PHYSICAL TREATMENT OPTIONS
(Removal of Chemicals from Wastewater by Adsorption, Filtration and/or Coagulation)

John C. Nye
Professor and Head
Agricultural Engineering Department
Louisiana State University Agricultural Center
and
Louisiana State University and A&M College
Baton Rouge, LA 70803

ABSTRACT

A two stage treatment system has been developed to remove pesticides from contaminated wastewater. The first step is primary flocculation and sedimentation. The pesticides in the supernatant can then be adsorbed to activated carbon. The system has been installed by several commercial pesticide applicators. The major problems that users have observed are related to: proper flocculation of the wastewater; selection of a small enough pump to pump the supernatant through the carbon columns; sealing the carbon columns to avoid leaks when under pressure; and disposal of the accumulated sludge and spent activated carbon. All of these problems are correctable with proper supervision. It would be extremely helpful if a commercial company would design and develop the physical equipment and sell the systems to pesticide applicators.

INTRODUCTION

During the past six years a two stage physical treatment system has been developed to remove pesticides from contaminated wastewater. The complete system is the result of four studies. The project was initiated under a USEPA Grant No. R 805 466010. This study (Whittaker, et al. 1982) was conducted to determine the extent of the problem of pesticide contaminated wastewater and evaluate alternative treatment means that might be acceptable to pesticide applicators. As an outgrowth of this project, K. F. Whittaker(1980) evaluated the effectiveness of activated carbon for removal of dissolved pesticides from water. T. J. Ruggieri(1981) then investigated the use of the two stage treatment system to remove 5 RPAR or near RPAR herbicides from a mixed solution of herbicides in water. This study was supported by the North Central Regional Pesticide Impact Assessment Program. The final study performed by K. L. Farrell(1984) investigated the feasibility of encapsulating the two wastes, sludge and spent activated carbon, in a portland cement matrix. This study was also supported by the Pesticide Impact Assessment Program. This paper summarizes the results of these four studies and projects the cost for installing and operating the treatment system.

PURPOSE

In the late 1970's several aerial pesticide applicators in Indiana were in disputes with local airport authorities regarding the handling of pesticide contaminated wastewater. As a result the Indiana Aeronautics Commission requested assistance from Purdue University to develop a system that would prevent ground water pollution or soil contamination around the areas that aerial applicators were using for loading and washing application equipment. A study was initiated to develop a method for collecting and treating the contaminated wastewater. The system was to be simple to operate and capable of producing an effluent that was free of detectable levels of pesticides. The system had to be flexible enough to handle the wide variety of agricultural chemicals currently in use and be equally applicable to ground applicators as well as aerial applicators. The final constraint was that the system must be economically acceptable.

APPROACH

The first step in the development was to characterize the wastewater that had to be treated. Samples were collected from several pesticide applicators during the course of the various research projects and the results were so dependent on the chemicals being applied and the techniques that were used to clean the application equipment that it is difficult to present any meaningful results except that any system that is developed to treat the pesticide contaminated wastewater must be capable of handling a wide variety of concentrations.

The variability in concentration and quantities of wastewater to be treated required that a system be developed that would not be sensitive to these factors. Since evaporation ponds and soil-gravel degradation pits were under investigation at other sites, a physical separation system was investigated. Particle size filtering systems were tested and were found to be either ineffective or of inadequate capacity to be useful in treating the wastewater.

Flocculation was then tested and found to be very effective. Alum, hydroxide coagulation and ferric chloride were evaluated as flocculents. Many other flocculent aids are available and should be considered by any applicator that installs this system. Alum was found to be effective on the wastewater samples that we studied. An anionic polymer (Watcon 1245) was added to enhance settling. Alum concentrations of from 200 to 500 mg/L and polymer concentration of .4mL/L were used throughout the study. Jar tests were performed prior to treatment to select the alum concentration for use.

After the wastewater was flocculated and allowed to settle, the supernatant was pumped through activated carbon columns. Filtrasorb 300 (Calgon Corporation) was used for carbon column with a surface loading rate of 1.5 gallons per minute per square foot of surface area and a 15 minute residence time. The initial carbon columns were made out of water softener columns. The resin was removed from these columns and they were filled with activated carbon.

The system was used in the agricultural engineering department's agricultural waste management lab on the Purdue University campus for one year. Samples were hauled to the lab in a 250 gallon tank mounted in the back of a pickup truck. The wastewater was pumped from the tank into four 100 gallon flocculation tanks. A variable speed mixer was used to mix the flocculent and polymer with the wastewater. The treated wastewater was analyzed for pesticide concentration. In addition to the field samples that were treated, synthetic wastewater solutions were prepared containing malathion, carbaryl and metribuzin.

The system was then mounted in an 8 x 10 trailer and pulled to an applicator's loading pad at Monon, Indiana for field test. The mobile system consisted of two 100 gallon flocculation tanks and two carbon columns. The system would treat 1 gallon per minute. A smaller system was constructed using four 4-inch diameter by 4-foot long carbon columns constructed of PVC pipe. The smaller unit would handle 0.2 gallons per minute.

Following the initial feasibility study, Whittaker(1980) investigated the adsorption of 30 classes of pesticides on activated carbon in isotherm and column studies.

Ruggieri(1981) then investigated the feasibility of using the entire system, flocculation and activated carbon columns, for removal of a mixture of alachlor, dinoseb, trifluralin, paraquat and 2,4-D from wastewater.

During the conduct of the various projects about 5000 gallons of wastewater were treated. As a result about 50 gallons of sludge had accumulated. This sludge was used in a study by Farrell(1984) on the feasibility of encapsulating the sludge with portland cement.

The four studies combine to form a feasibility analysis of a complete system for handling the pesticide contaminated wastewater that is produced by agricultural

TABLE 1. SUMMARY OF ADSORPTION ISOTHERM STUDIES(WHITTAKER, 1980)

Compound Name	Trade Name	Predominant Chemical Class	Molecular Weight	Water Solubility (mg/L @ 20 C)	Carbon Capacity[1] (mg/gm)
Propham	ChemHoe	Amide	179	250	289
Propanil	Stam	Amide	218	0.05%	191
Linuron	Lorox	Urea	249	75	222
Propachlor	Ramrod	Amide	212	580	251
Fluometuron	Cotoran Lanex	Urea	232	90	208
Cycloate	Ro-neet	Amide	215	85	170
Metolachlor	Dual	Amide	284	530	172
Metribuzin	Sencor	Heterocyclic Amine	214	1220	192
Prometone	Pramitol	Heterocyclic Amine	225	750	165
Ametryne	Evik 80W	Heterocyclic Amine	227	185	151
Cynazine	Bladex	Heterocyclic Amine	241	171	156
Diazinon	Basudin	Organophosphate	304	46	214
Fensulfothion	Dasanit	Organophosphate	308	1600	218
Methylparathion	(many)	Organophosphate	183	83	218
Carbaryl	Sevin	Carbamate	187	99	156
Carbofuran	Furadan	Carbamate	229	700	245
Dinoseb	Premerge	Phenolic	240	52	124
2,4-D	(many)	Carboxylic Acid	221	900	73
Naptalam	Alanap	Amide	291	230000	99
Diphenamid	Enide	Amide	239	260	131
Monocrotophos	Azodrin	Organophosphate	223	miscible	153
Phorate	Thimate	Organophosphate	260	85	159
Oxycarboxin	Plantvax	Amide	260	1000	155
Methomyl	Lannate	Carbamate	147	58000	167
CDAA	Pandox	Amide	174	2 %	184
Bentazon	Basagran	Heterocylic Amide	240	500	45
Malathion	Cythion	Organophosphate	330	145	118
Diquat	Ortho-Diquat	Quaternary Nitrogen		very soluble	-
Methamidophos	Monitor	Organophosphate		miscible	-
Dalapon	DowPon	Carboxylic Acid		very soluble	-

[1] Monolayer carbon capacity according the Langmuir theory.

chemical applicators. The complete system would require a collection system for collecting and storing the contaminated wastewater, the treatment system consisting of at least one flocculation tank and three activated carbon columns, and a small cement mixer for mixing the portland cement, activated the carbon and sludge to form the encapsulated final product.

PROBLEMS ENCOUNTERED

Flocculation of the wastewater is essential to the success of this treatment system. Numerous problems have arisen when the system was used in other parts of the country where alum would not form a floc. Since numerous flocculent aids are available and this technology is used in many municipal and industrial water and wastewater treatment plants one should be able to find an effective substitute for alum. It is recommended that the nearest water or wastewater treatment plant be contacted to obtain effective flocculent aids for your locale.

The carbon columns must be used periodically to prevent bacterial contamination. As a general rule, thumb water should be pumped through the columns at least once a week. If the system is going to be idle for more than a week the columns should be drained. Bacteria will form a slim layer over the carbon, preventing the pesticide molecules from being adsorbed on to the carbon. If the effluent from the carbon columns has an odor it will be necessary to replace the carbon in the columns.

RESULTS

The initial study produced two consistent results. First the wastewater could not be easily characterized because it was highly variable in both concentration of pesticide and quantity of wastewater. As a result a very broad based treatment system had to be employed. Flocculation was chosen for initial treatment and found to be very effective in reducing the concentration of the pesticide to its water solubility.

After treating numerous field produced samples, it was found that the system could reduce the concentration of pesticides to below the detection limits of the Indiana State Chemist Office's pesticide residue lab. Since it was difficult to obtain an accurate estimate of the pesticide concentrations and volume of wastewater, it was impossible to determine the capacity of the carbon columns used for the initial treatment system. The next two studies were conducted to determine the capacity of the activated carbon to remove a variety of pesticides.

Table 1 presents the isotherm data collected by Whittaker(1980) to determine the capacity of carbon for 30 classes of pesticides. Generally between 100 and 300 mg of pesticides can be adsorbed on to a gram of carbon. Three compounds, diquat, methamidophos and dalapon are not readily adsorbed to activated carbon and the Langmuir theory cannot be used to compute a capacity. Generally less than 10 mg of these three pesticides will be adsorbed on to one gram of carbon. Diquat can be easily removed by adding bentonite clay during the flocculation step. No wastewater that was made up of predominantly methamidophos and dalapon has been treated with the system.

TABLE 2. CARBON COLUMN CAPACITY
(Ruggeiri, 1981)

Herbicide	Carbon Capacity: Initial Breakthrough (mg/gm)	Carbon Capacity: Maximum Capacity (mg/gm)
Dinoseb	125	250
Alachlor	50	-
2,4-D	10	30

[1]No Alachlor was in the effluent.

Table 2 presents the adsorption capacity of carbon to remove dinoseb, alachlor and 2,4-D.(Ruggieri, 1981) The carbon becomes saturated with 2,4-D first as would be predicted by the results of Whittaker's study. Trifluralin and paraquat were removed during flocculation. This study showed that the carbon columns would become saturated with the most soluble and least adsorbable pesticide compound first. Carbon requirements would have to be based on the most difficult pesticide to adsorb.

TABLE 3. ECAPSULATION OF HERBICIDES

Cement: Sludge: Activated Carbon Ratio	Herbicide		
	Trifluralin (%)[1]	Dinoseb (%)	Alachlor (%)
3:2:0.10	99.7	2.5	0.0
3:2:0.15	99.9	69.4	78.6
3:2:0.20	99.9	69.1	66.9
3:2:0.40	100.	100.	99.8
3:2:0.80	100.	100.	99.9

[1] Percent of herbicide retained in the encapsulated samples that were crushed and subjected to the EPA Extraction Procedure.

Table 3 presents the results of the concrete encapsulation study conducted by Farrell(1984). Concrete cylinders were constructed by mixing the sludge from the flocculation procedure with portland cement and adding varying ratio of powdered activated carbon. The concrete was placed in an 8 oz. paper cup and allowed to set for 28 days. The EPA Extraction Procedure was used to determine the percent of pesticide encapsulation. The Indiana State Chemist Office analyzed the samples for dinoseb, trifluralin, and alachlor. Only 0.1% of the alachlor leached out of crushed samples of the concrete when a mixture of 3 parts cement, 2 parts sludge and 0.8 parts activated carbon was used. All of the other two herbicides were retained in the concrete encapsulate. This technique shows promise of providing a safe and simple method of handling the sludge and spent carbon.

In summary, primary flocculation and sedimentation followed by activated carbon adsorption appears to be a feasible means of handling pesticide contaminated wastewater. The system has been used on a variety of pesticide contaminated wastewaters. Proper flocculation is very important and it is sometimes necessary to receive assistance from a distributor of flocculent aids, such as Nalco Chemical Co. In test in Indiana, alum dosages of 300-500 mg/L were effective when used with an anionic polymer. The sedimentation step can be accomplished in a 55 gallon drum. A variable speed mixer is needed to assure proper flocculation and sedimentation. A flat blade paddle mixer, about 4 x 8 inches attached to the end of a 3 foot rod can be mounted on a variable speed electric motor and used as the mixer. The mixer should have at least 2 speeds. A 100-300 rpm mixing speed is necessary for mixing the chemicals for 15 minutes initially, followed by a 30 minute slow mix at 5-20 rpm to build the floc. Since the flocculation step is critical it is important to use the most effective polymer available. Persons interested in installing such a treatment system should seek advice from a local water or wastewater treatment plant or a supplier of flocculent aids to be sure that the initial flocculation step removes as much of the pesticides and carriers as possible. If the wastewater contains paraquat, bentonite clay should be added during flocculation.

The translucent supernatant that remains after the flocculated wastewater is allowed to settle will contain the dissolved pesticides. This liquid should be pumped through a series of activated carbon columns, usually 4. PVC or ABS pipe can be used to construct these columns. Four foot lengths of four or six inch diameter pipe will hold enough activated carbon to treat 2000 to 5000 gallons of most wastewater. The flow rate should be less than 1 gpm/ft^2 and the contact time should be at least 15 minutes. A pump that will deliver 0.1 to 0.2 gpm at 10 psi pressure should be used with the 4 or 6 inch diameter columns, respectively. Under these conditions approximately .25 grams of pesticide can be adsorbed on each gram of carbon.

Based on the results to date, a 55 gallon drum of flocculent will treat over 1000 gallons of wastewater. Four 6-inch diameter, 4-foot long columns will hold about 200 lbs. of carbon and will be capable of handling at least 5000 gallons of wastewater. The carbon costs about $1.00 per pound. Total cost of chemicals for treatment of the wastewater is about $.20 per gallon. A typical agricultural chemical applicator would produce 5000 gallons of wastewater per year. The cost of the mixer and tank would be less than $1000. The major cost would be the construction of a collection system to collect the wash water used to clean the application equipment.

The system produces two hazardous solid wastes. The sludge that accumulates from the flocculation and sedimentation and the spent activated carbon. The sludge can be reused in the sedimentation step until the volume of sludge limits the quality of supernatant. The total volume of pesticide contaminated waste is substantially reduced. Approximately 100 gallons of sludge and 200 pounds of spent activated carbon will be produced when 5000 gallons of wastewater is treated.

Using the simple encapsulation process that has been described in which the sludge is mixed with powdered activated carbon and portland cement, it would be possible to produce a concrete block that will meet the EPA Extraction Procedure test and would not be considered a hazardous waste. The 100 gallons of sludge and 200 pounds of spent activated carbon produced during the treatment of 5000 gallons of wastewater can be encapsulated in about 2 cubic yards of concrete.

The treatment system that has been developed can be used to remove the pesticides from the wastewater that is produced during cleanup of application equipment. The equipment is simple to operate and provides applicators with a realistic alternative for managing their contaminated wastewater.

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