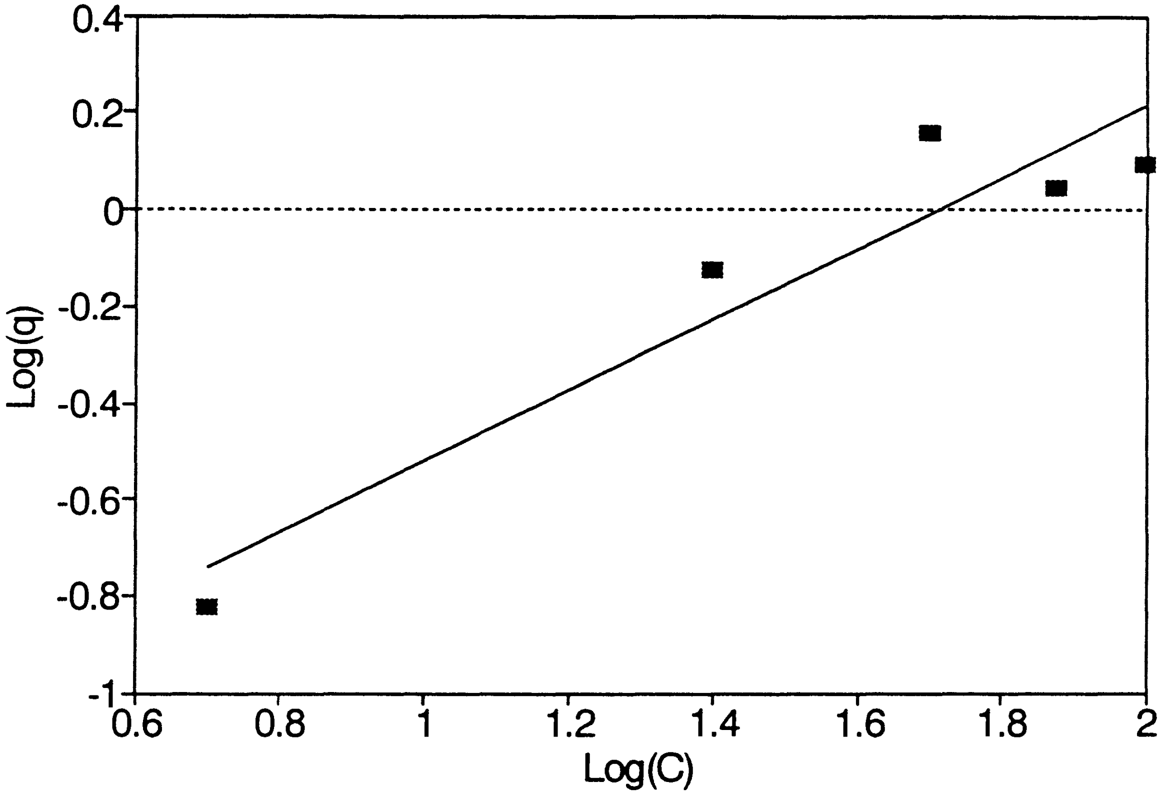

Figure 5. Linearized Freundlich Isotherm for Sorption of Alachlor onto Fe-Coated Sand

R squared.

These results point out that sorption of bromacil can be modeled by a Freundlich isotherm. The sorption capacity of Fe-coated sand can be determined from Isotherm data. The equation takes the form of:

$$X/M = 0.0075\ (C)^{1.12} \tag{2}$$

in which the variables X/M and C are the same as in equation 1. Each gram of Fe-coated sand can remove 0.0075 μg of bromacil. The breakthrough time for a column containing 100 grams of sand and subjected to an influent concentration of 50 μg/L of bromacil at flow rate of 20 ml/min can be estimated. Based on these values an initial estimated of the breakthrough time for bromacil was calculated to be about 60 minutes.

Experimental data for alachlor were fitted to linearized Freundlich equation in the form of:

$$X/M = 0.055\ (C)^{0.736} \tag{3}$$

The slope of linear regression line yields a value for 1/n of 0.736 and K, which is the antilog of the intercept, of 0.055. This line yields a value 0.90 for R squared. Each gram of Fe-coated sand can remove 1.36 μg of alachlor. In column studies containing 100 grams of sand; the estimated breakthrough time for alachlor at a flow rate of 20 ml/min is 98 minutes. Estimated times for alachlor and bromacil breakthrough to occur for 6.0 inches deep sand bed with an influent flow rate of 5 ml/min and influent concentration of 50 μg/l are 360 and 240 minutes, respectively.

Effect of pH

Figure 6 shows the effect of pH on alachlor and bromacil removal by Fe-coated sand. At pH of 4 only 4% of the bromacil was sorbed while at pH=7 about 30% of bromacil was removed. As it can be seen from Figure 6, there is a general trend of increasing removal at higher pH (up to 8.5). At pH of 4 about 22% of the alachlor was removed and at pH of 7 about 17% of alachlor is removed. In case of alachlor there was a general trend of decreasing removal as pH increases. It can be seen that the highest removal for bromacil is at pH=7.0 and for alachlor there is only a slight difference in the percent removal at pH values of 4 and 7.

Since these two pesticides were present together in solution used in this study, pH of 7.0 was chosen for all subsequent batch and column studies. The pH of 7 was an acceptable compromise based on the general removal trends of each pesticide.

Effect of Amount of Sand

One of the important factors which may influence the removal capacity is surface area. In batch studies, the

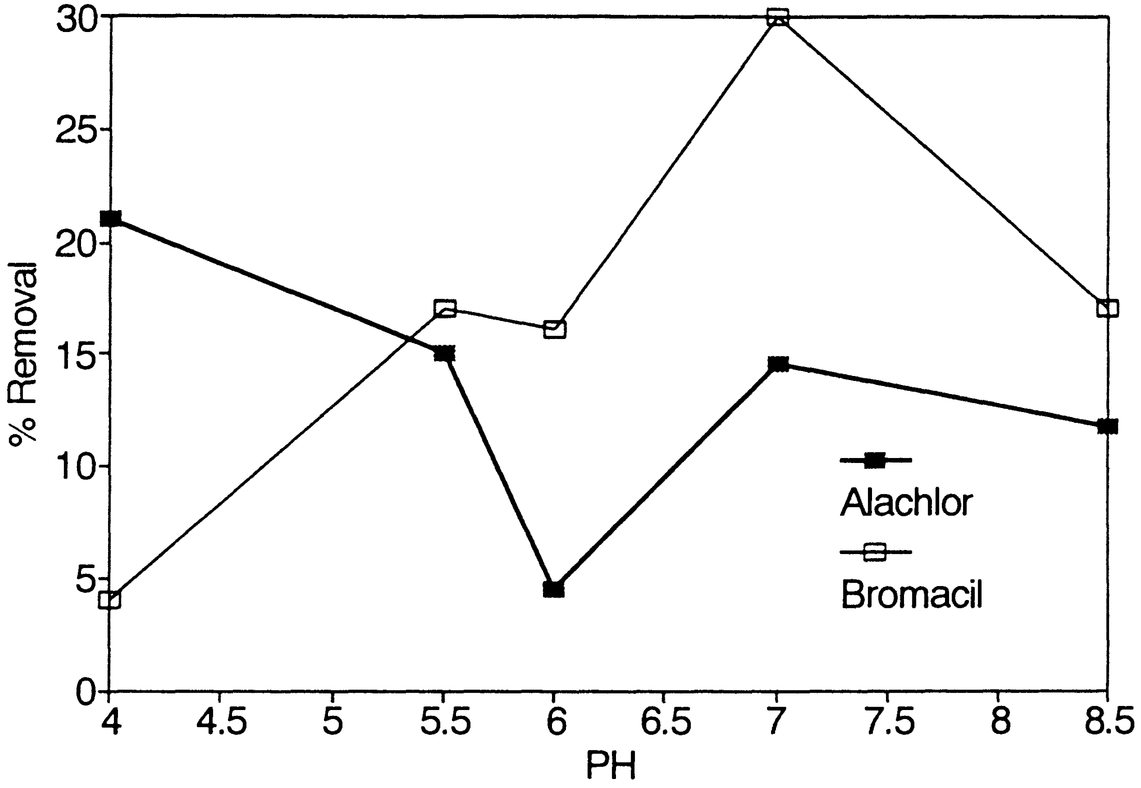

Figure 6. Effect of PH on Removal of Both Pesticides by Coated Sand

removal capacity of sand was investigated by increasing the amount of sand from the original 2.0 to 5.0, 10, and 15 grams. Figure 7 shows that, as the amount of sand increases from 2 to 15 grams, the removal of bromacil increased from 15% to 32%. Results indicated that the extent of alachlor removal increases by less than 8% for 5 grams of Fe-coated sand, decreased by approximately 15% for the 10 grams sample and then increased by 5% for 15 grams of sand. This may be experimental error for the alachlor samples. Figure 7 shows overall increase for removal of these two pesticides for higher quantity of sand.

Effect of Hydrogen Peroxide

Results (Figure 8) show that at a hydrogen peroxide osage of 20 mg/l, the alachlor removal reached its maximum. If the point at 20 mg/l is in error then the general trend shows that hydrogen peroxide has no effect on alachlor. Figure 8 also indicates that with an increases of hydrogen peroxide concentration from 1 to 5 mg/l, the extent of bromacil removal is increased sharply and maintained almost constant over the range of 5 to 100 mg/l. It was found (Figure 9) that hydrogen peroxide alone (no sand present) at low concentration was able to remove up to 18% of the alachlor and 28% of the bromacil. As the concentration of hydrogen peroxide increases from 20 to 50 mg/l, the extent removal was reduced by 10% for both alachlor and bromacil. It can be concluded from Figures 8 and 9 that the removal

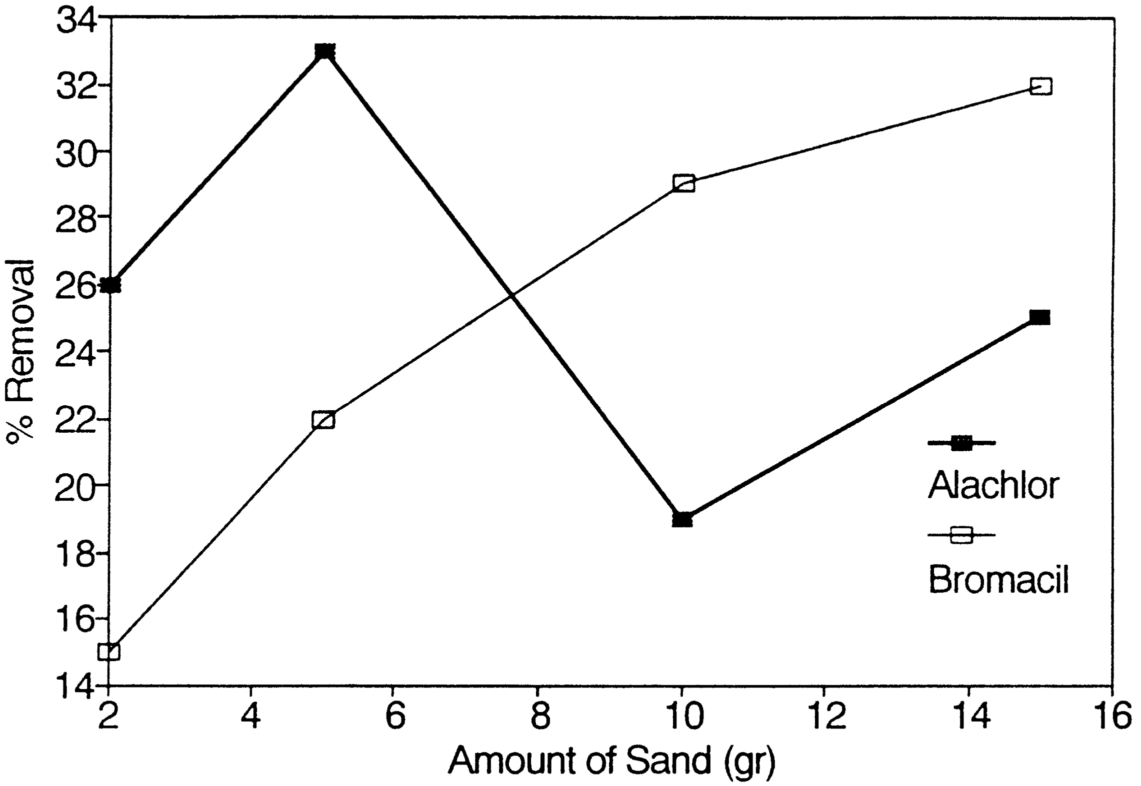

Figure 7. Effect of Amount of Sand in 100 ml Batch Exp.

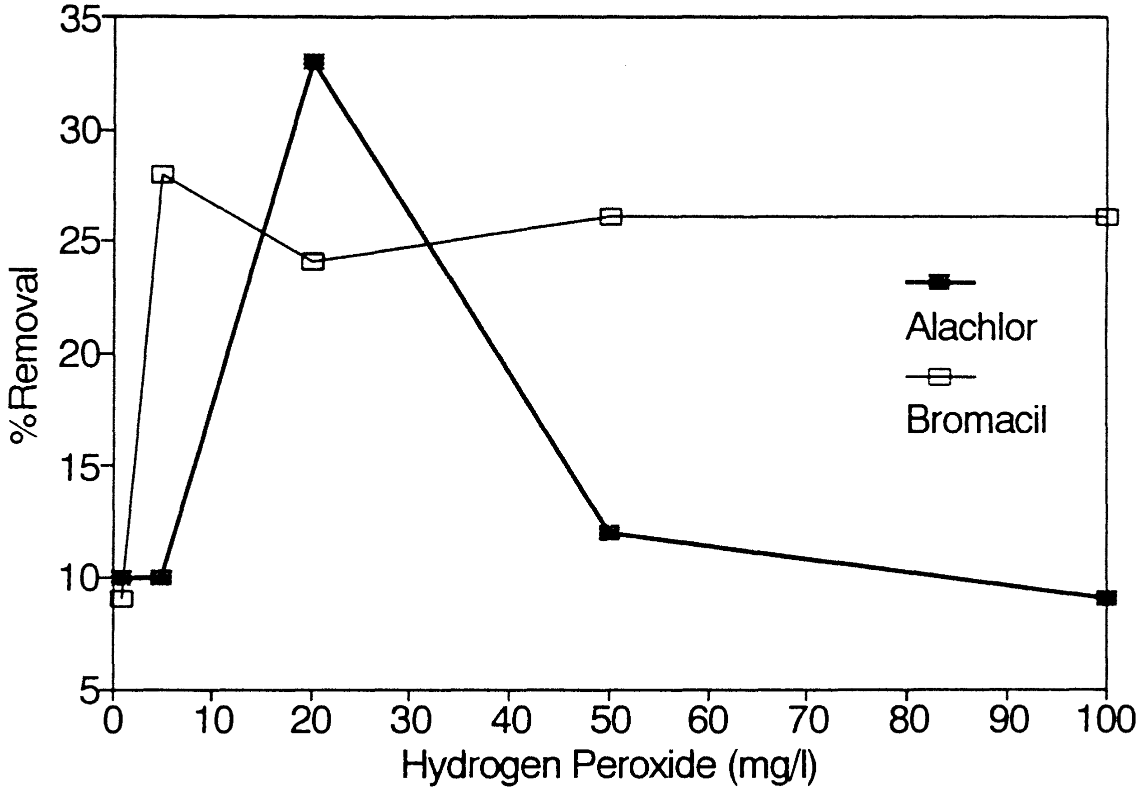

Figure 8. Effect of Hydrogen Peroxide on Removal of Pesticides with Fe-Coated Sand

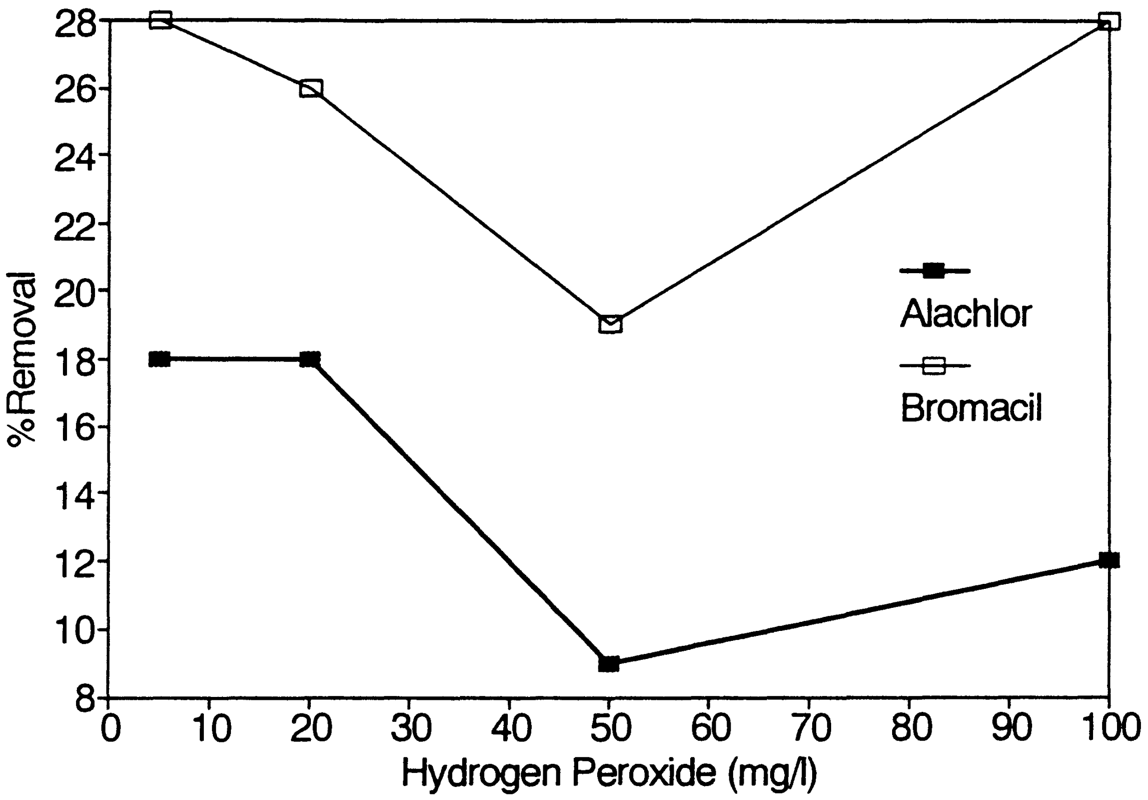

Figure 9. Effect of Hydrogen Peroxide on Removal of Pesticides with no Sand Present

has a general trend for alachlor 28% and for bromacil 12% when hydrogen peroxide (1 to 100 mg/l) and coated sand were used. Figure 9 indicates that the removal rate reduced as hydrogen peroxide dosage increased. This may be attributed to possible reaction between hydrogen peroxide and iron oxide. Since dosages of hydrogen peroxide higher than 20 mg/l are impractical due to expense, the column study was conducted with 5 mg/l of hydrogen peroxide in order to confirm the results from the batch experiment. All the results from batch experiments are presented in Tables 1-9 (Appendix).

Column Studies

Investigations using mini fixed-bed adsorbers were conducted to: 1) verify the predicted capability of the Fe-coated sand; 2) examine the impact of alachlor and bromacil on adsorber performance characteristics; 3) assess the extent of adsorbent capacity utilization; and, 4) verify the effect of hydrogen peroxide. The experiments were performed using alachlor and bromacil fed to the columns at two different flow rates (20 and 5 ml/min) which yielded two different empty bed contact time (EBCTs) of 4 and 16 minutes. The column operating conditions along with the adsorber influent and effluent concentrations are specified in Tables 10-15 (Appendix). One of the important consideration for mini-adsorber operations is wall effects because they can significantly affect the mass transfer of the pollutant along the adsorber. The wall effects are dependent on the column- to- particle size ratio. In this study this ratio was 50 which is greater than the minimum of 25 recommended by Conway and Ross (1980).

Fe-Coated Sand Column

The column studies were conducted to obtain an assessment of adsorber efficiency, and determine adsorbent capacity at two different EBCTs (flow rates) and run times. These assessments would be useful in determining adsorber service live as well as regeneration efficiency and replacement criteria of sand to meet treatment objectives. Thus an overall appraisal can be made on the economics and practicability of Fe-coated sand filter adsorbers. The first column study was performed using both pesticides each at an influent concentration of 50 μg/l, and flow rate of 20 ml/min (EBCT of 4 minutes and loading rate of 1 gpm/ft^2) for about one day. As evidenced from Figure 10 alachlor had a sharp decrease in removal, of about 10%, after 2 hours which may be attributed to the high flow rate causing inadequate contact time for sorption to occur. As it can be seen (Figure 11) bromacil has a sharp decrease in removal of about 12% at 200 minutes. After 450 minutes, bromacil has sharp increase of removal up to 10%. The removal reached its highest value (24%) at the end of experiment. The reason for improved performance of bromacil over time is not clear. When the EBCT was changed from 4 to 16 minutes by

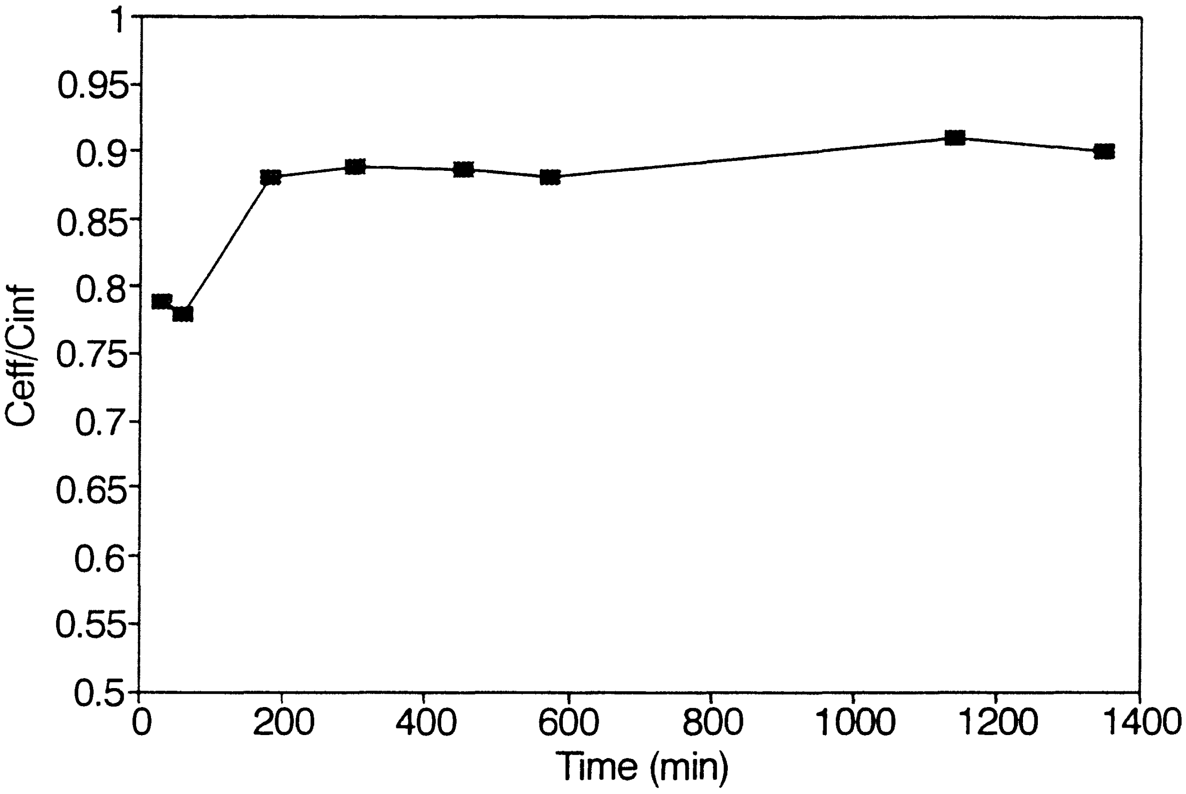

Figure 10. Performance of Fe-Coated Sand Column # 1 for Alachlor removal, Flow Rate = 20 ml/min

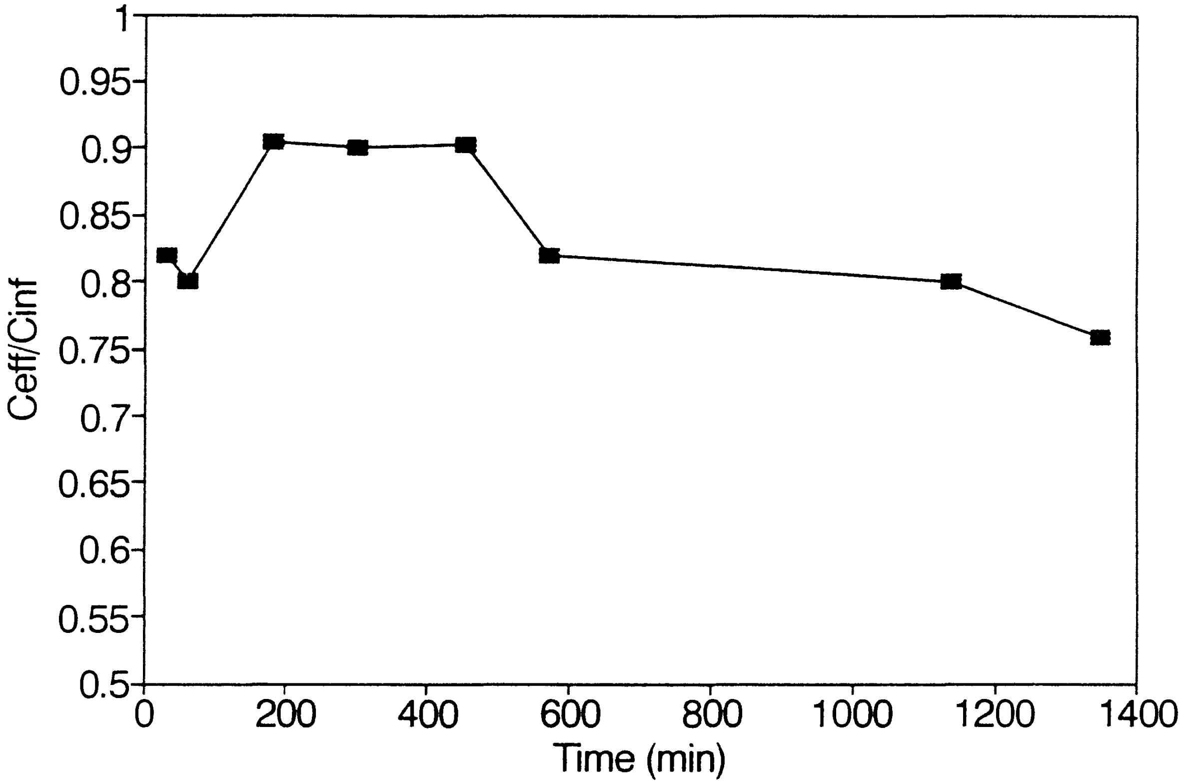

Figure 11. Performance of Fe-Coated Sand Column # 1 for Bromacil Removal, Flow Rate = 20 ml/min

reducing the flow rate to 5 ml/min, the removal for bromacil was less than 4% at first and gradually increased to 20% after 700 minutes of the experiment and remained constant at this level for the rest of one day experiment (Figure 12). When the flow rate was changed from 20 to 5 ml/min, the alachlor removal increased from 12% (Figure 10) to 23% (Figure 13). The increase of alachlor removal (12% to 23%) is attributed to increase of EBCT (4 to 16 minutes). It is believed that these patterns of sorption may be attributed to ripening of the filter sand. Since ripening phenomena (performance of filter improved over the time) was not expected, the same column was restarted after sitting for 4 days without any regeneration and operated for 1 more day under the same experimental conditions. Figure 14 shows the results for alachlor which reveal 55% removal immediately after restarting the column which may be due to 4 days of contact. After 200 minutes of the experiment run, the removal decrease to 30% removal. By the end of 24 hours the removal had increased to 45% and stayed almost constant. The general trend for alachlor suggested a fairly consistent 45% removal for alachlor. Figure 15 repeats the previous pattern for bromacil which shows almost no removal after 60 minutes and improvement removal up to 22% at the end of experiment run. In order to better view the alachlor and bromacil sorption patterns, the results from two previous run are shown together in Figures 16 and 17. The removals of bromacil (Figure 16) and alachlor (Figure 17) increased as filter sand ripened. This column was backwashed with

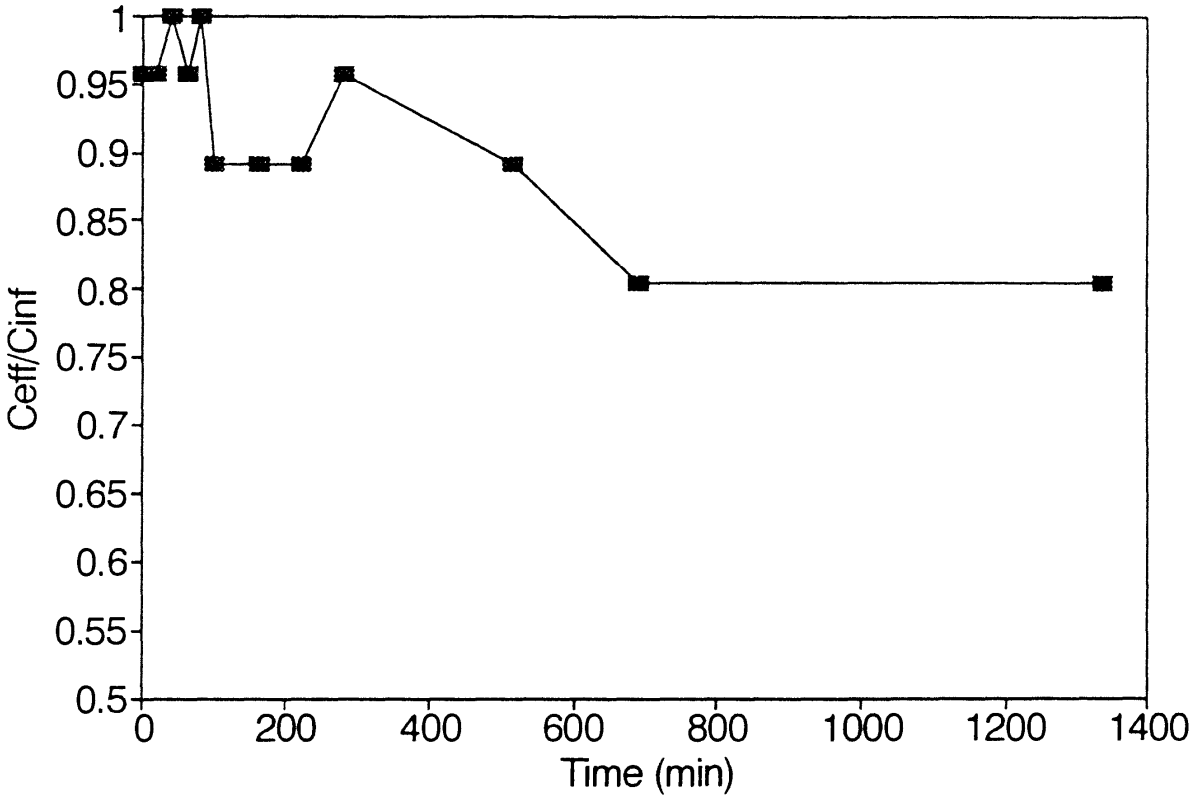

Figure 12. Performance of Fe-Coated Sand Column # 2 for Bromacil Removal, Flow rate = 5 ml/min

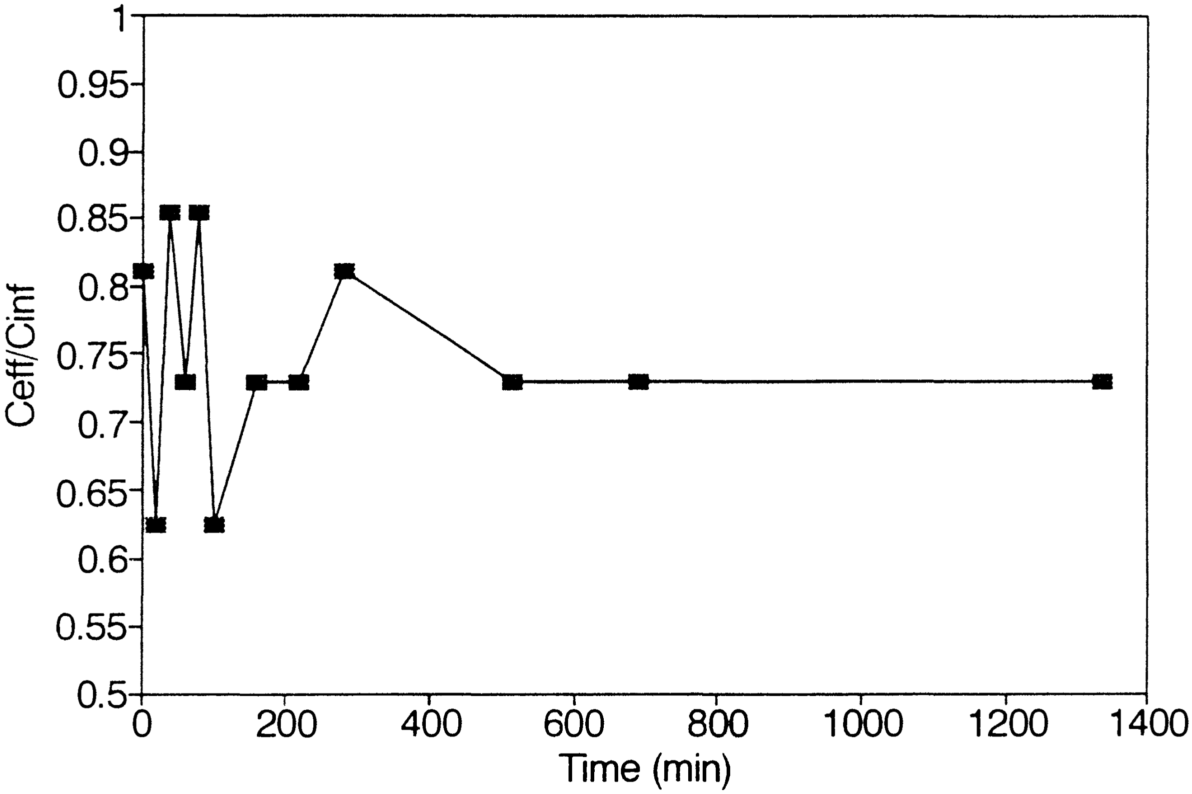

Figure 13. Performance of Fe-Coated Sand Column # 2 for Alachlor Removal, Flow Rate = 5 ml/min

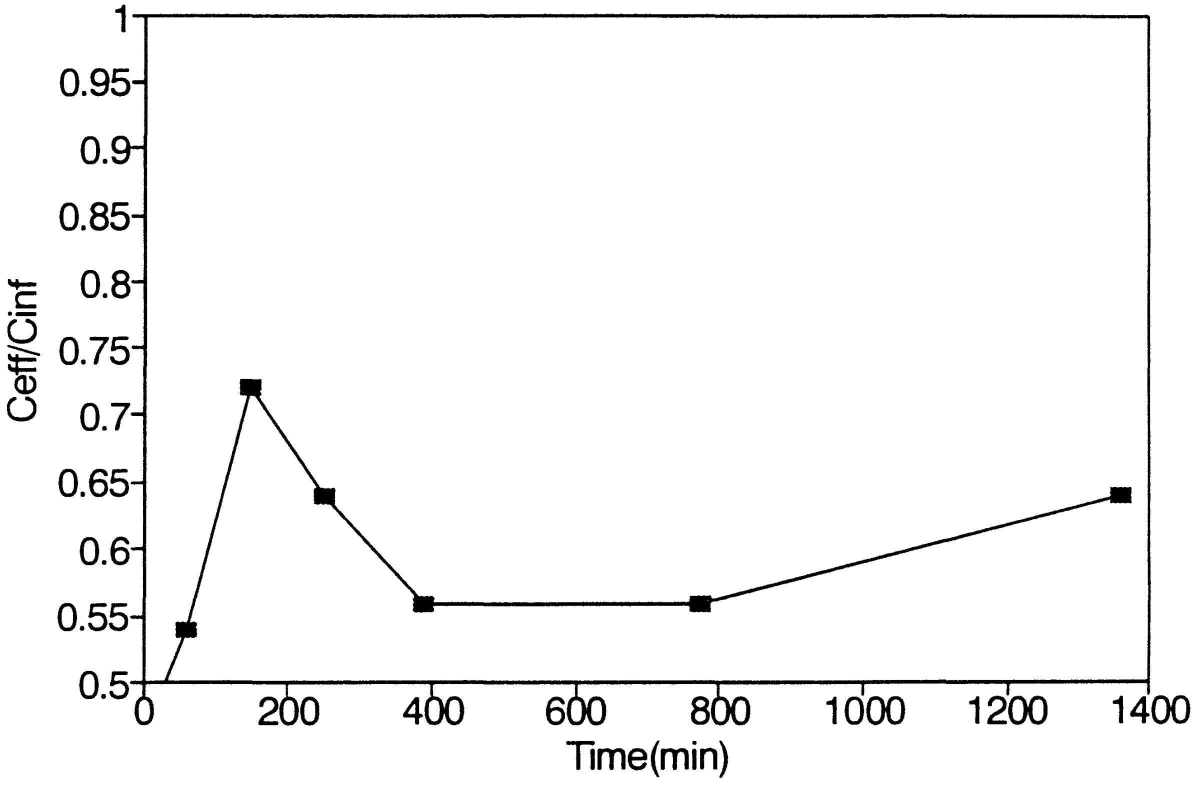

Figure 14. Performance of Fe-Coated Sand Column # 3 for Alachlor (Restarted After 4 Days Delay)

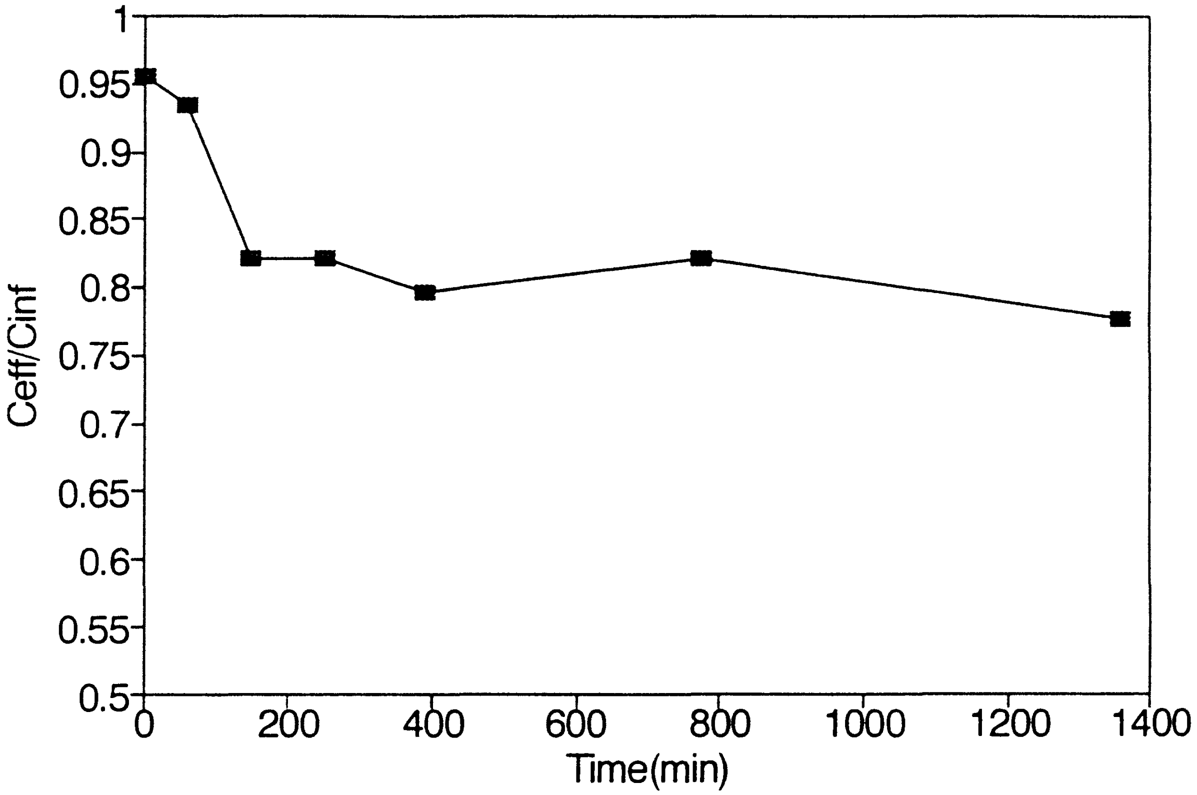

Figure 15. Performance of Fe-Coated Sand Column # 3 for Bromacil (Restarted After 4 Days Daley)

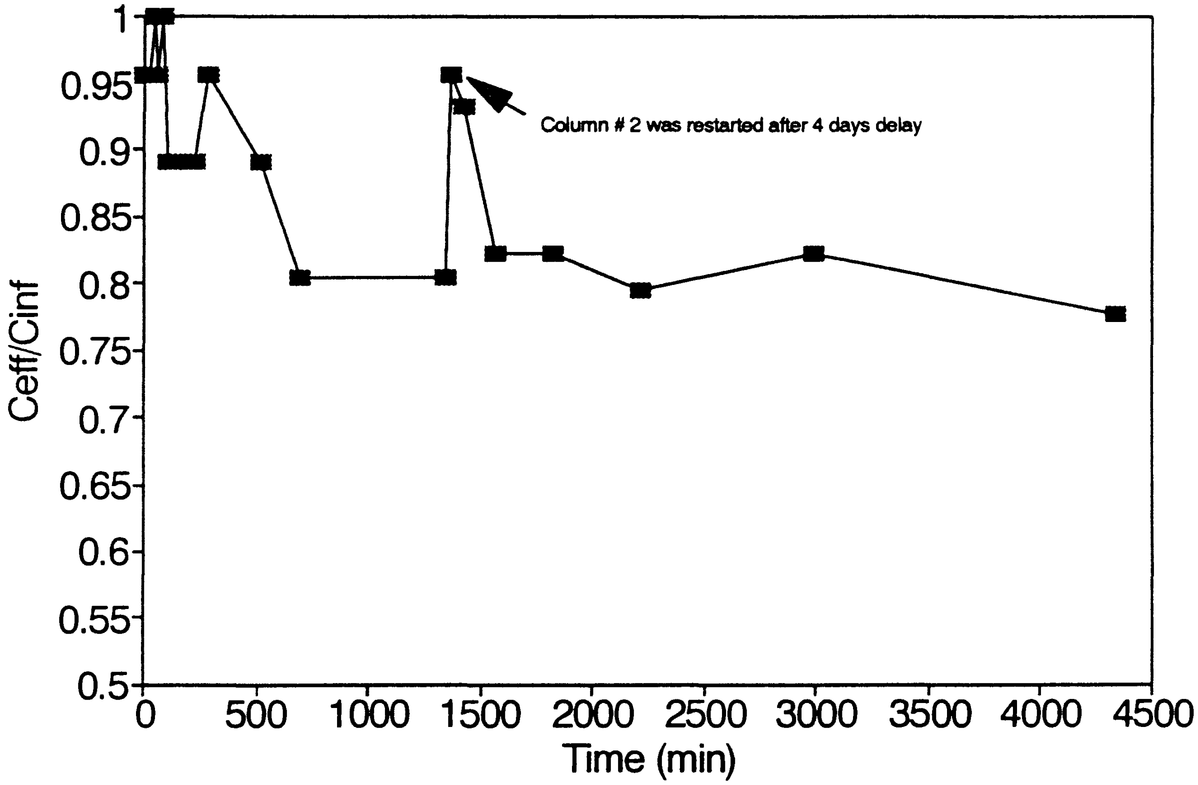

Figure 16. Performance of Fe-Coated Sand of Columns # 2 and 3 for Bromacil Removal

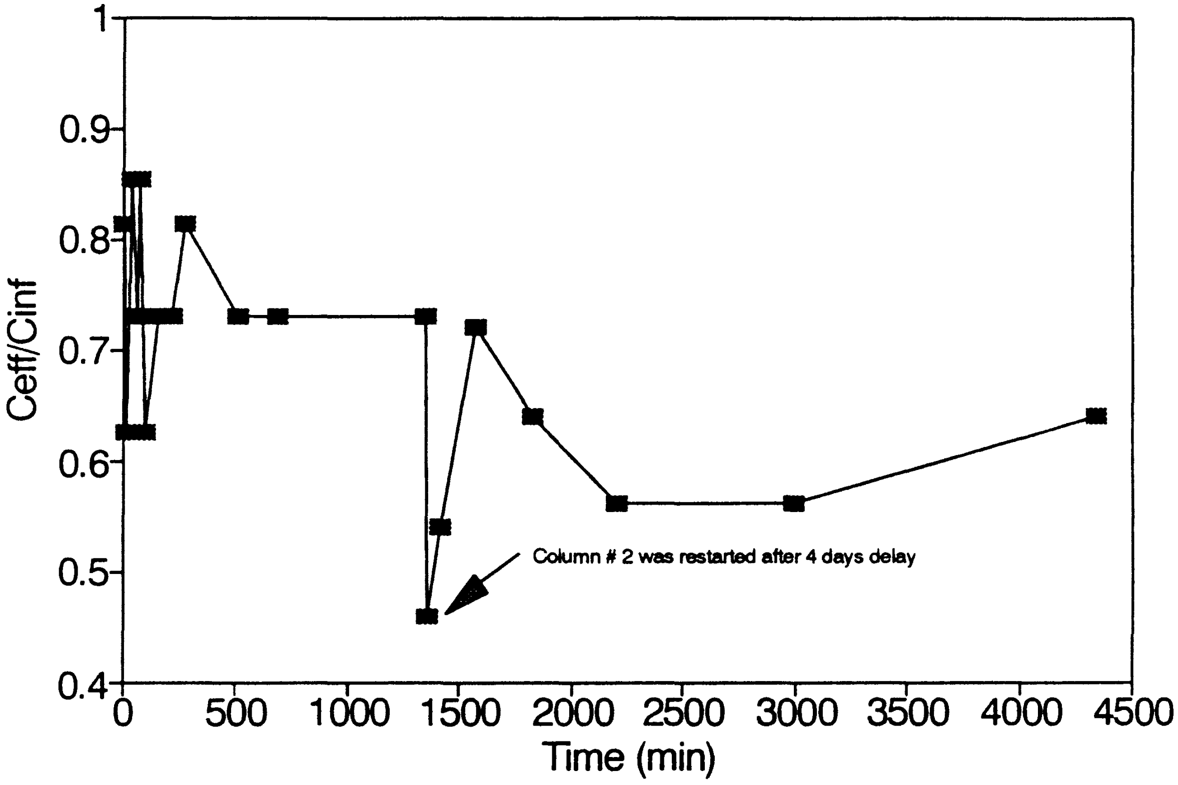

Figure 17. Performance of Fe-Coated Sand of Columns # 2 and 3 for Alachlor

(tap water) for 10 minutes, and then regenerated with acidic water (pH=3.0). Only 5.2% desorption took place for both pesticides in backwashed water (pH=7.2), while 67% and 43% desorption were obtained (through mass balance) from regenerated water (pH=3.0) for bromacil and alachlor respectively. In order to evaluate sorption efficiency, the regenerated sand was used for another column study. The same experimental conditions as used in the previous run were maintained except for time, in this case the column study was conducted for two continuous days. Figure 18 shows the performance of regenerated Fe-coated sand, which obtained 50% removal of alachlor from the water. This percent removal was highest ever obtained in this study. The removal stayed constant (27%) over the period for 500 to 1500 minutes and then slightly decreased by about 5%. After 2000 minutes the removal increased 15% and stayed constant for the rest of the experiment (33%). Figure 18 suggest a general trend of about 30% removal for alachlor. Figure 19 shows basically the same pattern as before for bromacil as far as removal is concerned. The highest removal was about 47% after 2700 minutes of experimental time. Figure 19 suggests a general trend of about 45%. As it can be seen from Figures 18 and 19 the highest removals of alachlor and bromacil were 50% and 45%, respectively. The last column study was conducted to evaluate the effect of hydrogen peroxide on removals of alachlor and bromacil from water. The column from the previous run was backwashed and regenerated as before. This column experiment evaluated

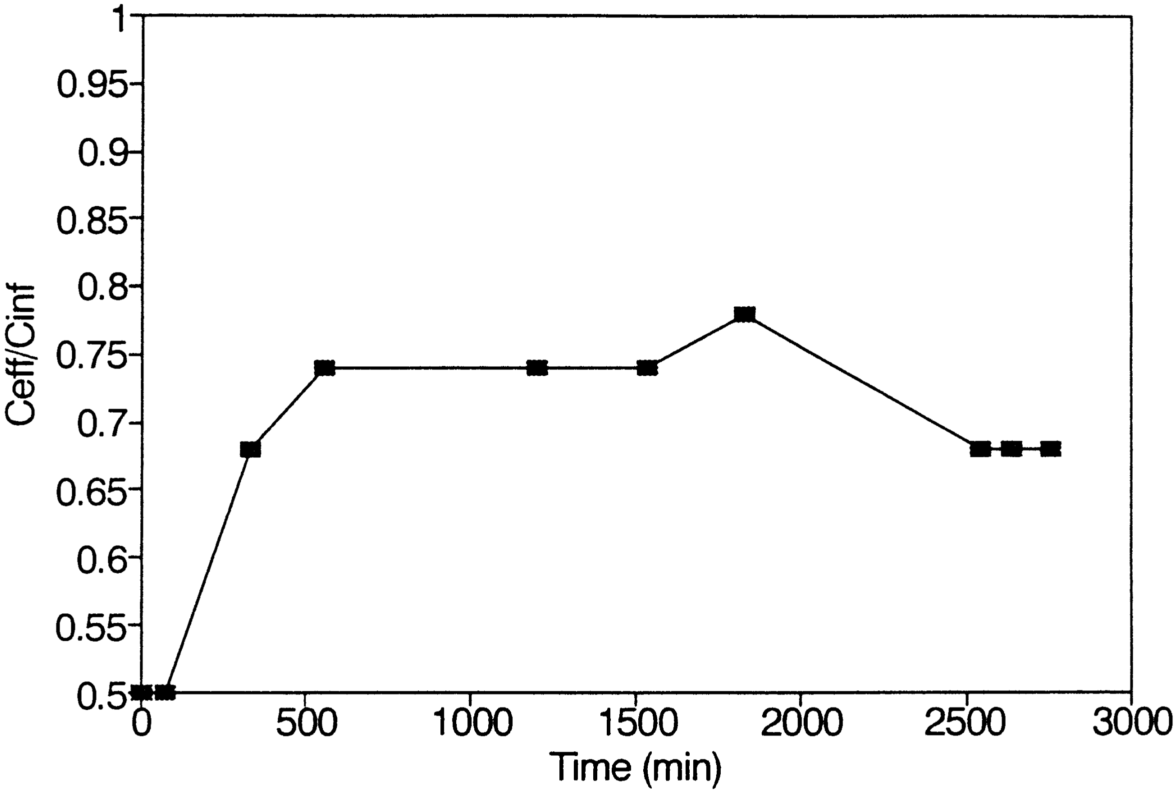

Figure 18. Performance of Fe-Coated Sand Column # 4 for Alachlor Removal

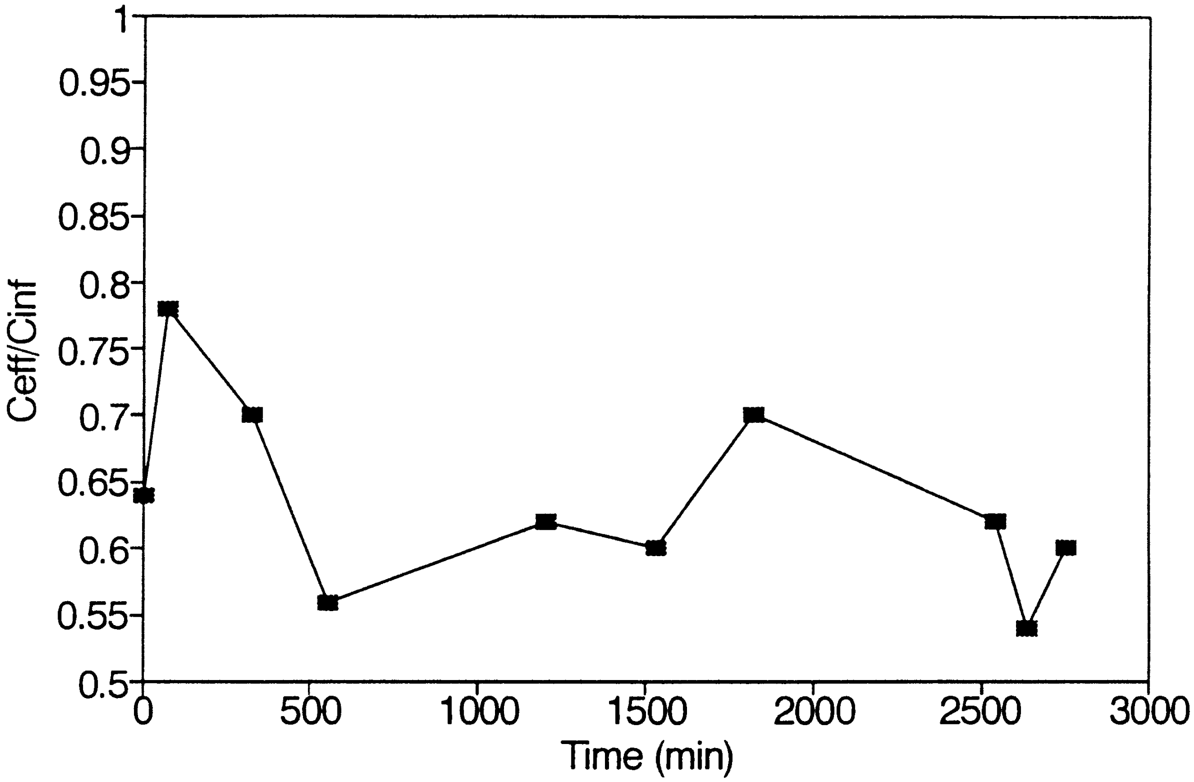

Figure 19. Performance of Fe-Coated Sand Column # 4 for Bromacil Removal

whether the removals of alachlor and bromacil were altered with addition of 5 mg/l of hydrogen peroxide to the water. As seen in Figure 20 the highest removal for alachlor was 24% when 5 mg/l of hydrogen peroxide was used. This represent about 26% reduction in removal of alachlor from previous experiment which was performed without hydrogen peroxide (Figure 18). As it can be seen in Figure 21 the highest removal for bromacil was only at 1255 minutes (48%) and it reduced to 5% removal over the next 700 minutes. After 1945 minutes of experiment, the previous pattern of removal from 0.0 to 1255 minutes was repeated and the removal of bromacil reached 46% after 2800 minutes. The points at 1145 and 1255 minutes could represent experimental error, if so the bromacil removal pattern (improved performance with time) was repeated once again. Overall the percent removal for alachlor and bromacil were higher when no hydrogen peroxide was used. Comparison between Figures 18 and 20 indicate that alachlor removal is higher and more consistent without hydrogen peroxide (30%). Comparison between Figures 19 and 21 also show that higher percent removal for bromacil was obtained without hydrogen peroxide addition (general trend of 40%).

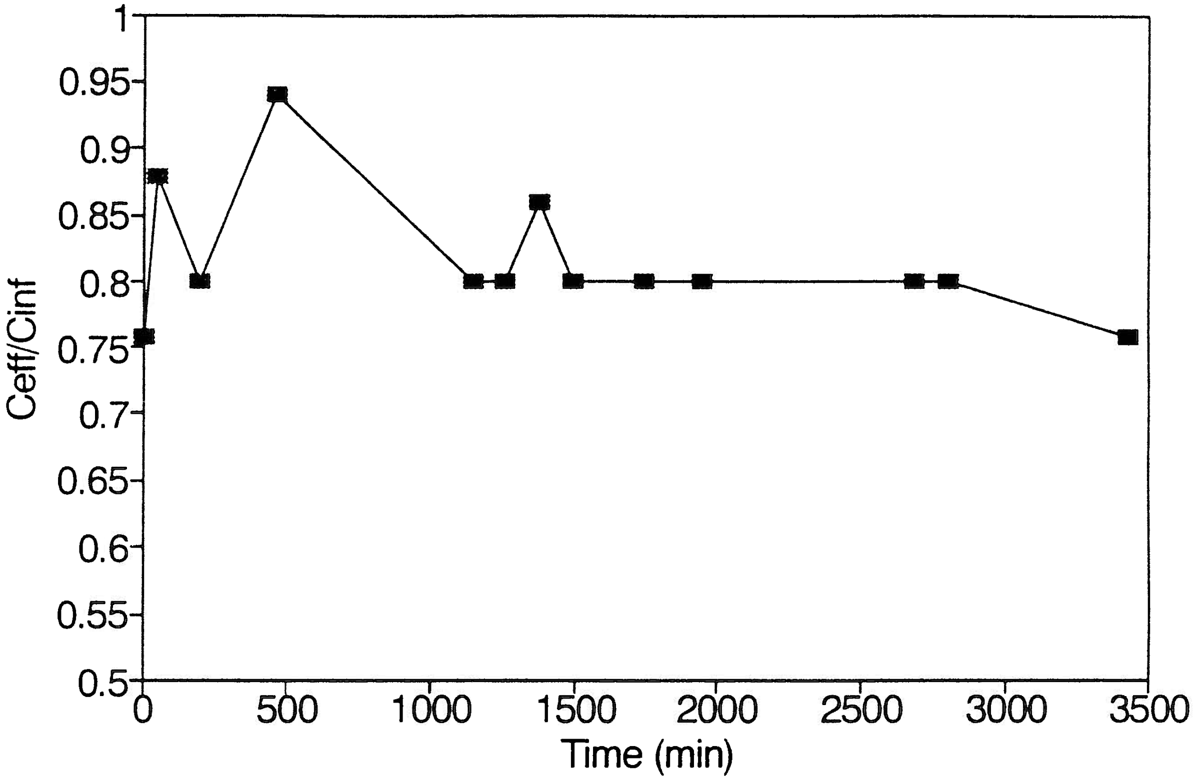

Figure 20. Performance of Fe-Coated Sand Column # 5 for Alachlor Removal with addition of 5 mg/l of Hydrogen Peroxide

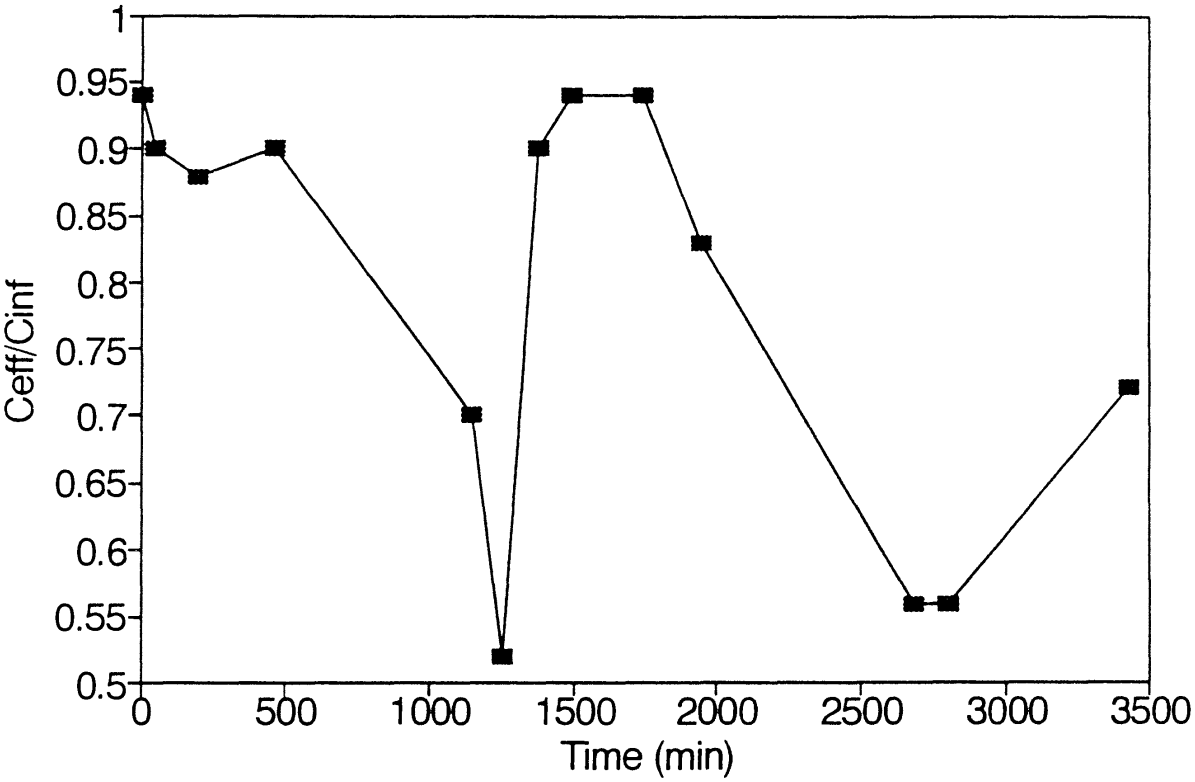

Figure 21. Performance of Fe-Coated Sand Column # 5 for Bromacil Removal with addition of 5 mg/l of Hydrogen Peroxide

CHAPTER V

CONCLUSIONS

Based upon the results of this investigation using an experimental Fe-coated sand, the following conclusions are made:

1. Fe-coated sand can be used successfully to remove alachlor and bromacil up to 45%.

2. The investigation of bromacil removal showed that sorption pattern of this compound under laboratory conditions is inconsistent. Therefore, caution should be exercised in evaluating the treatment efficiencies with respect to this pesticide.

3. The effectiveness of Fe-coated sand for alachlor and bromacil removal from water in practical applications is likely to be affected by process time and flow rate. At the highest flow rate (20 ml/min), Fe-coated media removed pesticides much less efficiently (alachlor 12% and bromacil 18%) than at lower flow rate (5 ml/min). At flow rate of 5 ml/min the removal were 33% for alachlor and 45% for bromacil.

4. Batch experiments were generally able to predict the process parameters such as pH, time, sand size, and effect of hydrogen peroxide. The sorption of pesticides to

Fe-coated sand follows the Freundlich isotherm. Sorption of alachlor and bromacil are pH-dependent (range 4 to 8.5). Performance can be increased through the use of smaller sand size because the distribution coefficient is directly proportional to surface area. The presence of hydrogen peroxide does not have a significant effect on the removal of these two pesticides by Fe-coated sand. In fact has a negative effect on alachlor and bromacil removal.

5. Removed pesticides were effectively recovered from coated media during backwashing and regeneration (up to 67%).

6. The sorption capacity of Fe-coated sand was not affected after four cycles of use in batch experiment (Table 9).

7. The parameters which are developed in this study form the basis of an equitable method for comparison between Fe-coated sand filtration and other fixed-bed treatment systems such as activated carbon treatment system for the removal of pesticides.

8. The concept and the technical feasibility of a regenerable Fe-coated sand filter appears to be an inexpensive approach to removing alachlor and bromacil, as demonstrated in both batch and column studies. Major advantages of this process include low cost of adsorbent preparation, low cost of regeneration, average sorption capacity of Fe-coated sand and simplicity of operation.

CHAPTER V

SUGGESTIONS FOR FUTURE STUDY

Based on the findings of this study, the following suggestions are presented for future studies involving application of Fe-coated sand for removal of pesticides from drinking water.

1. Conduct studies to evaluate the effect of differing water qualities and process operations on removal.

2. Studies should be undertaken to gain a better understanding of the mechanisms responsible for pesticides removal, particularly bromacil.

3. Additional investigations which evaluate the removal efficiency with respect to frequency of regeneration and backwashing procedures.

4. Perform studies which evaluate other oxide coating on the sand such manganese or aluminum oxides.

5. Conduct additional studies to determine if performance may be increased through the use of other types of sand.

6. Conduct studies to determine the effectiveness of this processes for removing one pesticide at a time.

In spite of these and other questions, the process can at least tried without a great investment of money.

LITERATURE CITED

Adams, J.Q., Clark, R.M., and Miltner, R.J. (1989). Controlling Organics: A Cost Performance Analysis. J. Am. Water Works Assoc., Vol. 81, No. 4, pp 132-140.

Dixon, D.R. (1985). Interaction of Alkaline Earth Metal Ions with Magnetite. Colloids and Surfaces, Vol. 13, p 273.

Edwards, M. and Benjamin, M.M. (1989). Regeneration and Reuse of Iron Hydroxide Adsorbents in the Treatment of Metal-Bearing Wastes. JWPCF, Vol. 61, p 481.

Edwards, M. and Benjamin, M.M. (1989). Adsorptive Filtration Coated Sand: A New Approach for Treatment of Metal-Bearing Wastes. JWPCF, Vol 61, p 1523.

Hallberg, G. (1985). Agricultural Chemicals and Ground Water in Iowa: Status Report 1985, Cooperative Extention Service, Iowa State Univer., Ames, Iowa, Circular CE-2158q.

Hebb, E. and Wheeler, W. (1978). J. Environ. Qual., Vol. 7, pp 598-601.

Herbicide Handbook, 5th edition, (1983). Weed Sci. Soc. Amer., Champaign, IL, 515 pages.

Mac Rae I.C. (1985). Removal of Pesticides in Water by Microbial Cells Adsorbed to Magnetite. Water Res., Vol. 19, No. 7, pp 825-830.

Mcbride, M.B. and Kung, K.H. (1991). Adsorption of Phenol and Substituted Phenols by Iron Oxides. Environmental Toxicology and Chemistry, Vol. 10, pp 441-448.

Miltner, R.J., Baker, B., Speth, F., and Fronk, A. (1989). Treatment of Seasonal Pesticides in Surface Waters. JAWWA, Vol. 81, No. 1, pp 43-52.

Pesticide Manual, 5th edition (1977). Biritish Crop Protection Concil, Worcestershire WR9 OHX, England.

Pfizer (1981). Color Oxide Technical Data, Pfizer Inc., Minerals Pigments and Metals Div., Clifton, NJ.

Pirbazari, M., Badriyha, N.B., and Miltner, R. (1990). Gas Adsorber Design for Removal of Chlorinated Pesticides. J. of Environmental Engineering, Vol. 117, No. 1, pp 88-100.

Remington, R.D. and Schork, M.A. (1970). Statistics with Applications the Biological and Health Sciences, Prentice. Hall Publ, Englewood Cliffs, NJ.

Ritter, W.F. (1990). Pesticide Contamination of Ground Water in The United States. J. Environ. Sci. Health, Vol. B25, No. 1, pp 1-29.

Robeck, G.G., Dostal, K.A., Cohen, J.M., and Kreissl, J.F. (1965). Effectiveness of Water Treatment Processes in Pesticide Removal. JAWWA, Vol. , pp 181-199.

Saleh, Y.F., Lee, G.F., and Wolf, H.W. (1982). Selected Organic Pesticides, Behavior and Removal from Domestic Wastewater by Chemical and Physical Process. Water Res., Vol. 16, pp 479-488.

Shirmohammahi, A., Knisel, W., and Faye, R. (1986). Effect of Irrigated Agriculture on Ground-Water Quality in the Southeast and Delta States. Proceedings of Am. Soc. of Civil Eng. Water Forum 86; World Water Issues in Evolution, Long Beach, CA.

Stewart, B., Woolhiser, D., Wischmeir, W., Caro, J. ,and Frere, M. (1975). Control of Water Pollution from Cropland. Vol. 1: A Manual for Guideline Development. Washington, DC. ARS, USDA, Report No. ARS-H-5-1.

Theis, T.L., Iyer, R., and Ellis, K.S. (1992). Evaluating a New Granular Iron Oxide for Removing Lead From Drinking Water. JAWWA, Vol. 84, No. 7, pp 101-105.

Van Rensburg, J.F.J., Hassett, A.J., Theron, S.J., and Wiechers, S.G. (1980). The Fate of Organic Micropollutant through an Integrated Wastewater Treatment / Water Reclamation System. Prog. Water Technology, Vol. 12, pp 537-552.

Valentine, R.L., Mulholiand, T., and Splinter, R.C. (1987). Radium Removal Using Sorption to Filter Sand. JAWWA, Vol. 79, No. 4, pp 170-176.

Valentine, R.L., Spangler, M.K., and Meyer, J. (1990). Removing Radium by Adding Preformed Hydrous Manganese Oxides. JAWWA, Vol. 82, No. 2, pp 66-71.

Wangen, L.E., Stalling, E.A., and Walker, R.D. (1982). Transport Contaminants from Energy Process Waste Leachates through Subsurface Soils and Soil Components. Laboratory Experiments Rep. LA-9406-MS, Los Alamos Natl. Lab., Los Alamos, N.M.

APPENDIX

TABLES

TABLE 1

EFFECT OF CONTACT TIME ON % REMOVAL OF PESTICIDES

	Alachlor		Bromacil	
Time Hr	Conc. µg/l	% Removal	Conc. µg/l	% Removal
0.25	44.0	12	40	21
1.00	40.0	20	36	27
2.00	41.0	18	44	13
10.00	39.0	22	43	16
22.00	33.5	33	43	15

TABLE 2

EFFECT OF SAND SIZE ON % REMOVAL

	Alachlor		Bromacil	
Sand Size mm	Conc. µg/l	% Removal	Conc. µg/l	% Removal
0.1	34.0	36	33.5	33
0.25	35.0	30	35.5	29
0.5	37.5	25	36.5	27

TABLE 3

EFFECT OF PH ON % REMOVAL

	Alachlor		Bromacil	
PH	Conc. µg/l	% Removal	Conc. µg/l	% Removal
8.5	44.3	11.7	41.5	17
7.0	42.7	14.6	35.0	30
6.0	49.0	4.5	42.0	16
5.5	42.5	15.0	41.5	17
4.0	39.5	21.0	48.0	4

TABLE 4

EFFECT OF AMOUNT OF SAND ON % REMOVAL

	Alachlor		Bromacil	
Amount of Sand gram	Conc. µg/l	% Removal	Conc. µg/l	% Removal
2	37.0	26	42.5	15
5	33.5	33	39.0	22
10	40.5	19	35.5	29
15	37.5	25	34.0	32

TABLE 5

EFFECT OF HYDROGEN PEROXIDE WITH FE-COATED SAND ON % REMOVAL

	Alachlor		Bromacil	
Hydrogen Peroxide mg/l	Conc. μg/l	% Removal	Conc. μg/l	% Removal
1	45.0	10	45.5	9
5	45.0	10	36.0	28
20	33.5	33	38.0	24
50	44.0	12	37.0	26
100	45.5	9	37.0	26

TABLE 6

EFFECT OF HYDROGEN PEROXIDE WITHOUT FE-COATED SAND ON % REMOVAL

	Alachlor		Bromacil	
Hydrogen Peroxide mg/l	Conc. μg/l	% Removal	Conc. μg/l	% Removal
5	41.0	18	41.0	18
20	41.0	18	37.0	26
50	45.5	9	40.5	19
100	44.0	12	36.0	28

TABLE 7

FREUNDLICH ISOTHERM DATA FOR ALACHLOR

C_{inf} µg/l	C_{eff} µg/l	Log(q)	Reg(q)	Log(C_{inf})
5	2	-0.824	-0.74392	0.699
25	10	-0.1249	-0.22926	1.398
50	21	0.1614	-0.00763	1.699
75	57	0.0458	0.122026	1.8751
100	75	0.0969	0.213988	2.000

TABLE 8

FREUNDLICH ISOTHERM DATA FOR BROMACIL

C_{inf} µg/l	C_{eff} µg/l	Log(q)	Reg(q)	Log(C_{inf})
5	4	-1.301	-1.34497	0.699
25	21	-0.699	-0.56488	1.398
50	36	-0.155	-0.22896	1.699
75	56	-0.0223	-0.03243	1.8751
100	74	0.113	0.106955	2.000

TABLE 9

BATCH DESORPTION AND REGENERATION DATA

		Alachlor			Bromacil		
Cycle No.	Washout pH	Conc. µg/l	% Rem.[a]	% Rec.[b]	Conc. µg/l	% Rem.	% Rec.
1		35	30		34	32	
	1.5			0			9
2		35	30		36	28	
	2.5			0			8
3		35	30		37	26	
	3.5			0			0
4		35	30		35	30	
	4.5			0			0

[a] removal

[b] recovered

TABLE 10

COLUMN STUDY #1
FLOW RATE = 20 ml/min
C_{INF} (FOR BROMACIL AND ALACHLOR) = 50 µg/l

	Alachlor		Bromacil	
Time min	C_{eff} µg/l	C_{eff}/C_{inf}	C_{eff} µg/l	C_{eff}/C_{inf}
30	39.5	0.790	41.0	0.820
60	39.0	0.780	40.0	0.800
180	44.0	0.880	45.3	0.906
300	44.4	0.888	45.0	0.900
450	44.3	0.886	45.2	0.904
570	44.0	0.880	41.0	0.820
1140	45.5	0.910	40.0	0.800
1350	45.0	0.900	38.0	0.760

TABLE 11

COLUMN STUDY #2
FLOW RATE = 5 ml/min
C_{INF} (FOR BROMACIL AND ALACHLOR) = 50 μg/l

	Alachlor		Bromacil	
Time min	C_{eff} μg/l	C_{eff}/C_{inf}	C_{eff} μg/l	C_{eff}/C_{inf}
0	39	0.8125	44	0.9565
20	30	0.6250	44	0.9565
40	41	0.8542	49	1.0000
60	35	0.7292	44	0.9565
80	41	0.8542	48	1.0000
100	30	0.6250	41	0.8913
160	35	0.7292	41	0.8913
220	35	0.7292	41	0.8913
280	39	0.8125	44	0.9565
515	35	0.7292	41	0.8913
690	35	0.7292	37	0.8043
1340	36	0.7292	37	0.8043

TABLE 12

COLUMN STUDY #3
CONTINUED COLUMN #2 AFTER 4 DAYS DELAY WITHOUT BACKWASHING AND REGENERATION,
FLOW RATE = 5 ml/min
C_{inf} = 50 μg/l FOR ALACHLOR
C_{inf} = 45 μg/l FOR BROMACIL

	Alachlor		Bromacil	
Time min	C_{eff} μg/l	C_{eff}/C_{inf}	C_{eff} μg/l	C_{eff}/C_{inf}
0	23	0.46	43	0.9556
60	27	0.54	42	0.9333
150	36	0.72	37	0.8222
250	32	0.64	37	0.8222
390	28	0.56	35	0.7955
775	28	0.56	37	0.8222
1360	32	0.64	35	0.7778

TABLE 13

COMBINATION OF COLUMNS #2 AND #3
FLOW RATE = 5 ml/min

	Alachlor		Bromacil	
Time min	C_{eff} $\mu g/l$	C_{eff}/C_{inf}	C_{eff} $\mu g/l$	C_{eff}/C_{inf}
0	39	0.8125	44	0.9565
20	30	0.6250	44	0.9565
40	41	0.8542	49	1.0000
60	35	0.7292	44	0.9565
80	41	0.8542	48	1.0000
100	30	0.6250	41	0.8913
160	35	0.7292	41	0.8913
220	35	0.7292	41	0.8913
280	39	0.8125	44	0.9565
515	35	0.7292	41	0.8913
690	35	0.7292	37	0.8043
1340	36	0.7292	37	0.8043
1360*	23	0.4600	48	0.9556
1420	27	0.5400	47	0.9333
1570	36	0.7200	41	0.8222
1820	32	0.6400	37	0.8222
2210	28	0.5600	35	0.7955
2985	28	0.5600	37	0.8222
4345	32	0.6400	35	0.7778

*column was restarted after four days.

TABLE 14

COLUMN STUDY #4
SPENT SAND FROM PREVIOUS RUN IS USED AFTER BACKWASHING AND REGENERATION,
FLOW RATE = 5 ml/min
C_{INF} (FOR BROMACIL AND ALACHLOR) = 50 μg/l

	Alachlor		Bromacil	
Time min	C_{eff} μg/l	C_{eff}/C_{inf}	C_{eff} μg/l	C_{eff}/C_{inf}
0	25	0.50	32	0.64
75	25	0.50	39	0.78
330	34	0.68	35	0.70
555	37	0.74	28	0.56
1200	37	0.74	31	0.62
1530	37	0.74	30	0.60
1825	39	0.78	35	0.70
2540	34	0.68	31	0.62
2635	34	0.68	27	0.54
2755	34	0.68	30	0.60

TABLE 15

COLUMN STUDY #5
SPENT SAND FROM PREVIOUS RUN IS USED AFTER BACKWASHING AND REGENERATION, HYDROGEN PEROXIDE = 5 mg/l
C_{INF} (FOR BROMACIL AND ALACHLOR) = 50 μg/l

	Alachlor		Bromacil	
Time min	C_{eff} μg/l	C_{eff}/C_{inf}	C_{eff} μg/l	C_{eff}/C_{inf}
0	38	0.76	47.0	0.94
50	44	0.88	45.0	0.90
195	40	0.80	44.0	0.88
460	47	0.94	45.0	0.90
1145	40	0.80	35.0	0.70
1255	40	0.80	26.0	0.52
1370	43	0.86	45.0	0.90
1490	40	0.80	47.0	0.94
1740	40	0.80	47.0	0.94
1945	40	0.80	41.5	0.83
2680	40	0.80	28.0	0.56
2800	40	0.80	28.0	0.56
3430	38	0.76	36.0	0.72

VITA

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