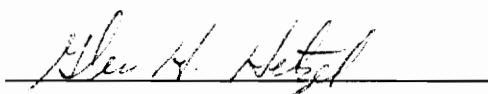


***Design Improvements to the Batch Demulsification and Sorption Equipment for  
Pesticide Rinsate Disposal***

by  
Patrick Phillips

Thesis submitted to the Faculty of the  
Virginia Polytechnic Institute and State University  
in partial fulfillment of the requirements for the degree of  
Master of Science  
in  
Agricultural Engineering

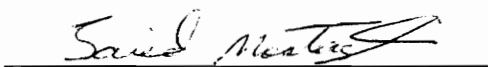
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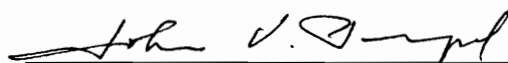
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September 14, 1994

Blacksburg, Virginia

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# **Design Improvements to the Batch Demulsification and Sorption Equipment for Pesticide Rinsate Disposal**

by

Patrick Phillips

Glen H. Hetzel, Chairman

Agricultural Engineering

(ABSTRACT)

Research currently being conducted at Virginia Tech has produced a viable pesticide wastewater clean-up procedure using biologically based materials. The system consists of two steps. First, pesticide laden wastewater is mixed with a lignocellulosic sorbent such as peat moss in a demulsification and sorption step. Second, the wastewater filtered rinsate is then passed through a packed column containing the same sorbent in a column sorption and filtration step.

Although the system yielded adequate results and performed the tasks commensurate with its design, the original batch demulsification and sorption phase of the process had several operational problems. Namely, the system was large and not very portable, the recirculation system was not very reliable, and the entire step one process was laborious and time consuming to execute. These problems and limitations prompted the redesign of the step one process into a new, more efficient system.

The new system consists of a steel frame similar to the old system. However, the new frame is smaller, lighter, more portable, and one person can easily operate and maneuver the new system. In addition, the new system provides a safer work environment for the operator. The frame surrounds the barrel and liner like a cage so that if the hand winch or the cable fails when lifting the liner out of the barrel, the operator is protected. The recirculation system has been automated such that it is self priming, and turns off when all the rinsate contained between the inner liner and outer barrel has been pumped dry. The come-a-long has been replaced with a hand wench that makes loading and unloading of the inner liner easier. Finally, the same pump that is used to recirculate the rinsate is used to transfer the rinsate onto the column for the second sorption and filtration step. There is now no need for additional pumps.

After the system was designed and developed, it was tested on two pesticides, atrazine and metolachlor, to determine if the new system yielded results comparable to the old system. The atrazine concentration in the rinsate was reduced from an initial 721 mg/kg (ppm) in step one to 2 mg/kg in the step two column sorption and filtration phase. This represents an atrazine reduction of 99.72% over the entire two step process. The metolachlor concentration in the rinsate was reduced from an initial 704 mg/kg in step one to 30 mg/kg in the step two column sorption and filtration phase. This represents a metolachlor reduction of 95.74% over the entire two step process. The percent reduction of pesticide from the rinsate in the new system is comparable to the 99% reductions obtained using the old system.



## **Acknowledgments**

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## **Chapter I**

### **Introduction**

Methods for aqueous pesticide waste reduction include rinsate recycling, on-site rinsate re-application, volume reduction using evaporation, and pesticide waste reduction [Mullins, et al., 1992(c)]. Inappropriate or inadequate pesticide waste disposal activities have been implicated as major sources of groundwater, soil, and surface water contamination [Mullins, et al., 1992(c)]. Development of effective pesticide disposal systems is understandably difficult; because pesticide wastes may include dilute rinsate solutions, concentrated materials, and even contaminated products such as soil. In addition, there are a multitude of pesticide formulations used by a variety of applicators. Procedures have been developed for pesticide contaminated rinsate disposal, however these procedures are extremely complicated, Gordian, and analytical [Mullins, et al., 1989; Berry, et al., 1993(a)]. The vast majority of disposal processes and concepts that have been

examined and presented over the last two decades involve the transfer of the potential pollutant to another matrix in conjunction with some detoxification or degradation technique [Hapemann-Somich, 1992]. In order for an applicator to be expected to use appropriate pesticide rinsate disposal methods, it is essential that the procedure be effective, simple to understand and operate, and safe. It is these types of pesticide rinsate disposal systems that an applicator and other pesticide users are likely to use. With these concerns in mind, an interdisciplinary team of researchers within the College of Agriculture and Life Sciences at Virginia Tech began to search for a means to safely dispose of pesticide containing wastewater [Hetzel, et al., 1992].

In order to more efficiently handle the hazardous material, a process was developed whereby the pesticide is sorbed to lignocellulosic materials resulting in a dramatic reduction in pesticide concentration [Hetzel, et al., 1992]. Various lignocellulosic materials have been examined; among them are peat-moss, steam exploded wood, steam exploded newspaper, peanut hulls, and rubber [ Hutchinson, et al., 1993; Mullins, et al., 1992(c)]. There are two major advantages to using organic material as the primary sorbent in treating pesticide contaminated rinsate. First, it acts as the sorbent, and in most situations is efficient in removing most of the pesticide from the rinsate. Second, the sorbent material is biodegradable as is the pesticide that is captured from the rinsate. Although, they do not necessarily degrade at the same rate. Work at Virginia Tech has proven this to be a safe and effective method for disposing of certain pesticides [Collins, et al., 1984; Mullins, et al., 1981]. The system consists of two steps. First, the pesticide laden wastewater is mixed with a lignocellulosic sorbent such as peat moss in the

demulsification and sorption step. Second, the wastewater or rinsate is passed through a packed column containing the same sorbent in a column sorption and filtration step.

The pesticide disposal system performs adequately and yields good results. Based on tests conducted on four pesticides, malathion, captan, lindane, and diazinon, the efficiency of pesticide removal from the rinsate was 99.995%, 99.996%, 99.997%, and 99.981% respectively. Despite these encouraging results there were mechanical parts of the system that could be improved, particularly the step one, batch demulsification and sorption phase of the process. The problems and limitations of the batch demulsification and sorption phase could be enumerated as follows: the system was big and not very portable, the recirculation system was not very reliable, and the entire step one process was laborious and time consuming to execute. These problems and limitations prompted the redesign of the step one process into a more efficient system.

## **1.1 Objectives**

This study is concerned with the redesign of the step one processing equipment in the pesticide rinsate bioremediation procedure. The redesign should address the problems associated with the batch demulsification and sorption step and fulfill the following requirements:

- The new equipment setup should be lighter and more portable,
- The recirculation components should be automatic and more reliable than the old design,
- The new equipment should be less labor intensive and safer to use than the old design,
- The new equipment should yield comparable results to the old design.
- The new equipment should be relatively inexpensive.

## **Chapter II**

### **Literature Review**

#### **2.1 General Pesticide Information**

Farming is one of the oldest professions and businesses in the world. Like any business, farmers are always looking for ways to improve their productivity. This may be in the form of new machinery, improved methods of tillage, improved crops and chemicals such as fertilizers and pesticides. All in the aforementioned list are designed to improve the productivity and output of the farmer. However, it is the pesticides and their persistence and detrimental effect to the environment that are of predominant interest in this thesis.

Pesticide is a generic term that includes several classes of chemicals designed to eliminate nuisances such as insects, rodents, and weeds that may inhibit the productivity of a farmer or any other crop producer. Insecticides, herbicides, fungicides, and rodenticides are a few of the more common classes used by applicators. Common pesticides can be classified chemically into three groups, inorganic, natural organic, and synthetic organic. Obviously, the synthetic pesticides are of primary interest here. These synthetic organic pesticides are best classified according to their persistence and behavior when introduced to waterways and the soil. The major types are the chlorinated pesticides, the organophosphorus pesticides, and the carbamate pesticides [Sawyer and McCarty, 1978].

Chlorinated pesticides are of many types, both insecticides and herbicides, and have been widely used for a variety of purposes. Chlorinated pesticides are extremely persistent in the environment, often requiring several months or years before they degrade. In addition to insects and plants, they are highly toxic to mammals including humans. Some common chlorinated pesticides are DDT, aldrin, chlordane, dieldrin, toxaphene, and heptachlor. Due to their extreme persistence and potential to harm the environment, DDT, chlordane, dieldrin, and toxaphene have been banned from use in the United States [Zakrzewski, 1991]. However, they are still manufactured for export to other countries such as Mexico and Central America where they are in common use [Zakrzewski, 1991].

Organic phosphorus pesticides are also used as both insecticides and herbicides. Typically, organophosphorus pesticides are quite toxic to both pests and humans alike. Parathion and malathion are two common organic phosphorus pesticides. Parathion is

very effective against certain pests, however, it is also highly toxic to humans. Malathion, on the other hand, while being highly toxic to a variety of insects, has a fairly low toxicity to mammals [Sawyer and McCarty, 1978].

Carbamate pesticides are amides having the general formula  $RHNCOOR$  [Sawyer and McCarty, 1978]. Carbamate pesticides may also be used as either insecticides or herbicides and generally exhibit low toxicity toward mammals. Some common carbamate pesticides are the fungicide captan and the insecticide carbaryl (liquid or dust) which is available in most department stores or hardware stores. A more comprehensive list of the major classes of pesticides, their persistence, and pathway to harm the environment is listed in Table 1.

With such a large variety of pesticides available and their extensive use in agriculture, growing concern has been exhibited over the effect of pesticide residues in the environment. In addition, a method by which unwanted pesticides and dilute pesticide formulations can be removed or destroyed needs to be investigated [Hetzl, et al., 1992; Bird, 1985].

**Table 1. Main Classes of Pesticides and Their Characteristics\***

<b>Class</b>	<b>Use</b>	<b>Persistence</b>	<b>Solubility in Water</b>	<b>Transport in Soil</b>
Chlorinated Hydrocarbons	Insecticides	High	Extremely Poor to Insoluble	Soil Erosion
Cationic Heterocycles	Herbicides	High	Good	Soil Erosion
Triazines	Herbicides	Moderate	pH Dependent	Soil Erosion
Phenylureas	Herbicides	Moderate	Variable	Leaching (If Highly Soluble)
Dinitroanilines	Herbicides	Moderate	Poor	Soil Erosion
Phenoxyacetic Acid Derivatives	Herbicides	Short	Good	Soil Erosion
Phenyl Carbamate Derivatives	Herbicides	Short	Good	Soil Erosion
Ethylenebis-(Dithiocarbamate) Metal Derivatives	Fungicides	Short	Moderate	Unknown
Pyrethroids	Insecticides	Short	Extremely Poor	Soil Erosion
Organophosphorus	Insecticides	Short	Good	Leaching
Carbamates	Insecticides	Short	Good	Leaching

\*Reference [Zakrzewski, 1991. p. 145.]



## 2.2 Pesticide Disposal Considerations

The vast majority of disposal processes and concepts that have been examined and presented over the last two decades involve the transfer of the potential pollutant to another matrix in conjunction with some detoxification or degradation technique [Hapemann-Somich, 1992]. Staffan Bengtsson, et al., 1994, used a solid phase extraction procedure to remove pesticides from surface water. The most widely used sorbent for non-polar interactions is octadecyl bonded silica matrix ( $C_{18}$ ). Since most organic molecules have some non-polar structure,  $C_{18}$  or octyl ( $C_8$ ) sorbents are well suited for non-polar and semipolar compounds. The bulk sorbent, with a particle size of 40  $\mu\text{m}$ , containing octadecyl ( $C_{18}$ ) bonded silica is manufactured by 3M (St. Paul, MN 55144) and is distributed by Varian Instrument Co. (Sample Preparation Products Division, Harbor City, CA). The cost of the  $C_{18}$  bulk sorbent is \$2 per gram in United States currency. Using the bonded silica matrix, mean recoveries of pesticide from the surface water were about 61% [Bengtsson, et al., 1994].

Agricultural pesticide application is predominantly targeted toward crop protection. The soil is the ultimate sink for pesticide residue in field application, minus that

portion of the pesticide that is lost to degradation and volatilization, crop uptake and runoff. There have been a number of studies concerning pesticide mobility in the soil, pesticide adsorption in the soil, and even pesticide degradation in the soil. Weber, et al., 1993, studied the mobility of fomesafen and atrazine in soil columns and determined that the relative mobility of pesticides in soil is affected by not only the properties of the chemical but also soil and hydrogeologic properties as well. In addition to these factors, application conditions, climatic, and meteorological conditions, likewise, affect pesticide mobility. Furthermore, saturated or unsaturated flow conditions also affect sorption of pesticides. Apparently, the rate of adsorption is time dependent and in fact sorption data of all pesticides showed an initial rapid rate followed by a slower rate of sorption [Kookana, et al., 1992(a)].

Not all the pesticides that come into contact with the ground are going to leach into the groundwater. Some of the chemical will adsorb to the soil matrix. Factors that affect the adsorption process are organic matter content, clay content, specific surface area, soil pH, and cation exchange capacity (CEC) [Hermosin and Carnejo, 1989]. The adsorption process can be described by the Freundlich isotherm equation [Frobe and Stengl, 1989]:

$$x/m = K_d * C_e^{1/n} \quad [1]$$

Where:  $x/m$  = the amount of pesticide sorbed per unit of sediment weight ( $\mu\text{g g}^{-1}$ )

$C_e$  = the equilibrium aqueous concentration ( $\mu\text{g ml}^{-1}$ )

$K_d$  = adsorption coefficient

$1/n$  = a constant for a given compound and sediment.

Hermosin and Carnejo also used the Freundlich isotherm equation to describe the adsorption process, but in the form:

$$C_s = K_f C_e^{nf} \quad [2]$$

Where:  $C_s$  = the amount of pesticide adsorbed

$C_e$  = the equilibrium pesticide concentration

$K_f$  and  $nf$  = regression parameters characteristic for each adsorbate/adsorbent system.

Obviously, these equations can be either linear or non-linear. In fact, both reports indicated that the isotherm plots may be either linear or non-linear depending on the particular pesticide modeled [Frobe and Stengl, 1989; Hermosin and Carnejo, 1989].

Gerstl and Kliger, 1990, determined that of the many components of the solid phase of soil, it is the organic matter that is generally found to be of major importance in the sorption of nonionic organic chemicals [Gerstl and Kliger, 1990]. Thus, the tendency of a soil or sediment to adsorb trace contaminants could be based on the percentage of organic carbon in the soil matrix. The percentage of organic carbon or  $K_{oc}$  partition coefficient is expressed as:

$$K_{oc} = (K_d * 100) / \% \text{ organic carbon} \quad [3]$$

Where:  $K_{oc}$  = the organic carbon partition coefficient

$K_d$  = the sorption coefficient of the chemical in a particular system expressed on a soil weight basis [Gerstl and Kliger, 1990].

Percent organic carbon is not the only parameter indicative of the adsorption capability of a soil or sediment. Gerstl and Mengelgrin, 1984, determined that correlation between adsorption (on an organic matter basis) and either solubility or the octanol / water partition coefficient,  $K_{ow}$ , enabled estimates of adsorption to within an order of magnitude [Gerstl, 1984]. The octanol / water partition coefficient or  $K_{ow}$  can be expressed as:

$$K_{ow} = \frac{K_{sd}}{6.3 \times 10^{-7} f_{oc}} \quad [4]$$

Where:  $K_{ow}$  = the octanol / water partition coefficient

$K_{sd}$  = the soil distribution coefficient

$f_{oc}$  = the fraction of organic carbon in the soil (g/g) [Tchobanoglous, et al., 1993].

Soil is not the only material that can adsorb trace chemical contaminants. In fact, in the process of adsorption, the first material that comes to mind is usually activated carbon. Activated carbon is prepared by first making a char from materials such as almond, coconut, walnut hulls and other woods, and coal. The char is produced by heating the material to drive off the hydrocarbons but with an insufficient supply of air to sustain

combustion (i.e., less than stoichiometric air). The char particles are then activated by exposure to an oxidizing gas at a high temperature. This gas develops a porous structure in the char and thus creates a large internal surface area [Metcalf and Eddy, 1991]. There have been several studies concerning the adsorption of pesticides to activated carbon e.g. Dalmacija, et al., 1992 and Heroes, 1982 who report a high rate of success with activated carbon, with removal efficiencies approaching 100 percent. Heroes, 1982, examined the capacity of activated carbon to remediate a ground and soil contamination site. Drums containing toxic liquid herbicide and pesticide had been buried in the ground. Corrosion of these drums led to contamination of the ground soil in the surrounding area. Remediation efforts consisted of injecting water into the soil and collecting the water in a storage reservoir. The contaminated water was then filtered through granular activated carbon and once purified, was used for reinjection. The remediation effort was conducted over several years. Table 2 illustrates the influent and effluent levels of chlorophenols and phenoxyacetic acids and the corresponding removal efficiencies obtained using activated carbon.

**Table 2. Efficiency of Treatment Using Activated Carbon\***

		12/1/77 to 12/31/78	1/1/79 to 12/31/79	1/1/80 to 12/31/80
Chlorophenols	Inlet	6.4 mg/l	1.3 - 3.2 mg/l	0.8 - 1.5 mg/l
	Effluent	3.8 µg/l	16.0 µg/l	2.6 µg/l
	Efficiency	99.94%	99.29%	99.27%
Phenoxy	Inlet	89 mg/l	113 - 129 mg/l	13 - 26 mg/l
	Effluent	57 µg/l	484 µg/l	77 µg/l
	Efficiency	99.93%	99.60%	99.60%

\*Reference [Heroes, 1982. p. 1530.]

## **2.3 Pesticide Sorption Using A Lignocellulosic Matrix**

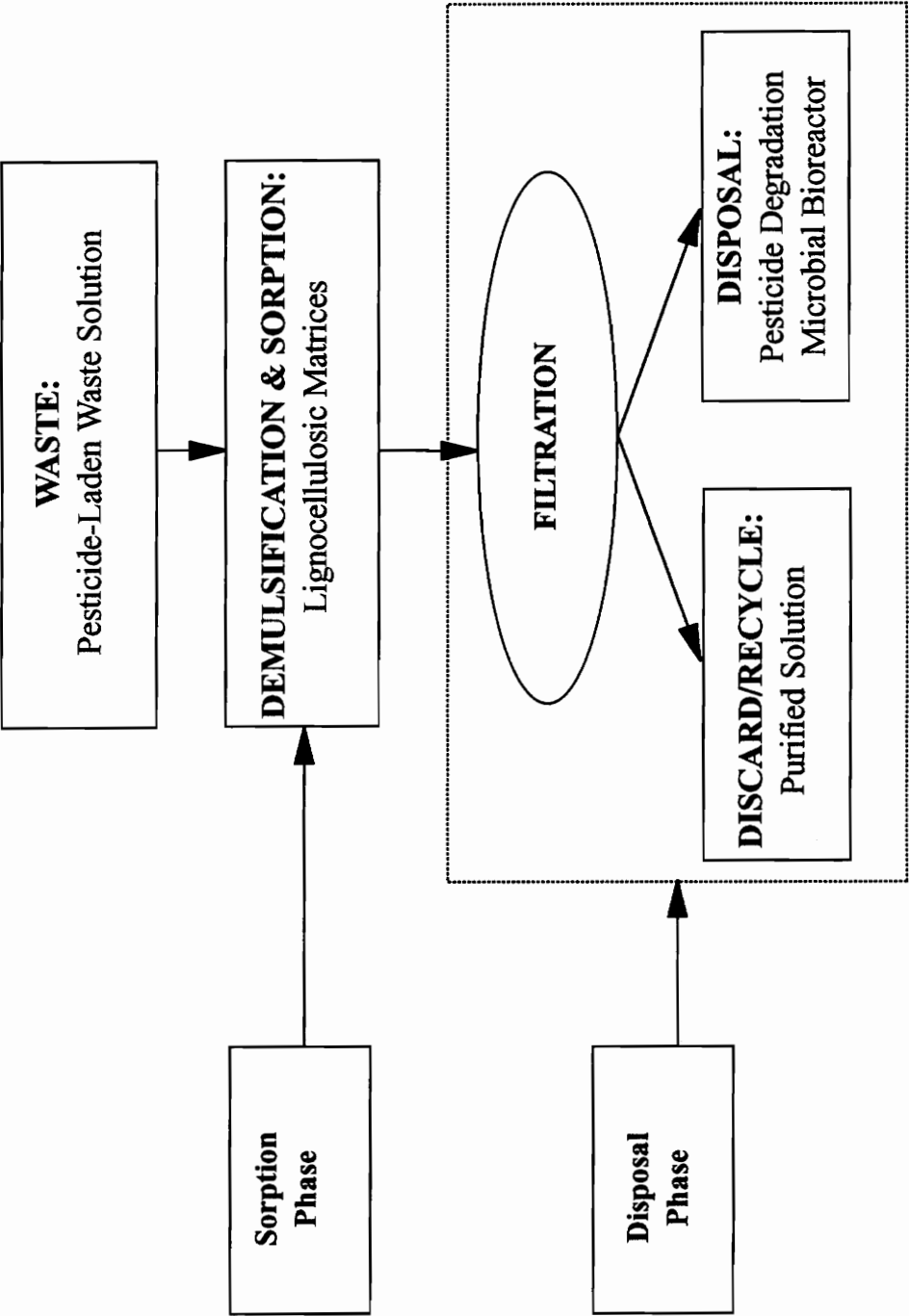
Other materials, besides activated carbon, have been examined for their adsorptive properties. Unwanted pesticide products and pesticide rinsate from agricultural applications have posed disposal problems for many years. Pesticide rinsate is the wastewater that results when the applicator cleans the spraying equipment after a particular pesticide application. Most rinsate contains only water with small or trace amount of contaminants. In addition, the volume of rinsate is typically large. Increased awareness of the environmental risks associated with pesticide rinsate has prompted applicators to seek adequate means of disposal. Ideally, the best method of handling potential contaminants is waste minimization. The less rinsate an applicator generates, the less there is for disposal. Another option is for the applicator or farmer to reuse the rinsate. However, if the rinsate is to be reused, the total applied pesticide cannot exceed the product label requirements [Hapemann-Somich, 1992].

Research currently being conducted by an interdisciplinary team of researchers within the College of Agriculture and Life Sciences at Virginia Tech is focusing on a means to dispose of pesticide containing wastewater. In order to more efficiently handle the hazardous material, a process was developed whereby the pesticide is sorbed to

lignocellulosic materials resulting in a dramatic reduction in pesticide concentration [Hetzel, et al., 1992]. Research carried out at Virginia Tech has shown that various lignocellulosic materials, such as peat moss, and steam-exploded wood fibers will sorb pesticides from the rinsate. This sorption is nearly as effective as using activated carbon [Hetzel, et al., 1992].

The model initially utilized for disposing of pesticide laden rinsate is illustrated in Figure 1. The process consisted of a single step in which demulsification and sorption occur in a batch type reaction [Hetzel, et al., 1991]. Rinsate and lignocellulosic sorbent were placed in a basket or liner that inserts into a 55 gallon drum. A motor driven stirrer was used to mix the rinsate and sorbent for approximately four hours. This ensured good wetting of the sorbent particles and also helped prevent flocculation of the sorbent. This is especially important because the next step was to add a demulsifying agent, like calcium hydroxide  $[Ca(OH)_2]$ , to the rinsate while mixing with the sorbent. Following the demulsification-sorption phase, the liquid was drained from the sorbent by raising the liner and allowing the liquid to drain from the sorbent for at least four hours. After draining, the liquid was allowed to settle an additional 12 hours or so to provide more time for the fines to settle. Following this settling phase, the liquid was passed through two or more filters to remove the fines left in suspension. Filters capable of removing particles of three microns were used for the final filtration [Hetzel, et al., 1992]. Good filtration was essential, because particles of lignocellulosic material remaining in the suspension had sorbed some pesticide from the mixture. In addition, even though the



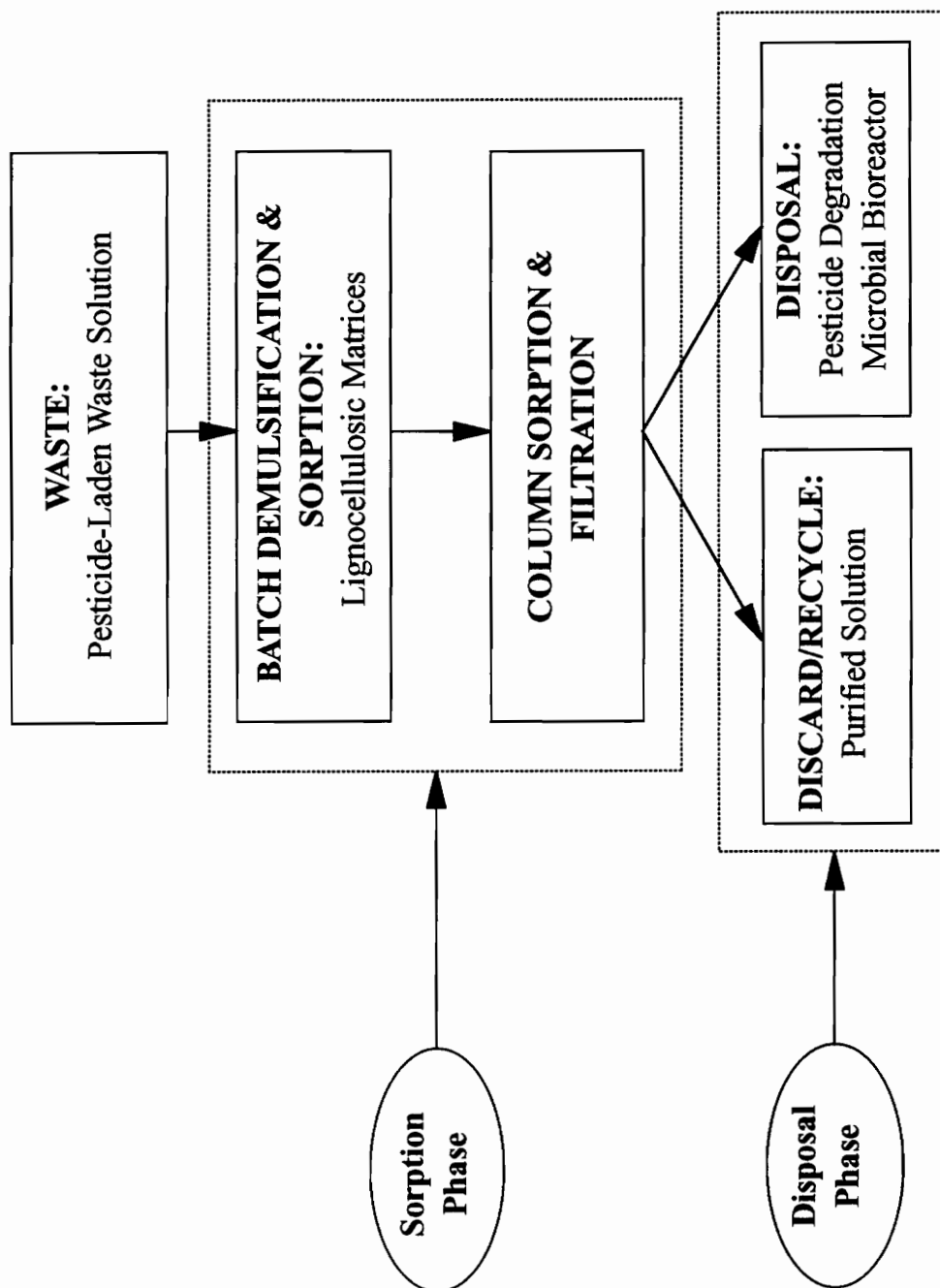


Ref. [Hetzel et al., 1992. p. 142.]

Figure 1. One-Step Demulsification and Sorption Process

mixing process inhibited flocculation, some flocculation may have occurred. Thus, it was necessary to provide a means of removing this flocculant. For the pesticides tested, it was possible to filter the solids from the mixture and reduce the residual pesticide levels in the rinsate to very low parts per million (or mg/kg) [Hetzel, et al., 1992]. It is likely that levels as low as parts per billion (or  $\mu\text{g/kg}$ ) can be achieved [Hetzel, et al., 1992].

Figure 2 represents the pesticide disposal scheme that is currently being used. It is a two step process in which demulsification and sorption occur the same as the one step process. The same equipment is employed to mix the rinsate, the sorbent, and the demulsifying agent  $[\text{Ca}(\text{OH})_2]$ . The rinsate is drained from the sorbent, the same as the single step procedure, however, it is not allowed to settle as in the single step system. After draining the rinsate from the mixture, it is then cycled through a column packed containing the same lignocellulosic sorbent as was used in the initial demulsification/sorption step. Recycling the rinsate through the column allows for additional pesticide to be sorbed from the rinsate that was not sorbed in the initial demulsification/sorption step. In addition, any fines that are remaining after the initial demulsification/sorption step will be removed by the packed column. This alleviates the need for an additional filter to remove the fines as was needed in the single step system. The system described can handle 133 - 151 L (35 - 40 gal) of rinsate [Hetzel, et al., 1992]. Between 0.057-0.085  $\text{m}^3$  (2-3  $\text{ft}^3$ ) of lignocellulosic material is mixed with the rinsate [Hetzel, et al., 1992]. The column was constructed from a piece of poly-vinyl-chloride (PVC) pipe 90 cm long by 20.3



Ref. [Hetzel et al., 1992, p. 142.]

Figure 2. Two-Step Pesticide Waste Disposal Process

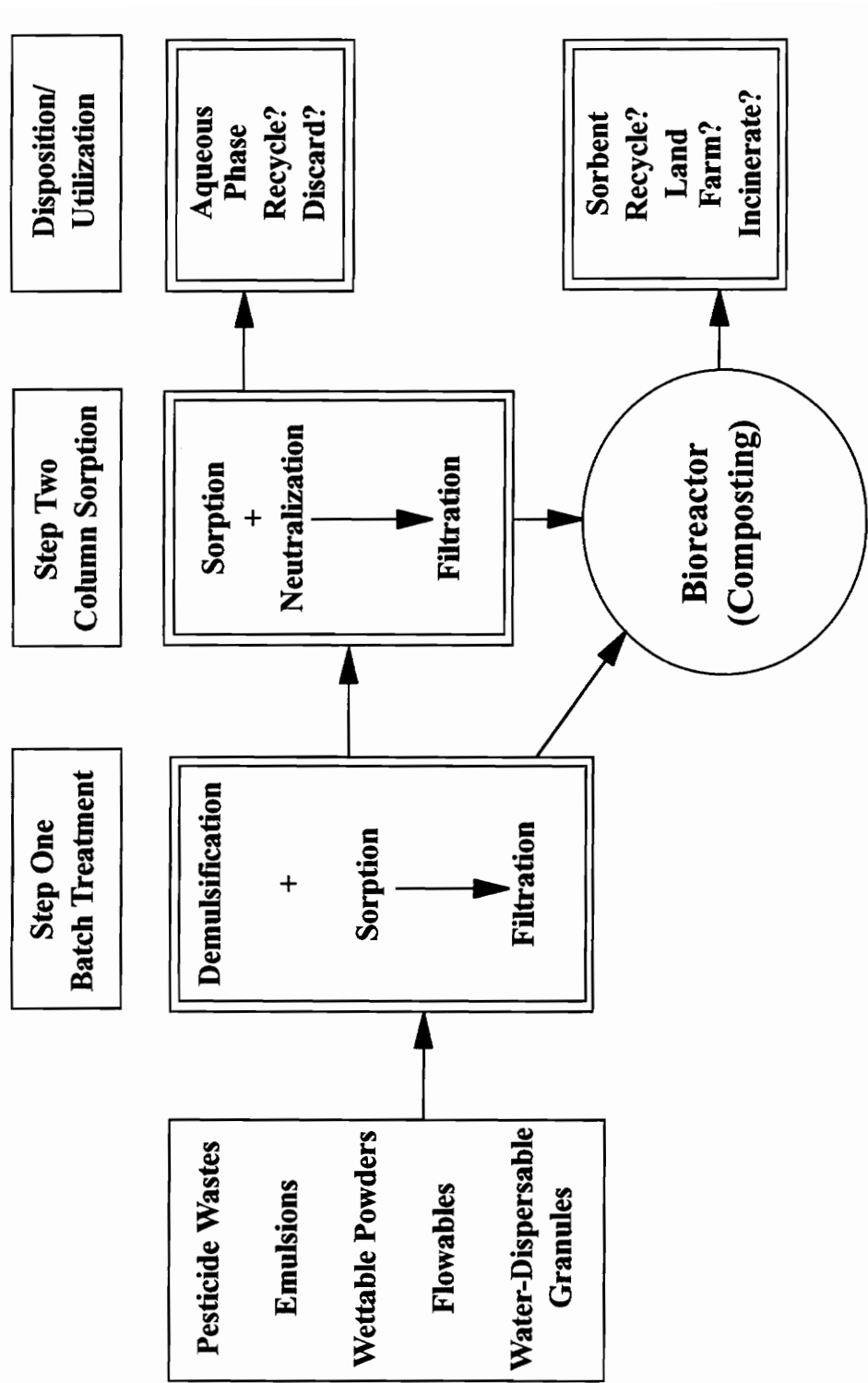
cm in diameter (35.5 in. long by 8 in. in diameter) with a 45 mesh stainless steel screen in the lower end. A float switch was installed to control the pump used in recycling the rinsate from the 55 gallon drum to the column. Approximately  $0.014\text{m}^3$  ( $0.5\text{ ft}^3$ ) of sorbent was placed in the column [Hetzel, et al., 1992]. After the solids of the sorbent are separated from the rinsate solution, both from the initial demulsification-sorption phase and the packed column, the sorbent is then placed in a bioreactor where solid-state fermentation occurs [Hetzel, et al., 1992; Berry, et al., 1993(a and b), Mullins, et al., 1992(b)].

## **Chapter III**

### **Rinsate Disposal System**

#### **3.1 The Pesticide Disposal System Before Equipment Modifications**

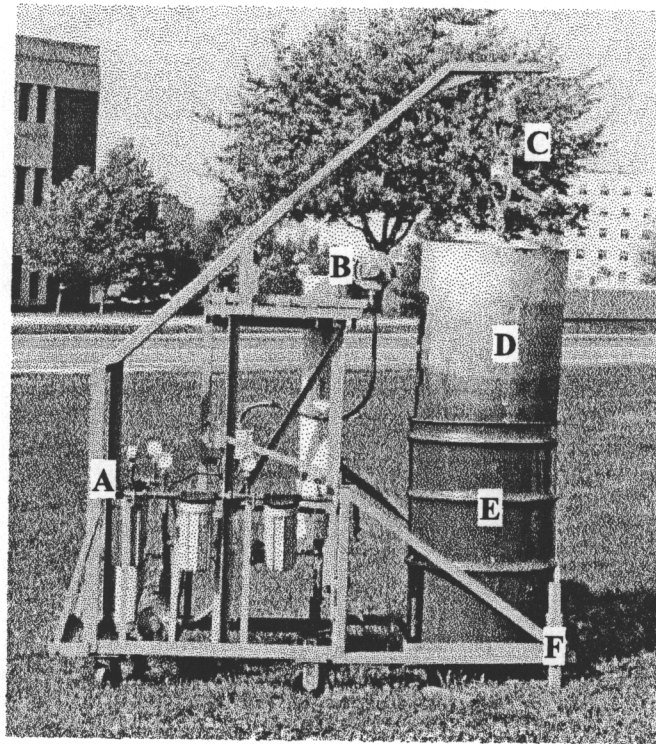
Figure 3 is a schematic representation of the pesticide disposal system. Only the equipment used to operate the pesticide disposal system was modified, the system itself remained unchanged by the design modifications. It was a two step process in which demulsification and sorption occur in the first step. The rinsate was mixed with the peat moss and a demulsifying agent  $[\text{Ca}(\text{OH})_2]$  and was stirred for approximately four hours. The rinsate was then drained from the sorbent and pumped into a PVC column, packed with the same sorbent as in step one. The packed column (step two) provides an



Ref. [Mullins et al., 1992(c), p. 115.]

Figure 3. Model For Pesticide Wastewater Disposal Using Organic Sorption And Microbial Degradation

additional opportunity for removal of the pesticide from the rinsate that did not occur in step one. In addition, the packed column serves as a filtration unit where any sorbent fines and any flocculant from step one is removed from the rinsate. Figure 3 also illustrates the final disposal method for the sorbent, which, in this case, is composting. This is an advantage of using an organic material as a sorbent, in that the sorbent is subject to biodegradation. The pesticide will also degrade, however, not always at the same rate as the sorbent material. After the sorbent and pesticide are allowed to degrade it is possible the levels of pesticide remaining in the peat moss are low enough that the material could be used for land application or as mulch on non edible crops or pastures. Figures 4 through 6 show the machinery setup for the first two steps of the process. Figures 4 and 5 illustrate the batch demulsification/sorption step (step one) and figure 6 illustrates the column sorption and filtration step of the process (step two). However, it was the first step of the process that was of interest because the equipment design for the demulsification/sorption phase of the process is the one that was modified.. This part of the system was mounted on a 61 cm (24 in.) wide by 152 cm (60 in.) long steel frame made from 6.35 cm by 6.35 cm by 0.64 cm angle iron (2 1/2 in. by 2 1/2 in. by 1/4 in.) [Mullins, et al., 1990-1993]. A 1/4 horsepower motor equipped with a gear reduction of 1725 to 99 rpm was mounted on a roller track on the steel frame. The motor used to stir the rinsate and the sorbent mixture was moved into place for mixing and recessed back into the steel frame when not in use. The paddle used to mix the rinsate and sorbent was a three stage system with paddles of 15 cm (6 in.), 25 cm (10 in.), and 38 cm (15 in.) in diameter. Figure 5 shows that the mixing container consisted of a standard 208 liter (55

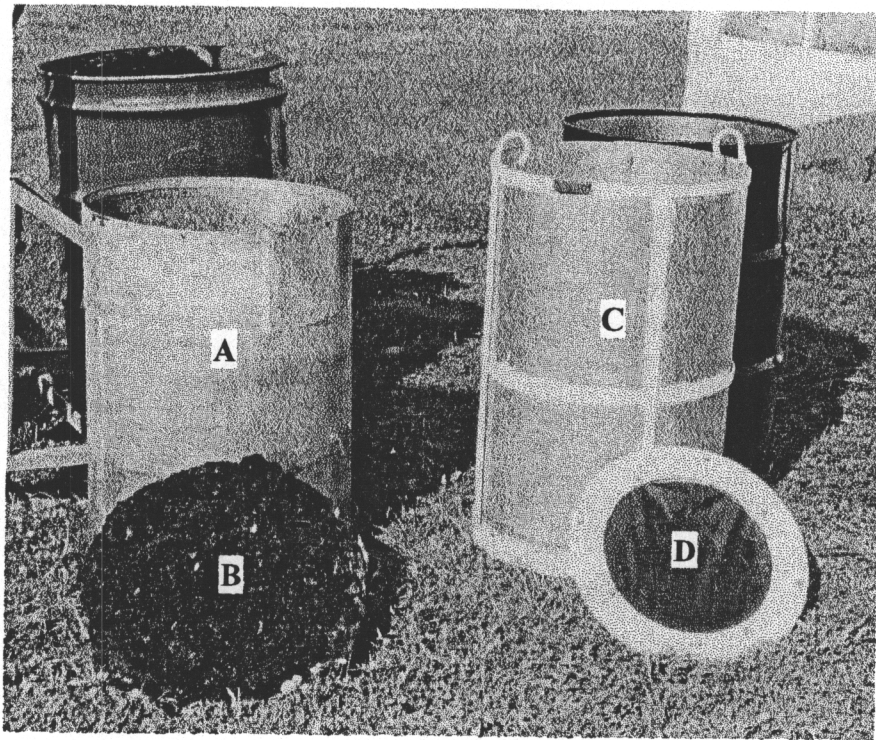


**Legend:**

- A. Steel Frame
- B. Gearmotor
- C. Come-a-long
- D. Inner Liner
- E. 55 Gallon Drum
- F. Retractable Legs

**Figure 4. Batch Demulsification and Sorption Step (Old System)**

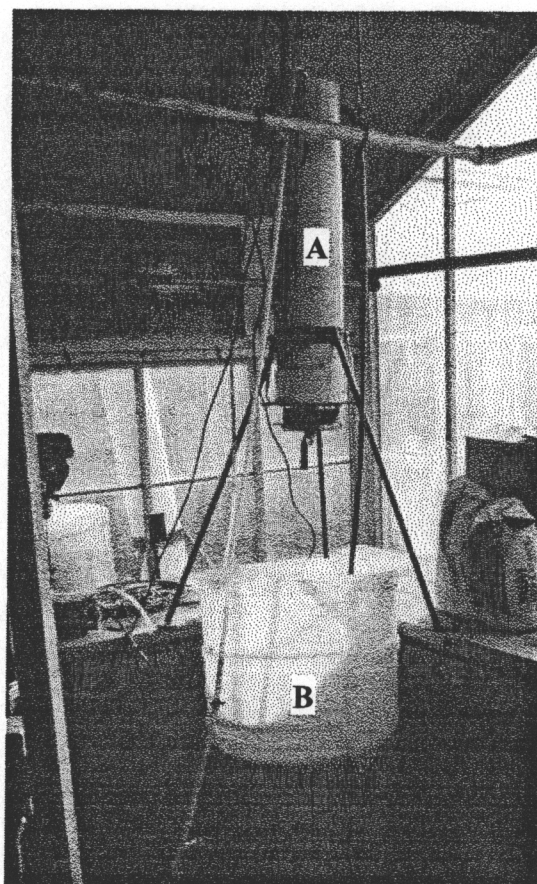




**Legend:**

- A. Inner Liner (Old System)**
- B. Inner Liner Screen (Old System)**
- C. Inner Liner (Current System)**
- D. Inner Liner Screen (Current System)**

**Figure 5. Inner Liner Setup (Old System on Left and New System on Right)**



**Legend:**

- A. Column Sorption and Filtration Unit**
- B. Barrel Containing Processed Rinsate**

**Figure 6. Column Sorption and Filtration (Old and New System)**

gallon) drum with a 56 cm (22 in.) diameter galvanized basket or liner that inserted into the 208 l (55 gallon) drum. In order to drain the rinsate from the sorbent, provisions had to be made for lifting the liner from the 55 gallon (208 l) drum. Thus, there is a 3.81 cm (1 1/2 in.) by 0.64 cm (1/4 in.) thick piece of square tubing that angled up out of the steel frame to a height of approximately eight feet. The liner was raised out of the drum by a half-ton come-a-long attached to the square tubing on one end and the liner. A 2205 kg (1000 pound) come-a-long is needed to lift the liner because not only is the liner being lifted out of the 55 gallon drum but also 151 liters (40 gallons) of rinsate and sorbent which weighs approximately 771 kg (350 pounds). Retractable legs were attached to the metal frame to keep the entire frame from over turning when the liner was lifted from the barrel. The legs were 107 cm (3 1/2 feet) long, thus the entire steel frame with the legs extended was 259 cm (8 1/2 feet) long. Since the inner liner had a screen in the bottom, the rinsate flowed into the space between the liner and the barrel. A recirculation system had been included in order to cycle the rinsate from the outside of the liner to the inside of the liner. This insured that all the rinsate had ample opportunity to mix with the sorbent material and thus improve the sorption process. The recirculation system consisted of a piece of copper tubing 0.95 cm (3/8 in.) in diameter and 76.2 cm (2 1/2 feet) long that was inserted between the liner and the barrel. This tubing was connected to a water pump on the steel frame by means of 0.95 cm (3/8 in.) tygon tubing. A return line from the pump emptied into the liner. In order to start recirculation, the pump had to be primed. This was accomplished by means of a "tee" connector in the tubing that split the

line going from the copper tubing to the pump. A funnel was attached to the "tee" and priming was accomplished with water from a standard garden hose.

### **3.2 Operational Procedure**

Four commercially available formulated pesticides: malathion (Dragon 4E; 319 ml, 50% ai), captan (Captan 50 WP; 319 g, 50% ai), lindane (Ortho 2.5 E; 760 ml, 20% ai), and diazinon (Diazinon 4 E; 320 ml, 50% ai) were used in this study [Mullins, et al., 1992(a)]. Each pesticide was added to 132.49 liters (35 gallons) of water in order to simulate a typical rinsate volume that might be expected if a farmer were to wash a pesticide application tank. The pesticide and water were agitated in the 55 gallon (208.20 l) drum with an inner liner for approximately two minutes to ensure thorough mixing. After thorough mixing occurred, 5.51 kg (2.5 pounds) of  $\text{Ca(OH)}_2$  and 14.11 kg (6.4 pounds) of sphagnum peat moss were added to the barrel and liner. The resulting mixture was then agitated for four hours. During mixing, a small amount of the solution contained between the inner screened liner and the 55 gallon (208.20 l) drum was recirculated into the screened container using a small 1.27 cm (1/2 in.) centrifugal pump, as described above. The recirculation flow rate was adjusted so that it did not exceed the

rinsate flow rate out of the screened inner liner. This ensured that there would still be rinsate in-between the inner liner and the 55 gallon (208.20 l) drum after four hours, and thus, prevent the pump from running dry and burning up.

After four hours of mixing, the inner liner was lifted out of the 55 gallon (208.20 liter) barrel using a hand powered hoist or come-a long. The solution was screened and filtered to remove the peat moss which remained in the screened inner liner. The inner liner had a three tier screening system. The inner liner itself had a 45 mesh screen covering the 40.64 cm (16 in.) diameter opening in the bottom, a piece of "shark skin" filtration paper was placed on this opening and a second, 40 mesh, screen was placed over this paper. The inner liner was raised out of the 55 gallon (208.20 l) drum using a come-a-long and allowed to drain for approximately 12 hours. The filtered rinsate was then pumped into the eight inch PVC sorption/filtration column containing 14.11 kg (6.4 pounds) of peat moss. The column was packed or tamped and then equilibrated with flowing water for several hours prior to use. The flow rate of the primary filtrate through the column was about 9.46 l/hr (2.5 gallons per hour) [Mullins, et al., 1992(a)]. Replicate samples of the initial solution, four hour mix solution, primary filtrate, mixing container rinsate (from the third rinse), primary filtrate solution, and the column sorption/filtrate were obtained for pH, conductivity, and pesticide concentration determinations [Mullins et al., 1992(a)]. Both the batch sorbents and the column sorbents, which were used to sorb the pesticides, were allowed to air dry to approximately 60 - 80% moisture content and then mixed and sampled prior to placement in bioreactors. The sorbents from each experimental series were mixed together along with 10%

vegetable oil, 8.38 kg (3.8lbs), 5% corn meal, 4.19 kg (1.9lbs), 15 grams of 15/30/15 (nitrogen/potash/phosphate) fertilizer, 240 grams nitrogen fertilizer, and 20 ml of an enrichment microbial culture [Mullins, et al., 1992(a)]. Experiments with lindane, captan, and malathion were replicated three times. Experiments with diazinon were replicated four times. Liquid samples (450 ml) were either held in a cold room at 2 - 4°C or frozen at -20°C until they could be extracted and analyzed. Samples from the primary filtration step of captan, lindane and diazinon were neutralized with HCl before cold storage [Mullins, et al., 1992(a)].

### **3.3 Results From Experiments on Premodified Equipment**

Table 3 provides data on solutions and sorbents obtained from the experimental series on malathion. The malathion concentration in the rinsate was reduced from an initial 1150 mg/kg (ppm) at the beginning of step one to 0.054 mg/kg after the step two column sorption and filtration phase. This represents a malathion reduction of 99.995% over the entire two step process. It should be noted that malathion is sensitive to alkaline hydrolysis and its disappearance from solution may be attributed to the high pH levels associated with the use of the calcium hydroxide demulsification agent in the step one demulsification/sorption phase [Mullins, et al., 1992(a)].

**Table 3. Removal of Malathion From 35 Gallons of an Aqueous Suspension**

**Using Chemical Destabilization and Sorption**

Solution	Malathion Conc. ppm	pH	Conductivity μMHO
Initial	1150±71	7.4±0.0	104±8
Step One (batch sorption)	0.022±0.020	12.2±0.2	5970±82
Step Two (column sorption)	0.054±0.016	3.9±0.1	539±20
Container Rinse (step one)	10.8±7.7	10.9±0.4	376
Tap Water	-----	7.1±0.1	107±6
Distilled Water	-----	5.5±0.4	7±2
0.00702 N KCl (standard)	-----	-----	978±118
Sorbent			
Step One (batch sorption)	N.D.	12.2±0.1	-----
Step Two	8.2±4.6	12.2±0.1	-----
Total (both steps)	8.2±4.6	-----	-----

Ref. [Mullins, et al., 1992(a)].

1. Values expressed as the mean ± the standard error of the mean, based on 3 replicated experiments
2. N.D. = not detectable at 0.001 ppm.

In addition, the pH and the conductivity of the rinsate was reduced from 12.2 to 3.9 and 5970  $\mu$ MHO to 539  $\mu$ MHO respectively after passing through both steps of the system. The conductivity of a solution is a measure of its ability to carry an electrical current, and varies with both the number and type of ions the solution contains. In this case, the conductivity is a measure of the salinity of the rinsate. Thus it should decrease with decreasing pH. Analysis of the primary sorbent apparently revealed no detectable level of malathion. However, a small amount (8.2 mg/kg) of malathion was detected in the step two column sorption and filtration sorbent. The reason there is no detectable level of malathion in the primary sorbent is probably due to the highly alkaline environment and the alkaline hydrolysis of the malathion as discussed above. The pH levels of the primary sorbent are high, much higher than in the packed column sorbent, due to the presence of the calcium hydroxide demulsification agent.

Table 4 provides data on solutions and sorbents obtained from the experimental series on captan. The captan concentration in the rinsate was reduced from an initial 1244 mg/kg at the beginning of step one, to non-detectable levels (below 0.001 mg/kg) after the step two column sorption and filtration phase. This represents a captan reduction of 99.996%. Captan is similar to malathion in its sensitivity to alkaline hydrolysis and its disappearance from the rinsate can also be attributed to the high pH level which resulted from the use of the calcium hydroxide demulsification agent in step one [Mullins, et al., 1992(a)]. In addition, the pH and the conductivity of the rinsate was reduced from 12.3 to 4.0 and 3763  $\mu$ MHO to 994  $\mu$ MHO, respectively,



**Table 4. Removal of Captan From 35 Gallons of an Aqueous Suspension Using Chemical Destabilization and Sorption**

Solution	Captan Conc. ppm	pH	Conductivity $\mu$ MHO
Initial	1244 $\pm$ 92	6.1 $\pm$ 0.3	130 $\pm$ 4
Step One (batch sorption) Not Neutralized	0.0003 $\pm$ 0.0003	12.3 $\pm$ 0.0	3763 $\pm$ 236
Neutralized	0.004 $\pm$ 0.001	8.2 $\pm$ 1.1	2593 $\pm$ 157
Step Two (column sorption)	N.D.	4.0 $\pm$ 0.3	994 $\pm$ 67
Container Rinse (step one)	3.8 $\pm$ 3.1	10.8 $\pm$ 0.5	807 $\pm$ 132
Tap Water	-----	7.1 $\pm$ 0.1	104 $\pm$ 5
Distilled Water	-----	6.2 $\pm$ 0.3	7 $\pm$ 1
0.00702 N KCl (standard)	-----	-----	1217 $\pm$ 6
Sorbent			
Step One (batch sorption)	286 $\pm$ 232 <sup>3</sup>	8.6 $\pm$ 0.3	-----
Step Two	0.119 $\pm$ 0.068	7.5 $\pm$ 0.1	-----
Total (both steps)	282 $\pm$ 232	-----	-----

Ref. [Mullins, et al., 1992(a)].

1. Values expressed as the mean  $\pm$  the standard error of the mean, based on 3 replicated experiments
2. N.D. = not detectable at 0.001 ppm.
3. One sample contained 856 ppm.

after passing through both steps of the system. Analysis of the sorbents revealed that some captan was detected in the primary sorbent on the order of 286 mg/kg. A small amount of captan was detected in the step two sorbent on the order of 0.119 mg/kg. The pH levels of the primary sorbent are high, much higher than in the packed column sorbent, due to the presence of the calcium hydroxide demulsification agent.

Table 5 provides data on solutions and sorbents obtained from the experimental series on lindane. The lindane concentration in the rinsate was reduced from an initial 1573 mg/kg at the beginning of step one, to 0.046 mg/kg after the step two column sorption and filtration phase. This represents a lindane reduction of 99.997%. Lindane is not as sensitive to alkaline hydrolysis as is malathion and captan. Thus, the disappearance of lindane from the rinsate after going through both steps of the system can be attributed mainly to sorption onto the peat moss matrices. This is corroborated by the relatively high levels of lindane that were found on the sorbent material. The amounts as listed in table 5 are 24,407 mg/kg of lindane in the primary sorbent and 3,496 mg/kg of lindane in the step two sorbent. In addition, the pH and the conductivity of the rinsate was reduced from 12.4 to 5.3 and 4590  $\mu$ MHO to 185  $\mu$ MHO, respectively, after passing through both steps in the system.

Table 6 provides data on solutions and sorbents obtained from the experimental series on diazinon. The diazinon concentration in the rinsate was reduced from an initial 1528 mg/kg at the beginning of step one, to 0.287 mg/kg after the step two column sorption and filtration phase. This represents a diazinon reduction of 99.981%.

**Table 5. Removal of Lindane From 35 Gallons of an Aqueous Suspension  
Using Chemical Destabilization and Sorption**

Solution	Lindane Conc. ppm	pH	Conductivity $\mu$ MHO
Initial	1573 $\pm$ 129	7.21 $\pm$ 0.1	96 $\pm$ 5
Step One (batch sorption) Not Neutralized	0.671 $\pm$ 0.0546	12.4 $\pm$ 0.0	4590 $\pm$ 242
Neutralized	7.28 $\pm$ 5.89	7.3 $\pm$ 0.0	2475 $\pm$ 43
Step Two (column sorption)	0.046 $\pm$ 0.03	5.3 $\pm$ 0.0	185 $\pm$ 3
Container Rinse (step one)	0.780 $\pm$ 0.114	9.6 $\pm$ 0.3	122 $\pm$ 7
Tap Water	-----	7.1 $\pm$ 0.1	89
Distilled Water	-----	6.5 $\pm$ 0.2	11
0.00702 N KCl (standard)	-----	-----	1,195
Sorbent			
Step One (batch sorption)	24,407 $\pm$ 1,878	9.0 $\pm$ 0.2	-----
Step Two	3,496 $\pm$ 2,098	8.0 $\pm$ 0.0	-----
Total (both steps)	27,902 $\pm$ 271	-----	-----

Ref. [Mullins, et al., 1992(a)].

1. Values expressed as the mean  $\pm$  the standard error of the mean, based on 3 replicated experiments
2. N.D. = not detectable at 0.001 ppm.

**Table 6. Removal of Diazinon From 35 Gallons of an Aqueous Suspension  
Using Chemical Destabilization and Sorption**

Solution	Diazinon Conc. ppm	pH	Conductivity $\mu$ MHO
Initial	1528 $\pm$ 54	7.7 $\pm$ 0.1	98 $\pm$ 2
Step One (batch sorption) Not Neutralized	102 $\pm$ 87	12.3 $\pm$ 0.2	5266 $\pm$ 709
Neutralized	83 $\pm$ 71	7.5 $\pm$ 0.4	3115 $\pm$ 355
Step Two (column sorption)	0.287 $\pm$ 0.08	5.7 $\pm$ 0.2	136 $\pm$ 9
Container Rinse (step one)	3.75 $\pm$ 0.54	9.1 $\pm$ 0.2	98 $\pm$ 8
Tap Water	-----	7.3 $\pm$ 0.0	114 $\pm$ 2
Distilled Water	-----	6.6 $\pm$ 0.0	11 $\pm$ 0
0.00702 N KCl (standard)	-----	-----	1228 $\pm$ 8
Sorbent			
Step One (batch sorption)	25,760 $\pm$ 1,791	10.8 $\pm$ 0.7	-----
Step Two	2,867 $\pm$ 974	8.0 $\pm$ 0.1	-----
Total (both steps)	28,627 $\pm$ 2,647	-----	-----

Ref. [Mullins, et al., 1992(a)].

1. Values expressed as the mean  $\pm$  the standard error of the mean, based on 3 replicated experiments
2. N.D. = not detectable at 0.001 ppm.

Like lindane, diazinon is not very sensitive to alkaline hydrolysis. Thus, the disappearance of diazinon from the rinsate after going through both steps of the system can be attributed mainly to sorption onto the peat moss matrices. This is evidenced by the relatively high levels of diazinon that were found on the sorbent material. In addition, the pH and the conductivity of the rinsate was reduced from 12.3 to 5.7 and 5266  $\mu$ MHO to 136  $\mu$ MHO, respectively, after passing through both steps in the system. Significant amounts of diazinon were found on both the step one, demulsification and sorption, and the step two, sorption and filtration sorbents. The amounts as listed in Table 6 are 25,760 mg/kg of diazinon in the primary sorbent and 2,867 mg/kg of diazinon in the step two sorbent.

Cost estimations have been made for the treatment of pesticide laden rinsate and are as follows: step one demulsification and sorption batch treatment, \$1.55/run; step 2 column sorption and filtration, \$1.05/run [Mullins, et al., 1992(a)]. These costs were based on the materials used in the field experiments such as sorbents and amendments. The cost of the equipment and machinery used to perform the field experiments; pumps, motor, steel frame, etc. has not been explicitly calculated. However, an economic analysis of these components, estimated the equipment cost to be about \$850.

### 3.4 Problems With The System

Obviously the system performed quite effectively as it was constructed. As was shown in the preceding section, it was possible to pare the four pesticides down to a concentration measuring in the low the parts per million. While there was nothing wrong with the theory behind the batch demulsification and sorption procedure, there were some operational parameters of the machinery itself that needed to be improved.

To begin with, the steel frame was too big. It weighed close to 400 pounds and with the legs extended, it was over eight feet long. These criteria prompt consideration that the portability of the machinery is limited. Indeed, even though the machine was on casters, it was almost impossible for one person to move the machine without a great deal of exertion. In addition, it was difficult to fit the setup through a standard door. If the machine needed to be relocated to another location it took at least three people to load it onto a truck.

The recirculation system was very difficult to set up and operate. Ideally the flow rate on the recirculation system should be equal to the flow of rinsate out of the inner liner. Unfortunately, the flow rate was very difficult to estimate and often varied during the step one mixing process as the screened inner liner clogged with sorbent fines. The result was that all the rinsate contained between the inner liner and the barrel was pumped into the inner liner before the four hour mixing time elapsed. With nothing but

air to recirculate, this could have seriously damaged the pump. In addition, the pump was not self-priming and required the presence of an operator to supply the initial priming and often to maintain the pump priming.

Finally, the entire step one demulsification and sorption setup took a great deal of time and labor on the part of the operator. If the operator could not lift the inner liner in order to place it in the 55 gallon barrel, then the come-a-long was used for the task. Additionally, the unreliability of the recirculating system necessitated the need for the operator to check on it during mixing. Since the machinery was so large and heavy, it is not always possible to position the setup in an advantageous location relative to the step two sorption and filtration setup. Thus, after the rinsate drained out of the inner liner, the barrel had to be moved to the step two setup. All total, it took two people 5 hours to thoroughly complete a step one run. This time includes one hour of preparation time and the four hour mixing time.

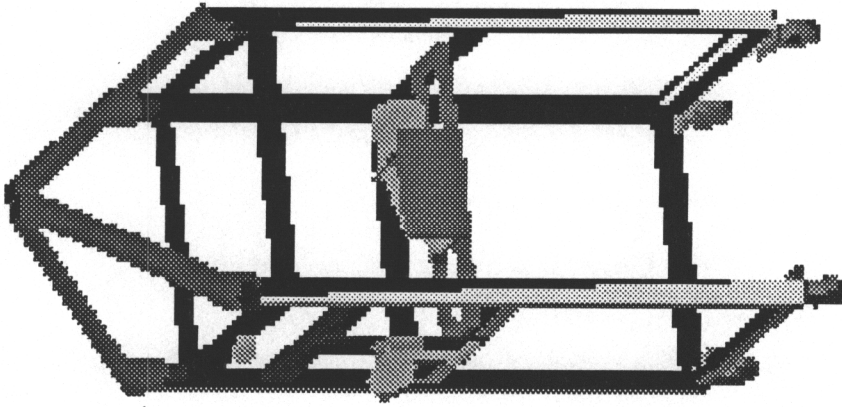
## **Chapter IV**

### **System Redesign**

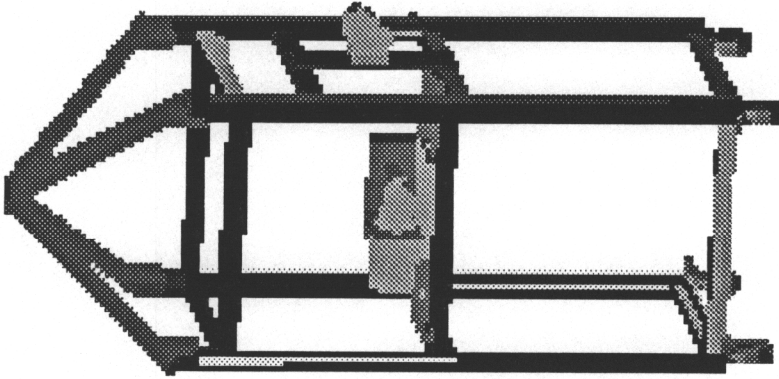
#### **4.1 Redesign of the Batch Demulsification and Sorption Step**

The redesign of the step one, batch demulsification and sorption step began with a conceptual design of the improved steel frame. AutoCAD release 12 was used to create a conceptual design of the new framework. Figure 7 illustrates a front view of the improved steel frame and Figure 8 illustrates a back view of the improved steel frame. Both figures are three dimensional solid models that have been rendered and exported using AutoCAD release 12. Figures 9, 10, 11, and 12 are standard line drafts of the steel frame top, side, front, and isometric views respectively. Based on the size and weight problems associated with the old system, the new frame was designed to be as small as

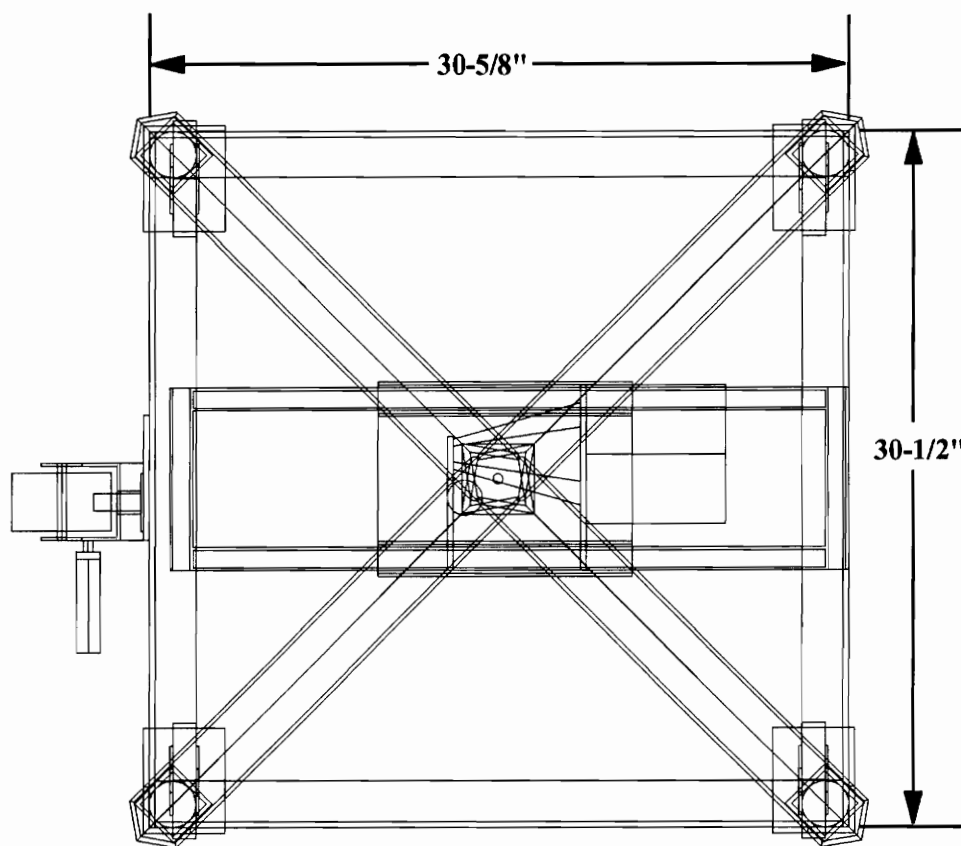




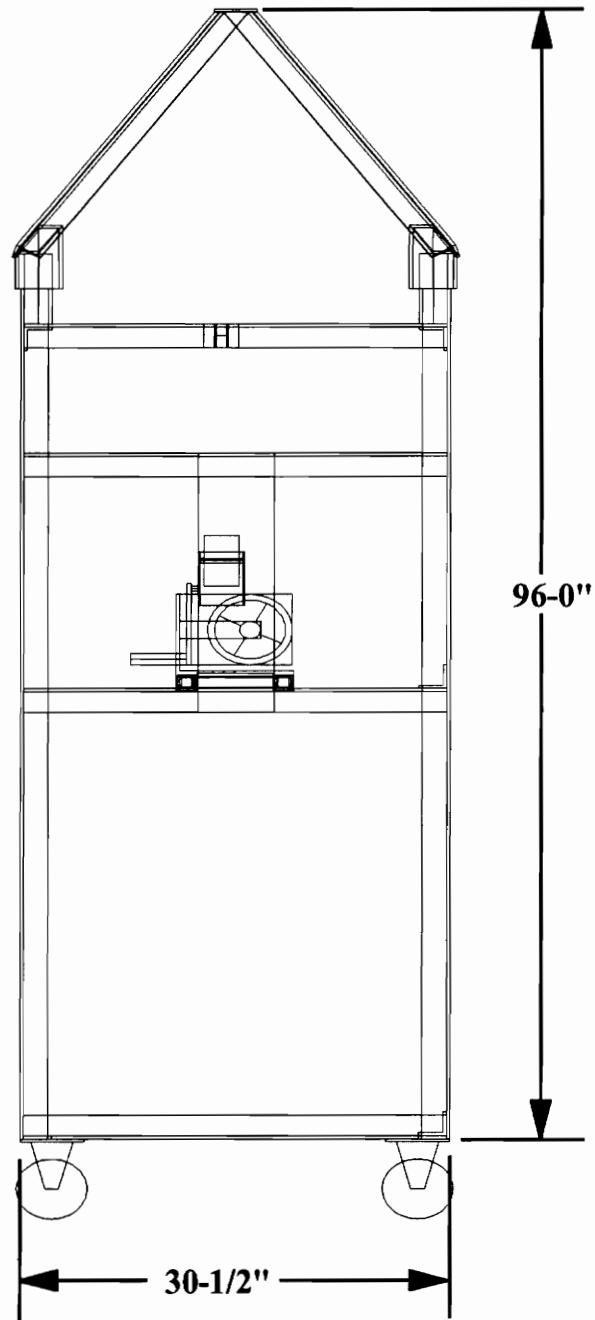
**Figure 7. Conceptual Design of the New System (Front View)**



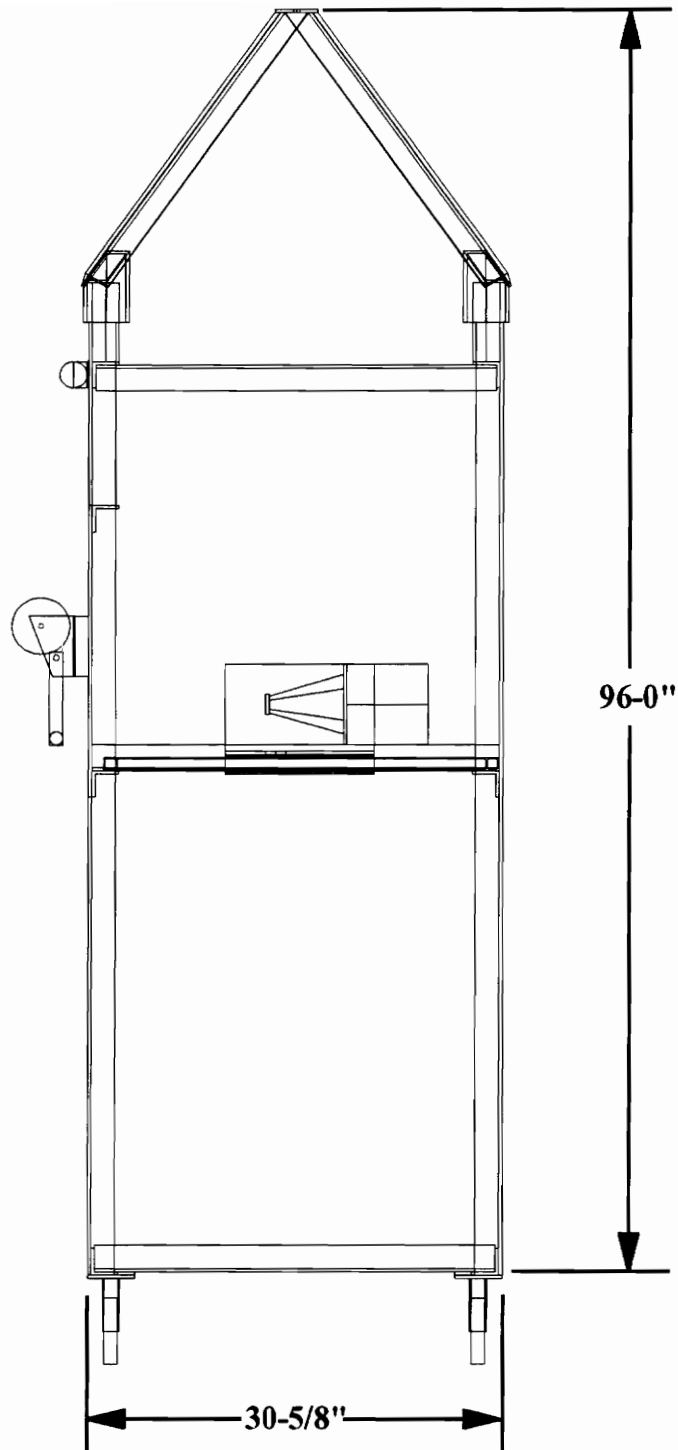
**Figure 8. Conceptual Design of the New System (Back View)**



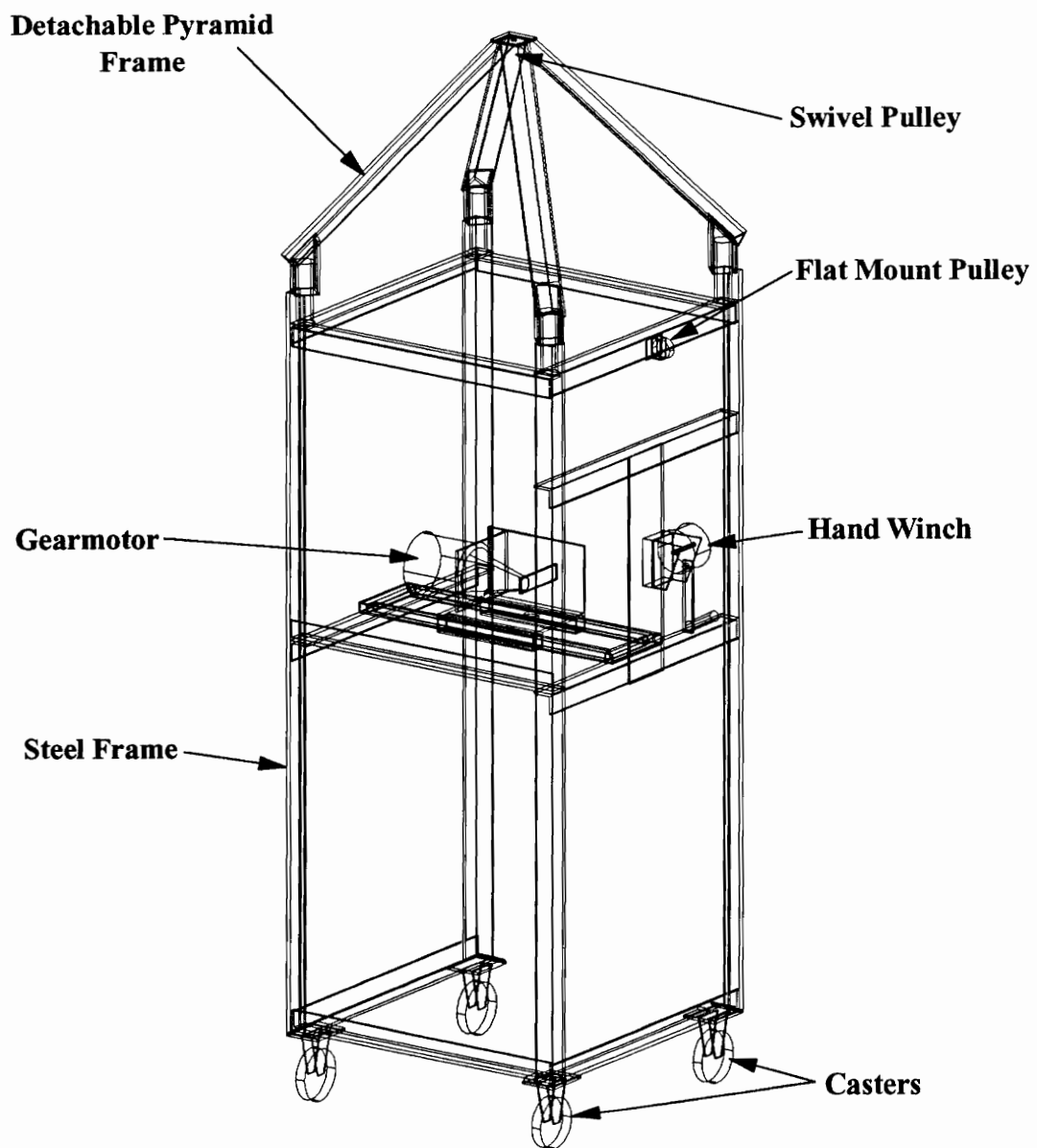
**Figure 9. AutoCAD Drawing of the New System (Top View)**



**Figure 10. AutoCAD Drawing of the New System (Side View)**

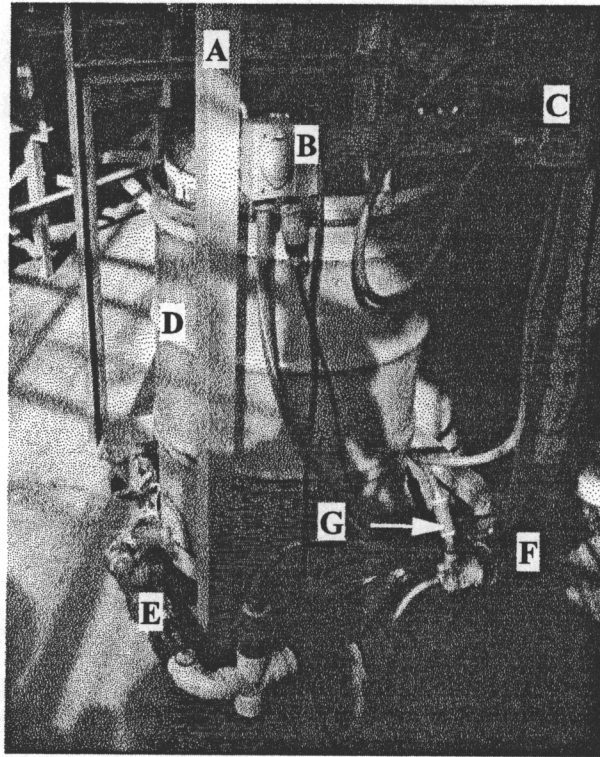


**Figure 11. AutoCAD Drawing of the New System (Front View)**



**Figure 12. AutoCAD Drawing of the New System (Isometric View)**

possible. The limiting factor in determining the size of the steel frame was the 55 gallon drum used to mix the rinsate and sorbent material. Thus, the new frame was designed only six inches wider than the diameter of the drum. Since the drum was mounted on a wheeled dolly, it can be moved inside the steel frame (Figure 13). The overall dimensions of the frame are 77.79 cm (30-5/8 in.) in width, 77.79 cm (30-1/2 in.) in length, and 243.84 cm (96 in.) in height. In addition, the frame was constructed out of 5.08 cm x 5.08 x 0.64 cm (2x2x1/4 in.) angle iron (ASTM A36 cold roll steel) instead of 6.35 cm (2-1/2 in.) angle iron, which reduces the weight of the system from 881.84 kg (400 pounds) to 551.15 kg (250 pounds). The 2 in. angle iron is extremely conservative for the strength requirements needed to support the inner liner full of rinsate. The 2 in. angle iron was selected not based on the strength requirements, but serviceability requirements. The 2 in. surface was needed to attach electrical outlets, switch box housings, idler pulleys, and mixing motor to the frame. The pyramid shaped top portion of the frame can be removed so that the unit can be rolled through a standard 91.44 cm x 203.20 cm (36 in. x 80 in.) door (Figure 14). The frame serves three purposes. First, it provides the framework and support necessary to raise the inner liner out of the drum (Figure 15). To this end, a hand winch replaces the come-a-long as the means of raising the inner liner. The hand winch, and pulleys are all rated at 2205 kg (1000 pounds) which is more than sufficient to support 771 kg (350 pounds) (132 liters {35 gallons} of rinsate, 14 kg {6.4 pounds} of sorbent material, and the 110 kg {50 pound} inner liner). The 0.48 cm (3/16 in.) wire rope was selected because it not only matched up with the pulleys but was also strong enough to support the inner liner full of rinsate. The 3/16" (0.48 cm) wire rope is

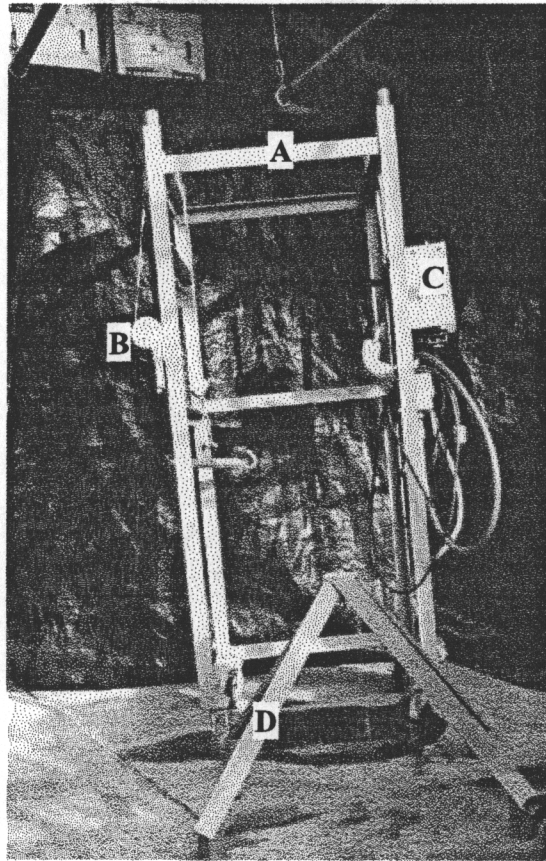


**Legend:**

- A. Steel Frame
- B. Relay Switch
- C. Switch for Gearmotor
- D. 55 Gallon Drum
- E. Recirculation System
- F. Recirculation Pump
- G. Check Valve

**Figure 13. Frame and Barrel Setup for the New System**

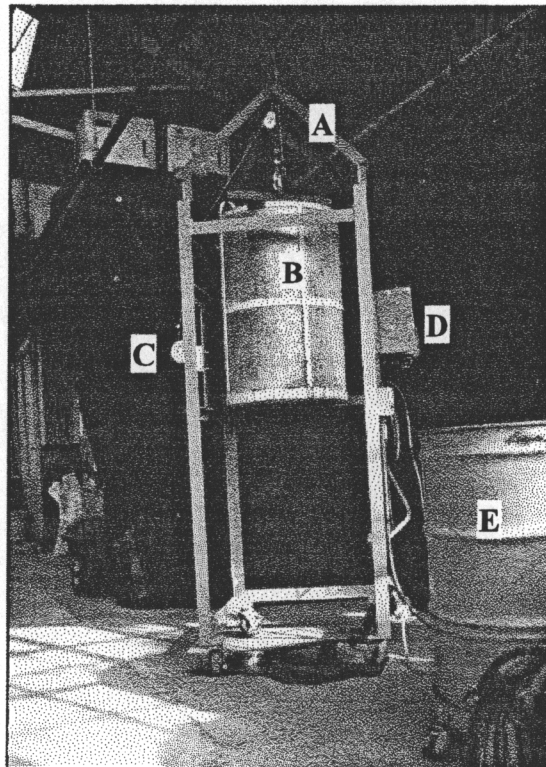




**Legend:**

- A. Steel Frame**
- B. Hand Winch**
- C. Gearmotor**
- D. Detachable Top Portion of Steel Frame**

**Figure 14. Separated Steel Frame (New System)**



**Legend:**

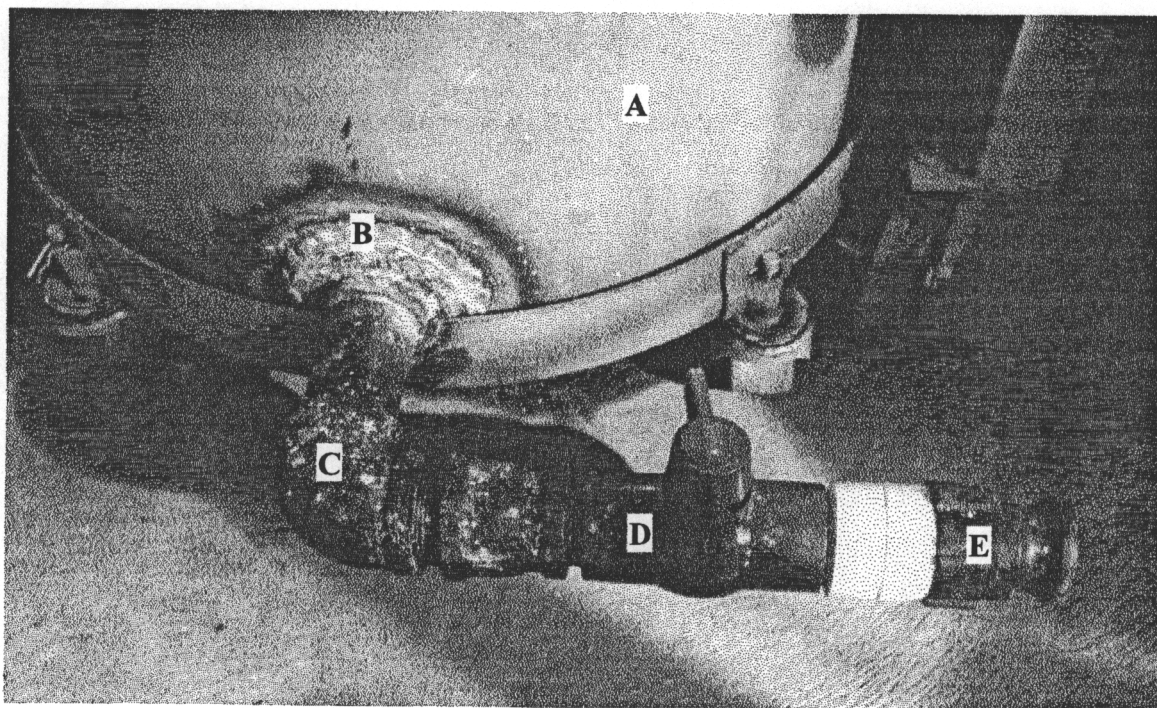
- A. Steel Frame**
- B. Inner Liner**
- C. Hand Winch**
- D. Gearmotor**
- E. 55 Gallon Drum**

**Figure 15. Raising the Inner Liner Using the New Steel Frame**

rated at 1851 kg (840 pounds). The next smaller size of wire rope, 0.32 cm (1/8 in.) is only rated at 617 kg (280 pounds), which is not strong enough to support the inner liner full of rinsate.

Second, the frame acts as a safety cage which protects the operator in the unlikely event that the hand winch or cable should fail while the inner liner is being raised. Third, the frame provides the foundation for all the supplementary equipment needed to complete a step one experiment. Thus, the mixing gearmotor, switches, and recirculation pump are all attached to the frame (Figure 13).

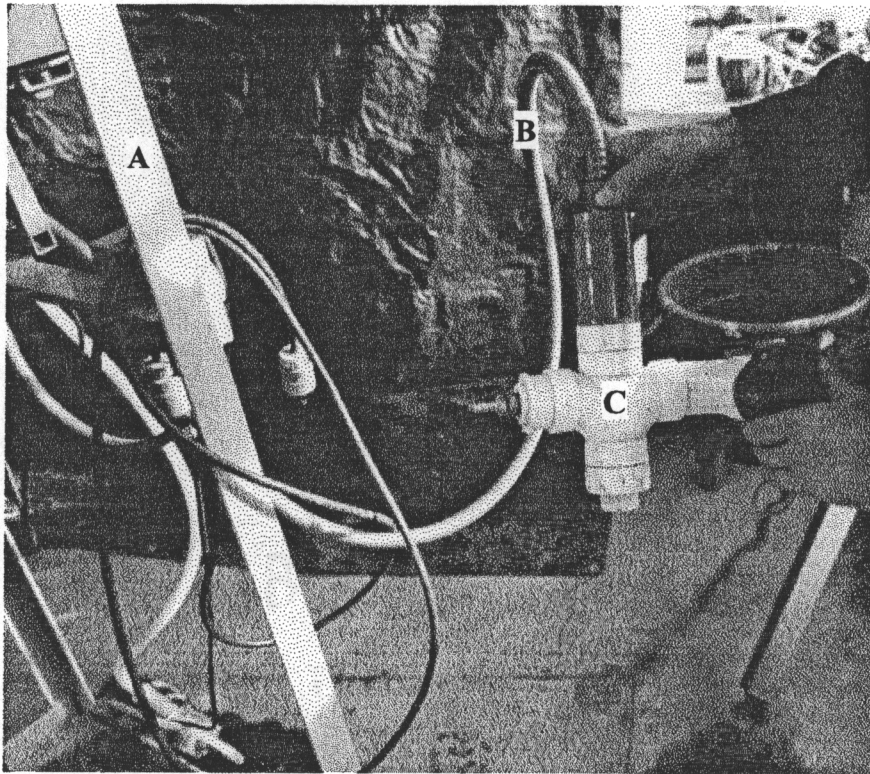
The 55 gallon (208.20 l) drum has been modified to improve the recirculation system. One of the criteria requisite to improving the recirculation system was that it should be self priming. The easiest way to accomplish this was to let the rinsate contained between the inner liner and the barrel do the priming by means of gravity and the pressure head of the rinsate. Thus, a 3.81cm (1-1/2 in.) hole was cut at the bottom of the barrel wall. A 3.81 cm (1-1/2 in.) threaded floor flange was then brazed onto the side of the barrel and then fitted with 3.81 cm (1-1/2 in.) cast iron pipe that extends around the side of the steel frame (Figure 16). A cut-off valve was installed in-line with the iron pipe so that the flow of rinsate out of the drum can be turned on and off by the operator when necessary (Figure 16). Another criteria for improving the recirculating system was, when the rinsate contained between the inner liner and the drum had been pumped dry, the recirculating pump would cut off. In order to accomplish this, a float valve was installed in a PVC double tee (Figure 17). The float switch operates at 0.28 amps which is not enough amperage capacity to directly activate the 1.5 amp water pump for



**Legend:**

- A. 55 Gallon Drum
- B. 1-1/2 in. Floor Flange
- C. 1-1/2 in. Cast Iron Pipe
- D. 1-1/2 in Ball Valve
- E. 1-1/2 in. Cam Coupler

**Figure 16. Barrel Alterations for Modified Recirculation System**



**Legend:**

- A. Steel Frame**
- B. Flexible Conduit Connecting the Float Switch to the Relay Switch**
- C. PVC double "Tee" Housing the Float Switch**

**Figure 17. Float Switch for Modified Recirculation System**

recirculation. Thus, the float switch is connected to a relay switch that provides up to 25 amps of current to turn on the pump. When rinsate flows through the pipe, the float switch activates the relay switch which then activates the pump, recirculating the rinsate into the inner liner. When the rinsate runs dry, the float switch cuts off, which activates the relay switch and turns off the pump.

A problem encountered with the new recirculation system was that after the rinsate between the inner liner and the drum ran dry and the pump shut off, rinsate contained in the output line of the pump would flow back through the pump and activate the float switch and the pump. Since the end of the output line is higher than the pump, the rinsate would continue to cycle back and forth through the pump as it turned on and off. This cycle would continue endlessly until enough rinsate leaked from the inner liner to activate the float switch and overcome the elevation head. In order to solve this problem, a check valve was installed in the pump output line to prevent rinsate flow back through the pump. A detailed account of the parts contained in the new system, and their corresponding cost, can be found in the results section of this thesis.

## **Chapter VI**

### **Results and Discussion**

The redesigned step one equipment adequately fulfills the requirements of the pesticide wastewater disposal system. Namely, it is still a batch demulsification and sorption step; after all, only the equipment to perform the process is new, not the process itself. In addition, the redesigned equipment addresses and satisfies the problems and limitations of the old system, discussed in a previous section, rather well.

Since the frame is based on the dimensions of the 55 gallon drum it measures only 78 cm x 78 cm x 244 cm (30-5/8 in. x 30-1/2 in. x 96 in.) rather than 61 cm x 244 cm x 244 cm (24 in. x 96 in. x 96 in.). The frame is constructed out of 5.08 cm x 5.08 cm x 0.64 cm (2 in. x 2 in. x 1/4 in.) angle iron rather than 6.35 cm x 6.35 cm x 0.64 cm (2-1/2 in. x 2-1/2 in. x 1/4 in.) angle iron. These two factors, size and material, greatly reduce the overall weight of the system. Whereas the old system weighed close to 882

kg (400 pounds), the new system weighs only 551 kg (250 pounds). In addition, the size and weight reduction means that the system is portable. It will roll through a standard door and one person can load the frame onto a truck for relocation.

Substitution of the hand winch for the come-a-long has made the job of loading the inner liner into the drum easier and less time consuming. The hand winch also makes the job safer because the operator does not have to risk injury trying to load the inner liner by hand. Raising the inner liner in order to allow the rinsate to drain is also much easier and safer. Since the steel frame acts as a safety cage around the drum and liner the operator is protected in the unlikely event that the hand winch or wire rope should fail.

Redesign of the recirculation system has yielded the greatest benefits, in terms of time, than any other part of the new system. The operator does not have to prime the recirculation pump, and then prime again if the first one was unsuccessful. No longer does the operator have to check on the mixing process to see if the rinsate has been pumped into the inner liner and run the risk of burning up the pump. In fact, after the mixing of the rinsate and sorbent begins, all the operator has to do is open a valve. The pump primes itself and recirculation begins automatically. In addition, the same pump that is used for the recirculation is used to transfer the rinsate to the packed column, no additional pumps are required. Using the old system, a step one experiment would take two people five hours to complete. One hour was used as preparation time and the remaining four hours was used for mixing. With the new system, a step one experiment takes only one person five hours to complete. Four hours is still consumed in the mixing process, however, it now only takes one person one hour to prepare for the experiment.



After construction of the new system, it was tested using two commercial pesticides, atrazine and metolachlor. The experiments were conducted using a procedure similar to that enumerated in the Operational Procedure section of this thesis, except that the experiments made use of the new equipment.

Table 7 provides data on solutions and sorbents obtained from the experimental series on atrazine. The results in Table 7 are based on four replicated experiments with atrazine. During the field experiments samples were collected from the rinsate and the sorbent material, for analysis. Three samples of the four hour batch demulsification were collected. Two of these samples were collected from the inner liner and one sample was collected from the rinsate being recirculated. Two samples were collected after filtering the rinsate through the inner liner. Three additional samples were collected after the rinsate had passed through the packed column. A final sample was obtained from the 55 gallon mixing barrel after it had been rinsed three times. One solution from the four hour batch demulsification, the recycled rinsate, and the filtered rinsate was neutralized with hydrochloric acid before freezing. The water samples were stored in freezer bags in a freezer, with the exception of the initial solution that was stored in a cold room. Storage blanks and spikes were frozen for analysis with the samples. Each of the water samples were analyzed for pesticide concentration, pH, and conductivity. The pesticide concentration was measured using gas chromatography, pH was determined by a pH meter, and conductivity was determined by a conductivity meter. The atrazine concentration in the rinsate was reduced from an initial 721 mg/kg in step one to 2 mg/kg in the step two

**Table 7. Removal of Atrazine From 35 Gallons of an Aqueous Suspension Using Chemical Destabilization and Sorption (Redesigned Step One)**

Solution	Atrazine Conc. ppm	pH	Conductivity $\mu$ MHO
Initial	721 $\pm$ 319	8.14 $\pm$ 0.67	160 $\pm$ 9
Step One (batch sorption)	13 $\pm$ 2	12.45 $\pm$ 0.03	7127 $\pm$ 340
Step Two (column sorption)	2 $\pm$ 1	4.06 $\pm$ 0.06	197 $\pm$ 13
Container Rinse (step one)	2 $\pm$ 2	9.28 $\pm$ 0.23	158 $\pm$ 13
Tap Water	-----	7.74 $\pm$ 0.12	161 $\pm$ 29
Distilled Water	-----	6.65 $\pm$ 0.2	23 $\pm$ 20
0.00702 N KCl (standard)	-----	-----	1423 $\pm$ 31
<b>Sorbent</b>			
Step One (batch sorption)	4070 $\pm$ 381	11.8 $\pm$ 0.02	-----
Step Two	6555 $\pm$ 272	7.6 $\pm$ 0.0	-----
Total (both steps)	10625 $\pm$ 503	-----	-----

1. Values expressed as the mean  $\pm$  the standard error of the mean, based on 4 replicated experiments

column sorption and filtration phase. This represents an atrazine reduction of 99.72%, in the rinsate, over the entire two step process.

Table 8 provides data on solutions and sorbents obtained from the experimental series on metolachlor. The field experiments on metolachlor were conducted the same as the atrazine experiments, and samples were collected and analyzed in the same manner. The metolachlor concentration in the rinsate was reduced from an initial 704 mg/kg in step one to 30 mg/kg in the step two column sorption and filtration phase. This represents a metolachlor reduction of 95.74%, in the rinsate, over the entire two step process.

These percent reductions are comparable to the reductions obtained from the old system, albeit a bit lower. It should be noted that all of the data for both pesticides and sorbents are not available at the present time. Thus, it is premature to draw any decisive conclusions about the degradation of these two pesticides. However, it is obvious from both Table 7 and Table 8 that the initial concentration of the pesticides is much lower, and the percent reductions are somewhat lower than those examined earlier in this thesis. One possible explanation for the lower removal rates, especially for metolachlor, lies in the use of calcium hydroxide as a demulsification agent. Research conducted by Lynn Hutchinson, 1991, concluded that  $\text{Ca(OH)}_2$  exhibits an inability to demulsify metolachlor. In fact, Hutchinson determined that addition of  $\text{Ca(OH)}_2$  as a demulsifying agent hinders the removal of metolachlor when contacted with peat. This is probably due to the solubilization of humic and fulvic acids, which sorbed the pesticide and held it in solution. Regardless of whether this is the case or not, the low initial concentration itself might

**Table 8. Removal of Metolachlor From 35 Gallons of an Aqueous Suspension Using Chemical Destabilization and Sorption (Redesigned Step One)**

Solution	Metolachlor Conc. ppm	pH	Conductivity $\mu$ MHO
Initial	704 $\pm$ 150	8.57 $\pm$ 0.48	163 $\pm$ 5
Step One (batch sorption)	235 $\pm$ 32	12.47 $\pm$ 0.08	6506 $\pm$ 312
Step Two (column sorption)	30 $\pm$ 14	3.89 $\pm$ 0.18	255 $\pm$ 48
Container Rinse (step one)	2 $\pm$ 2	8.82 $\pm$ 0.39	156 $\pm$ 16
Tap Water	-----	7.73 $\pm$ 0.07	148 $\pm$ 12
Distilled Water	-----	6.68 $\pm$ 0.22	20 $\pm$ 7
0.00702 N KCl (standard)	-----	-----	1335 $\pm$ 17
Sorbent			
Step One (batch sorption)	11497 $\pm$ 433	10.5 $\pm$ 0.6	-----
Step Two	6757 $\pm$ 299	7.7 $\pm$ 0.1	-----
Total (both steps)	18,254 $\pm$ 715	-----	-----

1. Values expressed as the mean  $\pm$  the standard error of the mean, based on 5 replicated experiments

account for the relatively low percent reductions in pesticide observed during these experiments. There is some research that supports the contention that a lower initial pesticide concentration yields lower adsorption rates and thus lower total reductions in pesticide concentration [Senesi, 1994; Kookana, 1992(a)]. However, this is apparently very pesticide and sorbent dependent and it is unclear whether atrazine and metolachlor fall into this category.

Table 9 illustrates an economic analysis of the redesigned equipment for the batch demulsification and sorption system. Not every component of the new system is covered in this analysis; some items such as screws, nuts, bolts, paint, etc., are grouped in a miscellaneous category . The total cost for the new system, as illustrated in Table 9, is approximately \$691, which is considerably less than the \$850 cost estimated for the old system.

**Table 9. Parts Listing and Cost Analysis of the New System**

Components	Cost (\$)
3 pcs. 2 in. x 2 in. x 1/4 in. x 20 ft. bar angle (ASTM A-36)	56
Miscellaneous scrap metal or "drops" (This included 2 in. round stock, 1 in. x 1 in. x 1/8 in. square tubing, and flat plate steel)	50
Miscellaneous hardware (saddles, u-bolts, paint, primer)	29
Cam Couplers: 1-1/2 in.	10
1-1/2 in. Ball Valve	15
3/4 in. Plastic foot/in-line check valve	10
PVC pipe, glue, bushings, nipples, elbows, tees, ball valve, check valve	25
Float Switch (Madison Liquid Level Control #M4300)	14
Relay Switch (Omron G4B Series #G4B112T1FDCUSRPAC120)	8
Hand winch 1000 pound capacity: 4.1:1 gear ratio	26
2 in. Swivel eye pulley rated at 1000 pounds: 3/16 in. cable size	9
2 in. Flat mount pulley rated at 1000 pounds: 3/16 in. cable size	6
3/8 in. slip hook rated at 2650 pounds	5
50 ft. 3/16 in. wire rope	18
Casters (4 rated at 240 pound, 5 in dia.)	75
Gearmotor (1725 to 99 rpm gear reduction)	210
Electrical supplies, bushings, flexible conduit, switch, waterproof switch housings, 3 prong plugs,	55
1/2 in. centrifugal water pump, tygon tubing	70
Total	691

## **Chapter VII**

### **Recommendations**

The following recommendations are proffered for further research in the area of pesticide rinsate bioremediation, clarification of results, and possible improvements to the current system.

1. In order to fairly and reasonably compare the old system to the new system, experiments should be conducted on the same pesticides. This would allow for a legitimate statistical analysis to be performed. Time constraints were the prohibitive factor to doing these experiments for this thesis.

2. At the current time, the results obtained from both the old and new systems in terms of pesticide reduction in the rinsate, actually have very little meaning outside the laboratory. Without some regulatory guidelines governing what level of pesticide is acceptable in the rinsate, there is no way to know if the current results are adequate. Thus,

the regulatory agencies should be prompted to set guidelines as to an acceptable pesticide residual level.

3. The redesigned system is partially automated and requires less operator time than its predecessor. The future of the pesticide rinsate bioremediation system might be a fully automated setup where all the operator needs to do is load and unload the sorbent material.



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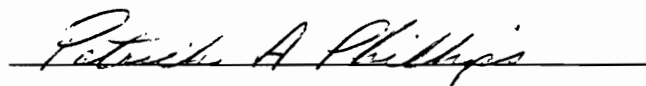
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## Vita

Patrick A. Phillips was born on March 1, 1967 in Radford, Virginia. Among the various positions and jobs he has held are: machinist, carpenter, truck driver, farmer, lumberjack, landscaper, data processor, and salesman. He received a B.S. in Agricultural Engineering from Virginia Polytechnic Institute and State University in 1990. Afterwards, he worked for a year and a half as a structural design engineer for Virginia Frame Builders, Inc. before returning to Virginia Tech in the Fall of 1992 to pursue an M.S. in Agricultural Engineering.

A handwritten signature in cursive script, reading "Patrick A. Phillips", is written over a horizontal line.