

## REMOVAL OF SPECIFIC CHLORINATED PESTICIDES FROM WATER BY CO - PRECIPITATION.

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### ABSTRACT

In the present work 5 widely used chlorinated pesticides were tested to assess the potential use of coagulation as a mean for reducing the load on advanced physicochemical processes such as activated carbon, ion exchange and membrane processes. The results indicated that the removal is through sweep floc adsorption mechanism.

The percentage removal increased with increase in coagulant dose and decrease in pH. The presence of Ca (II) and Mg (II) had a minor effect on the removal efficiency, while the increase in flocculation contact time slightly improved the removal efficiency.

### INTRODUCTION

The use of coagulants in water treatment practice is generally optimized for solids removal. In addition to removing turbidity, however, coagulation also reduces color, bacterial, viral and organic concentrations. These species are removed as they are colloidal in nature. However, soluble organics may also be removed by mechanisms such as specific adsorption to floc particles and co-precipitation.

It is clear that coagulation has the ability to reduce the concentration of organics in solution and as such it has an important role to play in pretreatment. If coagulation could be optimized for organics removal, considerable improvements could be expected in the life and performance of advanced treatment processes such as activated carbon, ion exchange and membrane processes.

There have been many attempts to achieve coagulation with Al (III) and Fe (III) salts for the removal of specific and dissolved organic compounds from water. For example, Sridharan and Lee (1972), studied the removal of phenol, citric acid and glycine by co-precipitation with iron from waters of differing quality. Concentrations of iron in the range of 0.005 to 0.025 molar ferric chloride removed approximately 60 to 90% of the phenol, 20 to 25% of the glycine, and 20 to 70% of citric acid spiked samples. Lower iron concentrations in the range of conventional coagulation practice

were not studied. The percentage organic removal was apparently not as sensitive to iron dosage as it was to solution pH, type of compound considered, and the quality of water studied. Carollo (1945) was able to remove 80 to 98% of 0.1 - 10 mg/l of DDT. Suspensions of DDT from water supplies were treated with various combination of carbon and chemical coagulation with aluminum and iron hydrous oxides. Complete removal of DDT was suggested when activated carbon was provided for a 15 min. contact period after coagulation and sedimentation but before sand filtration.

In another study, Whitehouse (1967), found that alum and ferric sulfate with and without anionic and cationic polyelectrolytes were ineffective in removing Malathion from water. Cohen (1966), investigated the removal of rotenone, toxaphene and various toxic substances from water. Concentrations of alum as high as 100 mg/l produced slight reduction in the quantities of these organics. Robeck et al. (1965) obtained a 55% removal of dieldrin and 35% removal of endrin via alum coagulation.

In all these studies on soluble organics removal, the systems studied were extremely complex and few conclusions may be drawn from these results other than the observation that iron has the potential for reducing the soluble organic concentration in a water.

In this study 5 of the most widely used chlorinated pesticides were selected for investigation in a very well defined and simple system in order to identify the influence of coagulant dosage, operating condition, and divalent ion concentrations on pesticides removal during coagulation. The ultimate objective of the present work is to assess the potential use of coagulation as a mean to minimize the load and extend the life and performance of costly advanced physicochemical processes such as activated carbon, ion exchange and membrane processes.

## MATERIAL AND METHODS

Five chlorinated pesticides were chosen for investigation: Hexachlorobenzene, Lindane, Heptachlor, Endrin, and Methoxychlor. These model compounds were selected based on their long term environmental persistence, widespread use, and public health implications. Pesticides were obtained in their neat form from Supelco and were employed without further purification.

A standard jar test procedure was employed in this study. Six clean one liter glass beakers were filled with approximately 800 ml of distilled organic free water. Known volumes of various stock solutions were added to each beaker to obtain the desired initial conditions and the volume of solution in each beaker was then adjusted to exactly one liter. When the solutions were made-up in this way, a predetermined amount of NaOH

was added to each beaker to neutralize the acidity of the coagulant to be added and to attain the desired final pH. All samples were spiked with pesticides at around 20 µg/l from a series of stock solutions. Analytical grade reagents were used to prepare stock solutions of 20,000 mg/l CaCl<sub>2</sub>, Mg Cl<sub>2</sub>, and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

Experiments were started by adding coagulant to the solutions while they were stirred at 100 r p m. The solutions were stirred rapidly for one minute and then flocculated at 40 r p m for variable intervals. Following sedimentation for 20 minutes samples of the supernatant were vacuum filtered using prewashed filter papers. The filtered samples were then extracted and analyzed for residual pesticides.

The analytical method used for the determination of the chlorinated pesticides is the standard USEPA method 608 (Longbottom and Lichenberg, 1982). All analysis were performed on a Varian 6000 GC equipped with a linearized electron capture detector and a 60 meter, 0.75 mm ID open tubular Supelco SPBS colum. Ultrapure nitrogen was used as a carrier at a flow rate of 35 ml/min. The column temperature was kept isothermal at 230°C, the injection temperature was set at 250°C and the detector heating block was maintained at 240°C. A Varian 4270 integrator was used for calculating peak areas and calibrating standards. A typical chromatogram for tested compounds is given in Figure (1).

## RESULTS AND DISCUSSION

The first experiment examined the influence of coagulant dosage on the percentage removals that could be obtained from solutions containing the following concentrations of pesticides: 23.8 µg/l of Hexachlorobenzene, 23.9 µg/l Lindane, 23.5 µg/l Heptachlor, 21.5 µg/l Endrin, and 40.2 µg/l Methoxychlor. The data obtained are plotted in Figure (2).

Between 2 and 5 percent removal have been observed in the control beakers and this probably resulted from adsorption to the glass walls of the beakers and stirrer. The observation that percentage removals increased with coagulant dosage was expected. The high degree of oversaturation resulted in the rapid precipitation of a large quantity of ferric hydroxide, enmeshing the pesticides in what has been termed sweep floc. Many investigators have reported similar observations (Rook, 1976). At pH 7.2 and 20 minutes flocculation, the percent removal of Hexachlorobenzene and Lindane were very similar. This might be due to their resembling molecular structures. The percentage removals for Lindane and Hexachlorobenzene were less than 10 percent at a 150 mg/l dose of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. The highest percent removal (31 percent) was achieved for Methoxychlor. Variations in solubility and affinity for surfaces were probably the reasons for these differences.

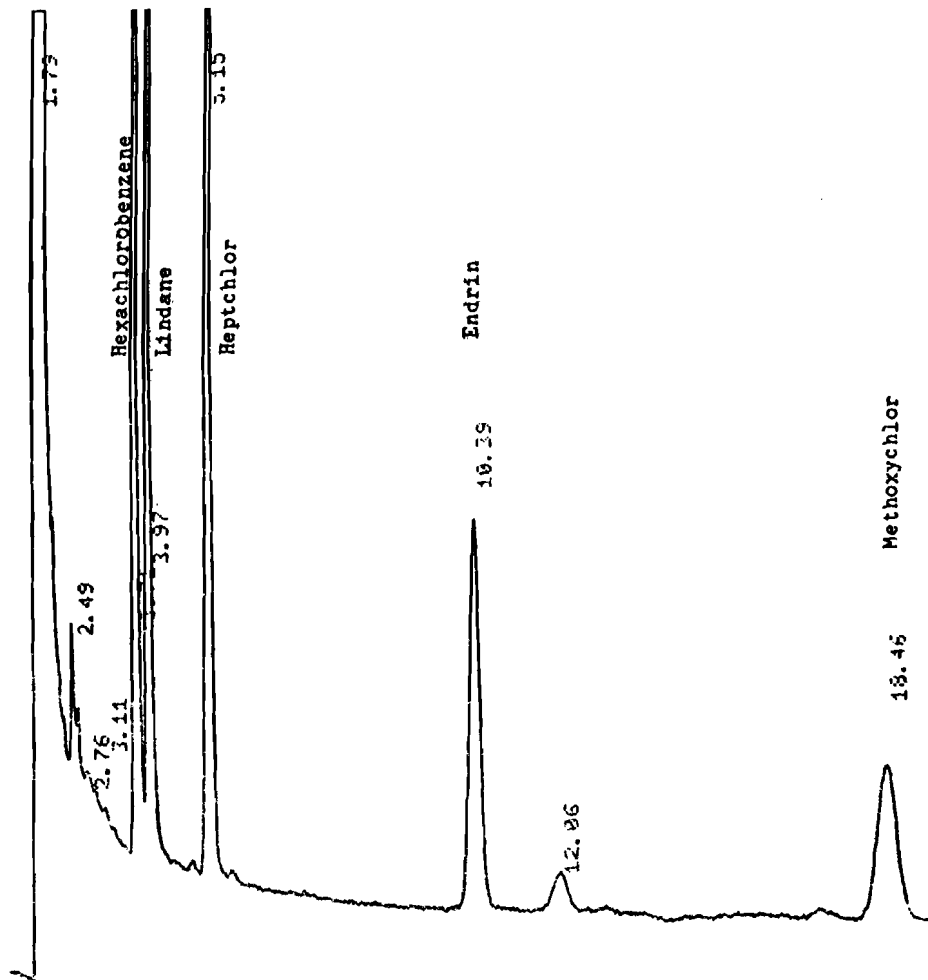


Fig. 1.  
Typical chromatogram of the tested compounds.

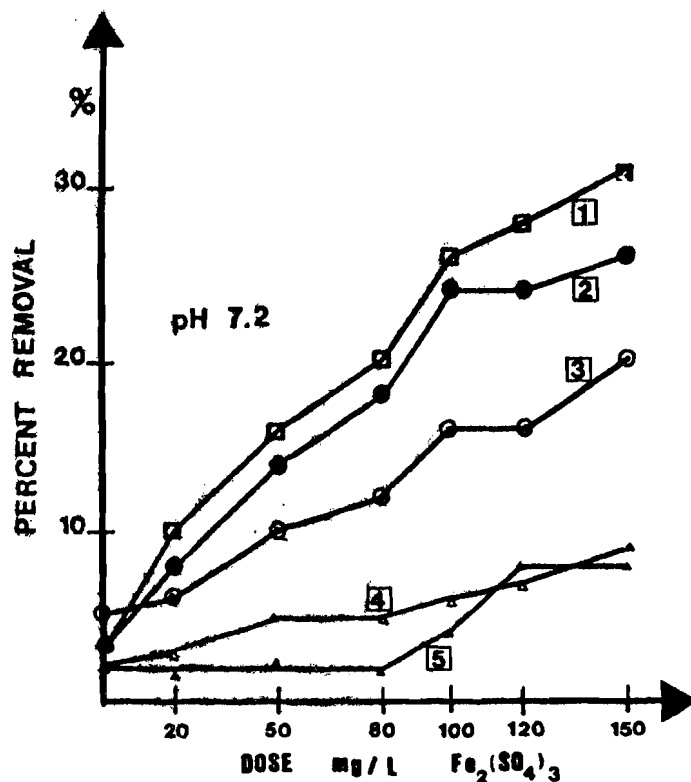


Fig. 2.  
Effect of coagulant dosage on percent removals of pesticides.  
1. Methoxychlor. 2. Endrin. 3. Heptachlor. 4. Lindane.  
5. Hexachlorobenzene.

The influence of pH on percentage removal was studied next. In Figure (3), the effect of final pH is presented for all compounds of concern. In this experiment, it is apparent that higher removals were obtained as the pH was lowered. All 5 pesticides showed a similar trend at a dose of 100 mg/l of  $Fe_2(SO_4)_3$ . The effect of pH on removals is interesting. The observed increase in pesticides removal with decreasing pH may be explained by improved adsorption or incorporation in the coagulant floc at lower pH. This may be facilitated by the favorable change in surface character of the floc. The larger polymeric species of iron present at low pH may have encouraged stronger Van der Waals interactions between the floc and pesticides. Similar results have been obtained by Semmens and Ocanas (1977). The pH of the water during coagulation has a profound

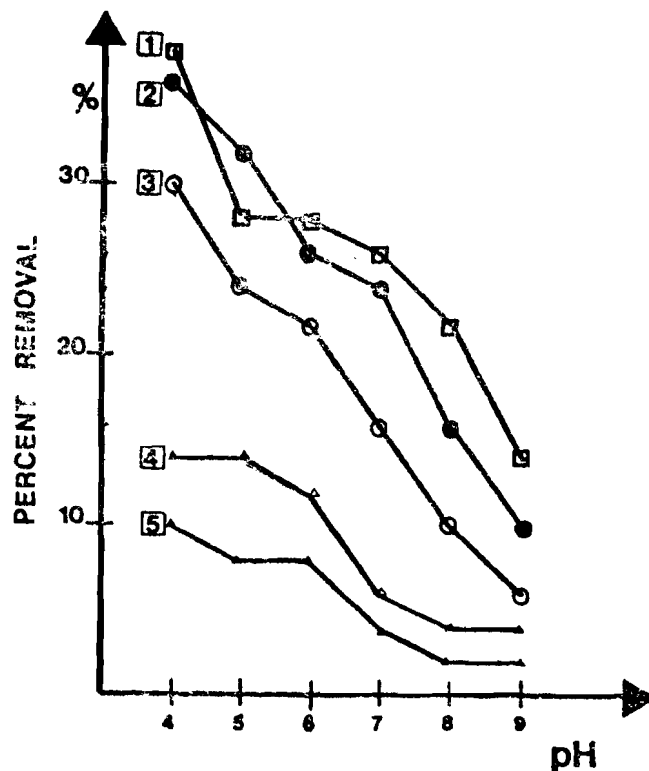


Fig. 3.  
Effect of pH on percent removals of pesticides.  
1. Methoxychlor. 2. Endrin. 3. Heptachlor. 4. Lindane.  
5. Hexachlorobenzene.

influence on the effectiveness of coagulation for pesticide removal. The chlorinated pesticides investigated in the present work are much better removed in slightly acidic conditions. The optimum pH range for  $\text{Fe}_2(\text{SO}_4)_3$  was from pH 4 to pH 5.

Extended flocculation time resulted in a slightly better removal. The influence of contact time on percentage removal of pesticides is illustrated in Figure (4). From the obtained results it seems that some benefit may be obtained by extending the flocculation time. However, the benefit is very limited and has to be determined in each individual case.

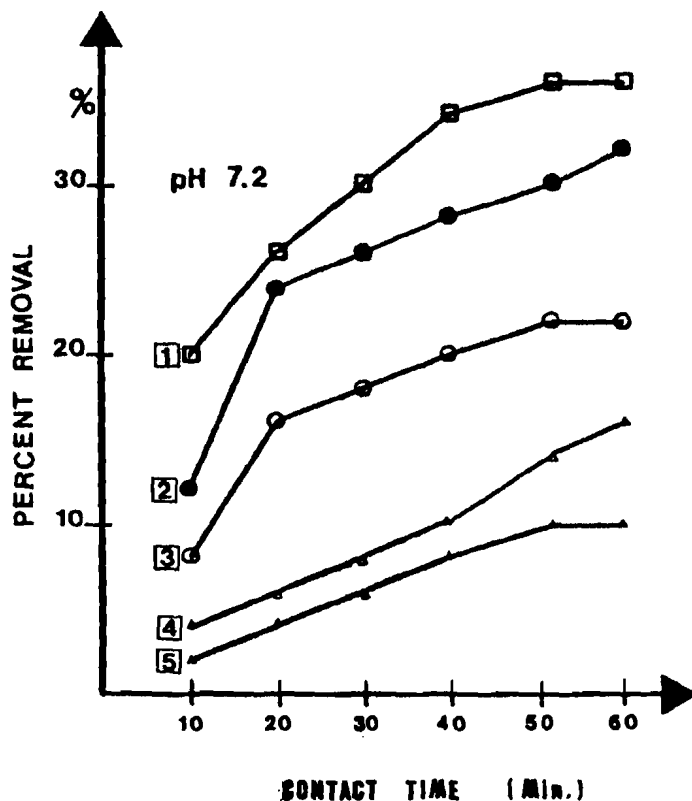


Fig. 4.  
Effect of contact time on percentage removals of pesticides.  
1. Methoxychlor. 2. Endrin. 3. Heptachlor. 4. Lindane.  
5. Hexachlorobenzene.

Finally, the influence of water hardness added to the tested solutions at 200 mg/L Ca (II) and Mg (II) on the removals at pH 7.2 and 20 minutes contact time was evaluated next. The effect of added Ca (II) and Mg (II) is shown in figure 5. The addition of the divalent metals slightly improved the removal percentage of pesticides. In the neutral pH range, relatively better removals were achieved in the presence of Ca (II) and Mg (II). The observed improvement in percentage removal can be attributed to the reduction of the electrical double layer surrounding the charge sites on the iron floc and in this way the calcium and magnesium salts may improve purely adsorptive interactions. From the observed patterns, it appears that the mechanism of chlorinated pesticides removal is purely adsorptive in nature. These findings are confirming Semmens and Ocanas (1977) observations, and contradicting Whitehouse (1967) findings.

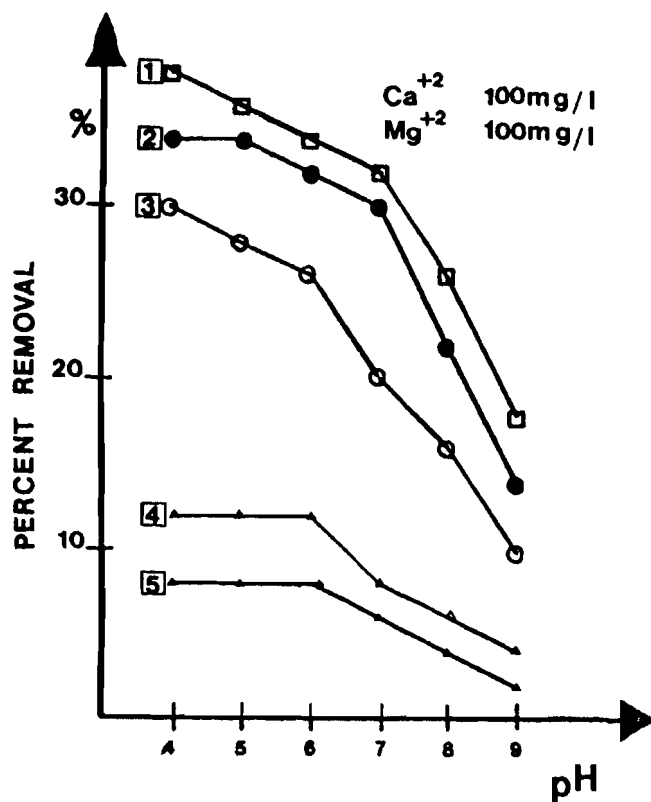


Fig. 5.  
 Effect of Ca (II) and Mg (II) on percentage removals  
 of pesticides.  
 1. Methoxychlor. 2. Endrin. 3. Heptachlor. 4. Lindane.  
 5. Hexachlorobenzene.

Under optimum circumstances for colloids removal from drinking water, the percentage removal of pesticides by co-precipitation will probably range from 4 percent for Hexachlorobenzene to 24 percent for Methoxychlor. It should be noted however that, the studies reported in this paper were all performed with distilled water. The percentage removals obtained do not therefore necessarily reflect the percentage removals that may be obtained under the same conditions with natural water containing a variety of inorganic and organic colloidal matter in suspension. Percentage removals may well be higher in natural waters since the colloidal material presents a large surface area for the sorption of both ferric hydroxide and low molecular weight organics. Studies are therefore needed to identify the influence of clays and humic acids on the removal of low molecular weight organic compounds.



## CONCLUSION

The study of  $\text{Fe}_2(\text{SO}_4)_3$  as a coagulant for removing selected chlorinated pesticides by co-precipitation revealed the following conclusions :

The extent of the pesticides removal increased to a considerable extent as the coagulant dosage was increased indicating a sweep floc adsorption mechanism.

The maximum percentage removals recorded in the systems studied following optimization ranged from 10 % for hexachlorobenzene to 38 % for Methoxychlor.

Removals decreased with increase in pH for all compounds. The general trend observed indicates that removal is achieved by purely adsorption forces rather than electrostatic interactions.

The presence of Ca (II) and Mg (II) had a minor effect on the removal efficiency. A very limited improvement in percentage removal of pesticides by  $\text{Fe}_2(\text{SO}_4)_3$  was observed when flocculation time was extended to 60 minutes.

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