

REMOVAL OF MICROORGANISMS AND PROTEINS FROM
SEWAGE AND INDUSTRIAL WASTE WITH
CHLORINATED SOLVENTS

by

Herbert Maxwell Dawson

Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute
in candidacy for the degree of

MASTER OF SCIENCE

in

Sanitary Engineering

August, 1962

Blacksburg, Virginia

LD

5655

V855

1962

D387

c.2

II. TABLE OF CONTENTS

| | Page |
|--|------|
| III. LIST OF TABLES | 4 |
| IV. INTRODUCTION | 5 |
| V. REVIEW OF LITERATURE | 8 |
| VI. OBJECT OF INVESTIGATION | 11 |
| VII. METHODS AND MATERIALS | 12 |
| Reagents | 12 |
| Apparatus and Materials | 15 |
| Key to Suppliers and Manufacturers of Reagents, Materials, and Apparatus | 17 |
| Analytical Methods | 18 |
| Primary Investigation | 18 |
| Screening Investigation | 20 |
| General Experimental Procedure | 21 |
| VIII. RESULTS (PRIMARY INVESTIGATION) | 23 |
| Applicability to Raw Sewage | 23 |
| Applicability to Settled Sewage | 23 |
| Applicability to Settled Trick- ling Filter Effluent | 28 |
| Applicability to Trickling Fil- ter Effluent | 30 |
| Applicability to Sewage Lagoon Effluent | 31 |
| Temperature Effect on Amount of Residue Produced by Extraction of Settled Sewage with a Chlor- inated Solvent | 32 |

| | Page |
|--|------|
| Effect of pH on the Amount of Residue Produced by Extraction of Settled Sewage with a Chlorinated Solvent. . . . | 34 |
| Solvent Extraction Effect on Micro- organisms in Sewage. | 35 |
| IX. RESULTS (SCREENING INVESTIGATION). | 41 |
| Comparison of Different Solvents on Different Wastes | 41 |
| Effect of Per Cent Butanol in Tri- chloroethane-Butane Mixture, on Extraction Performance | 43 |
| X. GENERAL DISCUSSION | 47 |
| XI. CONCLUSIONS. | 55 |
| XII. SUMMARY. | 56 |
| XIII. ACKNOWLEDGEMENTS | 57 |
| XIV. LITERATURE CITED | 58 |
| XV. VITA | 59 |

III. LIST OF TABLES

| | Page |
|---|------|
| Table 1. Results of physical and chemical investigation of solvent extraction as a waste treatment process. | 24 |
| Table 2. Effect of temperature on amount of residue separated by sedimentation with and without extraction | 33 |
| Table 3. Effect of pH on amount of residue separated by sedimentation with and without extraction | 36 |
| Table 4. Effect of solvent on microorganisms in sewage. | 40 |
| Table 5. Comparison of different solvents for treatment of various wastes by extraction | 42 |
| Table 6. Effect of per cent butanol in trichloroethane-butanol mixture, on extraction performance | 45 |

IV. INTRODUCTION

Solvent extraction has been of some interest in the waste treatment field for approximately ten years. However, it has not as yet been developed into a practical waste treatment process.

As early as 1934 Sevag (8) had developed and patented a process for removal of proteins from biological fluids with chlorinated solvents. More recently there has been some use of similar processes in removal of bacteria from fermentation media, virus purification, and protein removal from complex polysaccharides. Because solvents have been used successfully to remove bacteria and proteins from other fluids, it appears that solvents could possibly be used to remove bacteria and proteins from sewage and waste liquids.

Hennigan and Nemerow (5) have made use of solvent extraction in a study of biochemical oxygen demand (B.O.D.) analysis by solvent extraction. However, they were interested in developing a correlation between the five-day B.O.D. and the organic matter extracted by the solvent.

In Standard Methods for the Examination of Water, Sewage, and Industrial Waste (1) solvents are used in the analyses for the presence of grease in water and sewage.

The Robert A. Taft Sanitary Engineering Center (9) has investigated column extraction, of either water from the contaminant or the contaminant from the water, with solvents.

Carbide and Carbon Chemical Company (2) makes reference to the use of one of their organic chloride compounds for depression of solubility in the extraction of antibiotic "bacitracin" from fermentation broths.

Very few sewage and waste treatment effluents are free from microorganisms and proteins. This results in releases that require further treatment by the receiving stream and consequently lower stream quality. The increasing use of sewage lagoons for disposal of sewage and other wastes brings another problem to focus in the waste treatment field. The problem is dispersed algae growth. Contaminated streams and foul smelling sewage ponds are two of the many factors which indicates that present waste treatment processes are inadequate. Because present treatment processes are inadequate and new waste problems are appearing with increasing frequency new processes are needed.

There is a process now in the development stage, known as the "dispersed-growth aeration" process, in which the aerobic microorganisms do not coagulate into floc as they do in conventional biological treatment processes but remain dispersed in the waste liquids. Although this is a very promising process it is not desirable to release these large numbers of bacteria (4). It is possible that a process could be developed either to supplement "dispersed-growth aeration" or to improve conventional waste treatment by superior

removal of proteins and microorganisms at a key point in the treatment cycle by using a solvent extraction operation.

Previous use of solvent extraction in industrial waste treatment proved to be too expensive unless a valuable by-product could be extracted and reused (4). If a process is to be feasible in sewage and waste treatment it would have to be highly efficient and relatively inexpensive. Although previous solvent extraction processes have been too expensive and impractical for sewage and waste treatment, they have some qualities which indicate that a practical waste treatment process could be developed. Some of these qualities are: a) the coagulation of bacteria, b) the removal of proteins from biological fluids, and c) the extraction of fats. If an inexpensive solvent could be found that would produce efficient bacterial, grease, and protein removal by mixing and settling then a practical waste treatment process could possibly be developed.

V. REVIEW OF LITERATURE

Chlorinated hydrocarbons have been used for the removal of greases and proteins from sewage, and solvent extraction has been used in industrial waste treatment for some time, but neither process has been used very extensively or economically on a treatment plant scale (4).

Sevag (8), 1934, developed and patented a process for the removal of proteins from biological fluids. Sevag's process seems to be a good process for removing proteins on a small scale, but it appears that no attempt has been made to apply the process to protein removal from sewage or other waste on a large or small scale. The process as briefly described in the article cited would be too expensive for removing protein material from sewage and waste. The end effect produced would not justify the cost of freezing and centrifuging the waste to separate the solvent and protein material from the liquid portion.

Hennigan and Nemerow (5) have made use of solvent extraction in trying to shorten the time required to make B.O.D. analysis on waste material. Although they used seven different solvents, two of which were chlorinated, no reference was made of bacterial coagulation with the chlorinated solvents. Because Hennigan and Nemerow were trying to correlate the organic material removed by extraction to the

five-day B.O.D. of the waste, their methods were small scale and not adaptable to a treatment plant scale.

Rudolfs (7) reported that plant experiences indicated that small batches of spent solvents caused fluctuations in gas production and repeated discharges retarded greatly or may inhibit the sludge digestion process. He also stated that some solvents in concentrations of ten parts per million retarded gas production as much as fifty per cent in the sludge digestion process.

Carbide and Carbon Chemical Company (2) cited the use of one of their organic chloride compounds as a solubility depressant in the extraction of antibiotic "bacitracin" from fermentation broths.

Standard Methods for the Examination of Water, Sewage, and Industrial Waste (1) makes use of solvents for the analysis of greases in water, sewage, and waste; but the methods used are analytical and wouldn't be economical on a treatment plant scale.

The Robert A. Taft Sanitary Engineering Center (9) reports on the use of solvents in column extraction. The contaminant is either extracted from the water or the water from the contaminant. The investigators think that the solvents produce a greater contamination problem than the contaminants being removed, but they admit that solvent

extraction has a possibility of developing into a useable process if a solvent can be found that produces good extraction without contamination. No reference was made to studies of solvent extraction on sewage or waste in the Taft Center investigation.

Davison, Smith, and Hood (3) consider temperature to be an important variable in desalination by solvent extraction. Studies were made with selective solvents and temperature was considered very important.

VI. OBJECT OF INVESTIGATION

The object of this investigation was to evaluate chlorinated solvent processes for the removal of microorganisms, proteins, and other substances from sewage and other wastes.

VII. METHODS AND MATERIALS

Reagents*

Ammonium Chloride, (NH_4Cl), (General). Used to make up phosphate buffer solution for B.O.D. dilution water.

Ammonium Oxalate, ($\text{NH}_4\text{NH}_4\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$), (General). Used in making gram stains.

Asbestos, (fiber materia), (Baker). Used for filter mats in gooch crucibles.

1-Butanol, ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\text{OH}$), (Certified), (Fisher), Used in a solvent mixture.

Calcium Chloride, (Anhydrous), ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), (Baker). Used in making up calcium chloride solution for B.O.D. dilution water.

Calcium Hydroxide, ($\text{Ca}(\text{OH})_2$), (Baker). Used in varying pH.

Carbon Tetrachloride, (CCl_4), (Certified), (Fisher). Used as a solvent.

Chlorobenzene (Mono), ($\text{C}_6\text{H}_5\text{Cl}$), (Certified), (Fisher). Used as a solvent.

Chloroform, (CHCl_3), (Certified), (Fisher). Used as a solvent.

Crystal Violet, (National). Dye used in gram stains.

*Chemicals were C.P. grade unless otherwise noted.

Dichlorisopropyl Ether, (Union Carbide). Used as a solvent.

Ethylene Dichloride, $(\text{CH}_2\text{Cl})_2$, (General). Used as a solvent.

Ferric Chloride, $(\text{FeCl}_3 \cdot 6\text{H}_2\text{O})$, (General). Used in ferric chloride solution for B.O.D. dilution water.

Ferrous Ammonium Sulfate, $(\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2 \cdot 6\text{H}_2\text{O})$, (Baker). Used as titration agent in C.O.D. analysis.

Immersion Oil, (Fisher). Used in making microscopic examinations of gram stains.

Iodine, (Crystals), (I_2) , (General). Used in making gram stains.

Iron Sulfate, $(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})$, (General). Used in making ferrion indicator solution for C.O.D. analysis.

Magnesium Sulfate, $(\text{MgSO}_4 \cdot 7\text{H}_2\text{O})$, (Baker). Used in magnesium sulfate solution for B.O.D. dilution water.

Manganous Sulfate, $(\text{MnSO}_4 \cdot 7\text{H}_2\text{O})$, (Baker). Used in manganous sulfate solution for B.O.D. dilution water.

Nutrient Agar, (Difco). Used as medium for plate counts.

O-Phenanthroline, (Monohydrate), (Fisher). Used in making ferrion indicator solution for C.O.D. analysis.

Potassium bio-iodate, $(\text{KH}(\text{IO}_3)_2)$, (Smith). Used as a standardization agent for thiosulfate.

Potassium Dichromate, $(\text{K}_2\text{Cr}_2\text{O}_7)$, (Baker). Used as a standardization agent in the C.O.D. analysis.

Potassium Dihydrogen Phosphate, (KH_2PO_4), (Baker).

Used in buffer solution for dilution water for both plate count blanks and B.O.D. dilution water.

Potassium Iodide, (KI), (General). Used in alkalide iodide reagent for B.O.D. analysis.

Potassium Phosphate, Secondary, (K_2HPO_4), (Fisher).

Used in phosphate buffer solution for dilution water in B.O.D. analysis.

Proprietary Solvent, Cat. No. A 407, (Fisher). Used in making up dyes and also for 95 per cent alcohol solution for gram stains.

Safranin, (dye) (National). Used in making gram stains.

Silver Sulfate, (Crystals), (Ag_2SO_4), (Baker). Used as a catalyst in C.O.D. analysis.

Sodium Hydroxide, (NaOH), (Certified), (Fisher). Used in making alkalide iodide reagent for B.O.D. analysis.

Sodium Phosphate (dibasic heptahydrate), ($\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$), (Baker). Used in phosphate buffer solution for B.O.D. dilution water.

Sodium Thiosulfate, ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), (General). Used as titration agent in B.O.D. analysis.

Starch, (Potato Powder), (General). Used as an indicator in B.O.D. analysis.

Sulfuric Acid, (Concentrated), (H_2SO_4), (Fisher). Used in B.O.D., C.O.D. analysis and to adjust pH of samples.

Trichloroethane, (Technical), (Fisher). Used as a solvent.

Apparatus and Materials

Analytical Balance, (Satorius). Used to determine weights in suspended solids, residue, and settleable solids analysis.

Autoclave, (Will). Used to sterilize media for plate counts.

Beam Balance, (Ohaus), (Will). Used to determine weights of reagents put into mixtures.

Bibulous Paper, (Fisher). Used in making gram stains.

Darkfield Quebec Colony Counter, (American). Used in making colony counts of organisms plated on nutrient agar.

Desiccator, (Fisher). Used for cooling sample when removed from oven or furnace.

Hot Air Oven, (Despatch). Used to sterilize glassware for bacteriological investigation.

Incubator, (20°C), (Precision). Used to incubate B.O.D. samples.

Incubator, (35°C), (Will). Used to incubate agar plates in bacteriological investigation.

Incubation bottles, (300 ml.), (Fisher). Used for dilution and incubation of samples in B.O.D. analysis.

1-liter graduates and 1-liter bottle. Used as mixing and settling chambers.

Microscope, (No. LM3741), (Bausch). Used to examine gram stains.

Oven, (103°C), (Precision). Used to dry samples to constant weight in suspended solids, and residue determinations.

p.H. Meter, (glass electrode, Model N), (Beckman). Used to measure pH of samples.

Pittsburgh Non-Corrosive Microscopic Slides, (Fisher). Used in making gram stains.

Reflux Apparatus, six unit (Vari Heat) electric hot plate with manifold of six condensers attached. (Precision). Used to reflux C.O.D. samples.

Slide Box, (Adams). Used for filing gram stain slides.

Steam Bath Evaporator (eight unit), (Fisher). Used for evaporating samples in residue determinations.

Stereoscope (No. WP 7854), (Bausch). Used in examining colonies on agar plates.

Temco Electric Furnace, (Fisher). Used for ashing samples in suspended solids and residue analyses.

Torsion Balance, (Torsion). Used to weigh part of the reagents used.

Vacuum Pump, (Will). Used to filter suspended solids samples.

Key to Suppliers and Manufacturers of
Reagents, Materials, and Apparatus

(Adams). Clay Adams Company, Inc.

(American). American Optical Company; Scientific Instrument Division, Buffalo, New York.

(Baker). J. T. Baker Chemical Company; Phillipsburg, New Jersey.

(Bausch). Bausch & Lomb Optical Company; Rochester, New York.

(Beckman). Beckman Instruments, Inc.; South Pasadena, California.

(Despatch). Despatch Oven Company; Minneapolis, Minnesota.

(Difco). Difco Laboratories, Inc.; Detroit, Michigan.

(Fisher). Fisher Scientific Company; Pittsburgh; New York; St. Louis; Washington; Montreal; Toronto.

(General). General Chemical Division, Allide Chemical and Dye Corp.; New York, New York.

(National). National Aniline and Chemical Company, Inc.; New York, New York.

(Precision). Precision Scientific Company; Chicago, Illinois.

(Sartorius). Sartorius-Werke; Made in Germany.

(Smith). G. Fredrick Smith Chemical Company; Columbus, Ohio.

(Torsion). The Torsion Balance Company; Clifton, New Jersey.

(Union Carbide). Union Carbide Chemical Company; Division of Union Carbide Corp.; New York 17, New York.

(Will). Will Corporation; Rochester, New York.

Analytical Methods

Primary Investigation. Samples of flow from different points in the sewage treatment plant were mixed in a graduate with a definite volume of a chlorinated solvent. The volume of solvent mixed with the samples was five per cent of the volume of the sample. Mixing was obtained by making thirty inversions of the graduate containing the sample and the solvent. After mixing the mixture was settled in the graduate under quiescent conditions for a specified length of time. A blank consisting of the specific waste sample being analysed with no solvent added was processed along with the waste sample containing the solvent. After settling the supernatant was siphoned off with a rubber tube. Care was exercised in siphoning off the supernatant so that a major portion of the liquid was removed without disturbing the settled residue. The residue including scum, sludge, a major volume

of the solvent, and a small volume of supernatant was transferred to an ignited and tarred evaporation dish and evaporated to dryness. Evaporation was performed on a steam bath evaporator under a ventilation hood. After evaporation of the liquid the evaporation dish was transferred to a 103°C oven and dried to constant weight. Following drying the dish and residue were cooled in a desiccator and weighed. The residue in the evaporation dish was then ashed in a 600°C furnace, cooled, and reweighed to determine the ash content. When transferring the residue from the settling chamber to the evaporation dish, approximately the same volume of material was transferred each time. This was to compensate for the solids in the supernatant transferred to the evaporation dish with the residue.

In determination of suspended solids, total solids, chemical oxygen demand (Dichromate Reflux Method), (C.O.D.) biochemical oxygen demand (B.O.D.) and the standard plate count analyses; the procedures followed were the procedures specified by Standard Methods for the Examination of Water, Sewage, and Industrial Waste (1) for sewage; with the modifications as stated below.

1. In the C.O.D. analysis the samples that were mixed with a solvent were boiled until approximately one-half of original volume had evaporated, to remove dissolved solvent,

and rediluted to original volume with distilled water.

2. In the B.O.D. analysis the samples that were mixed with a solvent were boiled until approximately one-half of original volume had evaporated, to remove the dissolved solvent, and rediluted to original volume with distilled water. When the dilutions were made with the boiled-down samples one milliliter of settled primary sewage was added to each dilution bottle for reseed. Three-hundred milliliter B.O.D. incubation bottles were used for diluting and incubating the B.O.D. samples. The dilution water used was seeded with three milliliters of settled primary sewage per liter of dilution water. Dissolved oxygen determinations were made using the Aesterberg (Azide) Modification of the Winkler Method.

3. In the standard plate count analysis nutrient agar was used as the growth medium.

Screening Investigation. In this investigation different solvents were added to different waste samples containing suspended solids. The waste sample and solvent were mixed and allowed to settle for 1.5 hours. Three settling chambers were set up for each waste and solvent. One chamber contained the solvent and the waste sample. Another chamber contained waste sample, solvent, and 200 mg/l. of lime. The third chamber contained waste sample, solvent, and 200

mg/l. of sulfuric acid. Three blank settling chambers were set up for each different waste sample analysed. One blank chamber consisted of the waste sample, another consisted of the waste sample and 200 mg/l. of lime and the third consisted of the waste sample and 200 mg/l. of sulfuric acid. Mixing was accomplished with thirty inversions of the mixing and settling chambers. One liter bottles were used as mixing and settling chambers instead of one-liter graduates. Residue determinations were performed according to the procedure described in the primary investigation section.

General Experimental Procedure. In making this thesis investigation the procedures used in performing the extractions were limited to operations that could be reasonably performed on a treatment plant scale.

The general experimental procedure used in the primary investigation was:

1. Obtain sample.
2. Add solvent and mix.
3. Allow mixture to settle.
4. Siphon off supernatant.
5. Evaporate, dry, and weigh residue.
6. Determine ash content and calculate volatile matter in residue.

7. Make suspended solids, total solids, C.O.D., B.O.D., standard plate count, and gram stain analysis on some samples.

The general experimental procedure used in the screening investigation was:

1. Obtain sample; check pH and temperature.
2. Dose with 200 mg/l. of lime or sulfuric acid.
3. Add solvent and mix.
4. Allow mixture to settle.
5. Siphon off supernatant.
6. Evaporate, dry and weigh residue.
7. Determine ash content and calculate the volatile matter in the residue.
8. Check pH of supernatant.

VIII. RESULTS (PRIMARY INVESTIGATION)

The purpose of this investigation was to obtain a mass of physical and chemical data that would help to evaluate a chlorinated solvent process for the removal of suspended matter in different wastes.

Applicability to Raw Sewage

Raw sewage was investigated because it is a common type of waste containing suspended solids and bacteria.

The modifications made in the general procedure described under Analytical Methods were as follows:

1. The solvent used was ethylene dichloride.
2. The volume of sample used was 500 milliliters.
3. The settling time used was seven hours.

The results from the raw sewage investigation are presented in Table 1. The raw sewage results indicated that more residue settled from raw sewage without the addition of ethylene dichloride than with the addition of ethylene dichloride. Since the results indicated little promise for the process, experimentation with this waste was discontinued.

Applicability to Settled Sewage

Settled sewage was investigated because it contains fewer solids than raw sewage. Because the settled sewage contained

Table 1: Results of physical and chemical investigation of solvent extraction as a waste treatment process.

| Type Waste | Series | Description of Sample | T E S T | | | | | | | | | Comments | | |
|-----------------------------------|-----------------------------|---|--------------------------|-----------------|----------------|-----------------------------|-------|------------------|-------------------|---------------------------|---------------------|----------|-----------------------------------|---|
| | | | Suspended Solids (mg/l.) | | | Residue Settled Out (mg/l.) | | | C.O.D. (mg/L) | 5-day-20°C B.O.D. (mg/l.) | Total Solids (mg/L) | | | |
| | | | Total | Vola. | Ash | Total | Vola. | Ash | | | Total | | Vola. | Ash |
| Raw Sewage | A | Blank | -1 | - | - | 181 | 140 | 41 | - | - | - | - | - | Samples were settled for 7 hours. |
| | | Sample+5% Ethylene Dichloride | - | - | - | 64 | 42 | 22 | - | - | - | - | - | |
| Settled Sewage | A | Blank | 150 | - | - | - | - | - | 241 | 128 | - | - | - | Samples were settled for 3 hours. |
| | | Sample+5% CHCl ₃ | 12 | - | - | 106 | - | - | 1525 ^b | 137 ^a | - | - | - | |
| | | Distilled H ₂ O - 5% CHCl ₃ | - | - | - | 3 | 3 | 0 | 930 ^c | - | - | - | - | |
| | B | Blank | 43 | - | - | - | - | - | 321 | - | - | - | - | Serial extracted. Three extractions, 1 hour each. |
| | | Sample+5% CHCl ₃ | 0 | - | - | 38 | - | - | 1000 ^a | - | - | - | - | |
| | C | Blank | 75 ^f | 72 ^f | 3 ^f | 63 | 39 | 24 | 264 | 171 | 473 | 232 | 241 | Samples were settled for 3 hours. |
| | | Blank boiled (h) | - | - | - | - | - | - | 260 ^c | 115 ^c | - | - | - | |
| | | Sample+5% CHCl ₃ | 10 ^f | 9 ^f | 1 ^f | 74 | 54 | 20 | 182 ^h | 129 ^h | 437 | 237 | 200 | |
| | D | Blank | 90 | 45 | 45 | - | - | - | - | - | 414 | 166 | 248 | Samples were settled for 1 hour. |
| | | Sample+5% CHCl ₃ | 15 ^c | 15 ^c | 0 ^c | 48 | 37 | 11 | - | - | 377 | 137 | 240 | |
| E | Blank | 92 | 84 | 8 | 42 | 22 | 20 | 202 | 96 ^d | - | - | - | Samples were settled for 4 hours. | |
| | Sample+5% CHCl ₃ | 31 | 30 | 1 | 83 | 57 | 26 | 153 ^h | 45 ^{e,h} | - | - | - | | |
| Settled Trickling Filter Effluent | A | Blank | 11 ^c | 11 ^c | 0 ^c | - | - | - | - | - | 334 | 96 | 238 | Samples were settled for 1 hour. |
| | | Sample+5% CHCl ₃ | 3 | 3 | 0 | 25 | 16 | 9 | 1375 ^a | - | 302 | 82 | 220 | |
| | B | Blank | 18 ^f | 17 ^f | 1 ^f | - | - | - | 128 ^c | 15 | - | - | - | Samples were settled for 3 hours. |
| | | Sample+5% CHCl ₃ | 0 ^c | 0 ^c | 0 ^c | 41 | 25 | 16 | - | - | 324 | 131 | 193 | |
| | C | Blank | 10 | 9 | 1 | - | - | - | 82 | 26 ^g | - | - | - | Samples were settled for 4 hours. |
| | | Sample+5% CHCl ₃ | - | - | - | - | - | - | 73 ^h | 9 ^{g,h} | - | - | - | |
| Trickling Filter Effluent | A | Blank | - | - | - | 42 | 20 | 22 | - | - | - | - | - | Samples were settled for 7 hours. |
| | | Sample+5% Ethylene Dichloride | - | - | - | 35 | 19 | 16 | - | - | - | - | - | |
| Sewage Lagoon Effluent | A | Blank | 18 | - | - | 37 | 21 | 16 | - | - | - | - | - | Samples were settled for 7 hours. |
| | | Sample+5% Ethylene Dichloride | 20 | - | - | 30 | 17 | 13 | - | - | - | - | - | |

- a) Sample was brought to a boil in an attempt to remove CHCl₃.
- b) No attempt was made to remove CHCl₃ from sample.
- c) Average of two valves.
- d) Average of six valves.
- e) Average of seven valves.

- f) Average of three valves.
- g) Average of four valves.
- h) Sample boiled down to 1/2 original volume to remove dissolved CHCl₃ and rediluted to original volume.
- i) "-" No analyses made.

fewer solids than the raw sewage, better results were expected from the solvent extraction process with this waste than was obtained with the process on raw sewage.

The modifications made in the general procedure described under Analytical Methods were as follows:

Series A:

1. The solvent used was chloroform.
2. The volume of sample used was one liter.
3. The settling time employed was three hours.
4. When making C.O.D. analyses no attempt was made to remove dissolved chloroform from C.O.D. samples that had been solvent extracted.

5. The B.O.D. samples containing dissolved chloroform were only brought to a brief boil in an attempt to remove the chloroform.

6. A check sample consisting of one liter of distilled water and fifty milliliters of chloroform was analysed.

Series B:

1. The solvent used was chloroform.
2. The volume of sample used was one liter.
3. The samples were serial extracted using three extractions. The procedure for the serial extraction was as follows. One per cent of chloroform was mixed with one liter of settled sewage and allowed to settle for one hour. The

supernatant from the first extraction was transferred to another graduate, mixed with two per cent of chloroform, and allowed to settle for another hour. The supernatant from the second extraction was transferred to a third graduate, mixed with two per cent of chloroform, and allowed to settle for an hour. The residues from the three extractions were combined.

4. When making the C.O.D. analyses no attempt was made to remove the dissolved chloroform from the samples that had been solvent extracted.

Series C:

1. The solvent used was chloroform.
2. The volume of sample used was one liter.
3. The settling time used was three hours.
4. Samples of settled sewage were boiled until approximately one-half the original volume had evaporated and then rediluted to original volume with distilled water.

Series D:

1. The solvent used was chloroform.
2. The sample volume used was one liter.
3. The settling time used was one hour.

Series E:

1. The solvent used was chloroform.
2. The volume of sample used was one liter.

3. The settling time used was four hours.

The results from the settled sewage investigation are presented in Table 1, page 24. The results indicated that chloroform extraction in conjunction with settling produced an average suspended solids removal of eighty-four per cent. Seventy-three per cent of the suspended solids removed were volatile. The average residue that settled out with the chloroform was 70 mg/l. as compared to 53 mg/l. for the sample settled without chloroform. The total solids of a sample settled with chloroform was 36 mg/l. less than the total solids of a sample settled without chloroform. The average C.O.D. of two samples settled without chloroform was 233 mg/l. as compared to 167 mg/l. for a sample settled with chloroform. The results also showed that dissolved chloroform in the C.O.D. samples greatly increased the C.O.D. of the sample. The C.O.D. of a sample of supernatant taken from a settled mixture of distilled water and five per cent of chloroform was 930 mg/l. The dissolved chloroform in the B.O.D. samples caused variable results if it was incompletely removed before making the B.O.D. analyses. All of the dissolved chloroform apparently was not removed by just bringing the sample to a brief boil because such samples had very high C.O.D.'s. A major portion of the dissolved chloroform appeared to be removed from the samples by boiling away one-half of

the original volume of the sample. Evaporation of the sample had no material effect on the magnitude of the C.O.D. or B.O.D. as compared to unevaporated samples.

The results from the settled sewage investigation indicated that chloroform was not too effective for extracting material from the settled sewage. Although the suspended solids removal appeared to be relatively good the C.O.D., B.O.D., and total solids results failed to verify the suspended solids removal.

Applicability to Settled Trickling

Filter Effluent

Settled trickling filter effluent was investigated because it is a common waste and has very little suspended matter in it.

The modifications made in the general procedure described under Analytical Methods were as follows.

Series A:

1. The solvent used was chloroform.
2. The samples volume used was one liter.
3. The settling time used was one hour.
4. When making the C.O.D. analyses no attempt was made to remove the dissolved chloroform from the C.O.D. sample that was chloroform extracted.

Series B:

1. The solvent used was chloroform.
2. The volume of sample used was one liter.
3. The settling time used was three hours.

Series C:

1. The solvent used was chloroform.
2. The volume of sample used was one liter.
3. The settling time used was four hours.

The results from the investigation on settled trickling filter effluent are presented in Table 1, page 24. The results indicated that chloroform extraction in conjunction with settling produced an average suspended solids reduction of eighty-five per cent, and that approximately ninety-two per cent of the reduced suspended solids were volatile. The average amount of residue that settled out with the chloroform was approximately three times the average suspended solids removed. The chloroform extraction in conjunction with settling resulted in an average C.O.D. reduction of thirty per cent and an average B.O.D. reduction of fifty-five per cent. The average total solids reduction effected by extraction and settling was approximately equal to the average amount of suspended solids removed by the same process.

The settled trickling filter effluent investigation results indicated that the chloroform extraction and settling

processes were about as effective in removing material from settled trickling filter effluent as it was in removing material from settled sewage. Again the C.O.D. and B.O.D. reductions produced by the processes did not verify the good suspended solids reductions realized with the same processes. However, the residue and total solids results indicated that the solids concentration of the settled trickling filter effluent had been reduced by an amount equal or greater than the amount of suspended solids that appeared to be removed from the effluent.

Applicability to Trickling
Filter Effluent

Trickling filter effluent was investigated because it is a common waste and has suspended matter composed of biological cell substance that should be easily extractable with a solvent extraction process.

The modifications made in the general procedure described under Analytical Methods were as follows.

1. The solvent used was ethylene dichloride.
2. The sample volume used was 500 milliliters.
3. The settling time used was seven hours.

The results from the trickling filter effluent investigation are presented in Table 1, page 24. The trickling

filter results indicated that ethylene dichloride did not improve the settleability of suspended matter in the trickling filter effluent. Since the results indicated little promise for the process, experimentation with this waste was discontinued.

Applicability to Sewage Lagoon Effluent

Sewage lagoon effluent was investigated to determine if the chlorinated solvent extraction process would remove the dispersed algae in the lagoon effluent.

The modifications made in the general procedures described under Analytical Methods were as follows.

1. The solvent used was ethylene dichloride.
2. The sample volume used was 500 milliliters.
3. The settling time used was seven hours.

The results from the sewage lagoon effluent investigation are presented in Table 1, page 24. The suspended solids and residue results from the sewage lagoon effluent investigation showed that ethylene dichloride did not extract the dispersed algae growth in the lagoon effluent. Since the results indicated little promise for the process, experimentation with this waste was discontinued.

Temperature Effect on Amount of Residue Produced by
Extraction of Settled Sewage with a
Chlorinated Solvent

The purpose of this investigation was to determine if variations in the temperature of the sample would produce a noticeable change in the amount of residue that was settled out with the chlorinated solvent extraction process.

Previous investigations in this study indicated that the chlorinated solvent extraction processes were of limited effectiveness in removing suspended material from settled sewage. Since temperature is known to effect extraction efficiency, the effect of sample temperature on the extraction process efficiency was investigated.

The modifications made in the general procedure described under Analytical Methods were as follows.

1. The sample volume used was 100 milliliters.
2. The solvent used was chloroform.
3. The settling time used was fifty-two hours.
4. The different temperatures that samples and blanks were settled at were; (a) 8° C, (b) 20° C, and (c) 35° C.

The results of the investigation of temperature effect on the solvent extraction process are presented in Table 2. The results showed that much more material was extracted

Table 2: Effect of temperature on amount of residue separated by sedimentation with and without extraction.

| Description of Sample ^a | Temperature (°C) | Settling Time (Hr) | Residue Settled Out (mg/l.) | | |
|------------------------------------|------------------|--------------------|-----------------------------|----------|-----|
| | | | Total | Volatile | Ash |
| S. Sewage ^b | 8 | 52 | 99 | 68 | 31 |
| S. Sewage + 5% CHCl ₃ | 8 | 52 | 87 | 71 | 16 |
| S. Sewage | 20 | 52 | 38 | 78 | 0 |
| S. Sewage + 5% CHCl ₃ | 20 | 52 | 118 | 94 | 24 |
| S. Sewage | 35 | 52 | 53 | 38 | 15 |
| S. Sewage + 5% CHCl ₃ | 35 | 52 | 89 | 60 | 29 |

a) Samples were settled in 100 ml. graduates.

b) S. Sewage = Settled Sewage.

from settled sewage with chloroform when the temperature of the sample was 20° C than was extracted when the temperature of the sample was 8° C or 35° C.

The results were not too conclusive because the sample volume analysed was insufficient to produce completely reliable results. However, the temperature range of all the waste samples used in the entire investigation was from 22° C to 27° C, so temperature was not considered to be the reason for poor extraction efficiencies of the solvent processes.

Effect of pH on the Amount of Residue Produced by
Extraction of Settled Sewage
with a Chlorinated Solvent

The level of pH is known to affect the efficiency of extraction processes. A series of experiments were made to evaluate the effect of pH on the performance of the chlorinated solvent process.

The modifications made in the general procedure described under Analytical Methods were as follows.

1. The waste used was settled sewage.
2. The solvent used was chloroform.
3. The sample volume used was 500 milliliters.
4. The volume of the two blanks was one liter rather than 500 milliliters.

5. The settling time used was fifteen hours with the exception that the blank at pH 12.0 was settled for twenty-four hours.

6. The pH range investigated was from 2.0 to 12.0.

7. Sulfuric Acid and sodium hydroxide were used to adjust the pH of the samples.

The results from the pH investigation are presented in Table 3. The results indicated that approximately 300 mg/l. more solids were extracted by the chloroform in the sample with pH at 12.0 than were settled from the blank at the same pH, with no chloroform added.

The results from the pH investigation showed that samples that were very alkaline were extracted much more effectively with the chloroform extraction process than samples that were neutral or acid. Although good extraction was produced at a pH of 12.0, the alkaline condition was not desirable to have in a waste treatment process, so no further investigations were made at high pH conditions.

Solvent Extraction Effect on Microorganisms in Sewage

The poor extraction efficiencies produced by the chlorinated solvent extraction process in previous investigations of this study indicated that the solvent was not extracting

Table 3: Effect of pH on amount of residue separated by sedimentation with and without extraction.

| Description of Sample | pH | Settling Time (Hr) | Residue Settled Out (mg/l.) | | |
|---|-------|--------------------|-----------------------------|----------|-----|
| | | | Total | Volatile | Ash |
| S. Sewage ^a | 12.0 | 24 | 337 | 100 | 237 |
| S. Sewage | 7.1 | 15 | 93 | 47 | 46 |
| S. Sewage ^b + 5% CHCl ₃ | 2.0 | 15 | 85 | 58 | 27 |
| S. Sewage + 5% CHCl ₃ | 3.0 | 15 | 48 | 24 | 24 |
| S. Sewage + 5% CHCl ₃ | 6.0 | 15 | 84 | 51 | 33 |
| S. Sewage + 5% CHCl ₃ | 7.1 | 15 | 87 | 57 | 30 |
| S. Sewage + 5% CHCl ₃ | 9.2 | 15 | 73 | 43 | 30 |
| S. Sewage + 5% CHCl ₃ | 110.2 | 15 | 105 | 48 | 57 |
| S. Sewage + 5% CHCl ₃ | 12.0 | 15 | 631 | 92 | 539 |

a) S. Sewage = Settled Sewage. Settling was in one-liter graduates.

b) Settled sewage sample with CHCl₃ added was settled in 500 ml. graduates.

all of the microorganisms from the waste liquids. Therefore, several bacteriological analyses were made to determine the extent of removal of bacteria.

The modifications made in the general procedure described under Analytical Methods for making the bacteriological investigation were as follows.

Standard Plate Count:

1. Settled sewage was plated on nutrient agar growth medium using the following dilutions; (1) $1:10^3$, (2) $1:10^4$, (3) $1:10^5$.

2. Settled sewage that had been solvent extracted was plated on nutrient agar medium using the following dilutions; (1) $1:10$, (2) $1:10^2$, (3) $1:10^3$.

3. Settled trickling filter effluent was plated on nutrient agar medium using the following dilutions; (1) $1:10$, (2) $1:10^2$, (3) $1:10^3$.

4. The plated samples were incubated for twenty-four hours at 35° C.

Gram Stains:

1. Slide smears were made of the following waste samples:

- a. Supernatant and sludge of settled raw sewage.
- b. Supernatant and sludge of extracted and settled raw sewage.

- c. Supernatant and sludge of resettled, settled sewage.
- d. Supernatant and sludge of extracted and resettled, settled sewage.

2. The slide smears were stained according to the following procedure (6).

- a. Crystal violet was applied to fixed smear for one minute.
- b. Then fixed smear was washed with tap water.
- c. Following washing iodine solution was applied to smear for one minute.
- d. Fixed smear was again washed with tap water, then blotted dry.
- e. Following second washing the smear was discolored for 30 seconds in a 95 per cent solution of ethanol.
- f. After discolorizing smear was blotted dry.
- g. The final steps were counterstaining for ten seconds with safarin, washing in tap water and blotting dry.

Interpretation: Gram-positive bacteria stained dark blue. Gram-negative bacteria stained red.

3. Stains were observed under an oil immersion objective of a microscope.

The results from the bacteriological investigation are presented in Table 4. The results showed that all of the microorganisms were not extracted with chlorinated solvent process but a substantial removal was indicated.

Table 4: Effect of solvent on microorganisms in sewage.

| Type Waste | Description of Sample | T E S T | | | Gram Stains Description of organisms (size, shape, stain) |
|---|-----------------------|-------------------|------------------|---------------------------|---|
| | | Plate Counts | | | |
| | | Dilution factor | Colonies Counted | Organisms per Milli-liter | |
| Raw Sewage | Supernatant | - | - | - | Small spheres, in pairs, gram - negative. |
| | | - | - | - | Large spheres, in pairs, gram - negative. |
| | | - | - | - | Rods, large and small, in chains and separate, gram - positive. |
| | Sludge | - | - | - | Small spheres in pairs, and separate, gram - negative. |
| | | - | - | - | Small rods in chains, gram - negative. |
| | | - | - | - | Large single spheres, gram - positive. |
| Raw Sewage (Settled with a Solvent) | Supernatant | - | - | - | Large rods in chains, gram - positive. |
| | | - | - | - | Same as raw sewage except fewer organisms present. |
| | | - | - | - | Same as raw sewage except more organisms present. |
| | Sludge | - | - | - | Same as raw sewage except more organisms present. |
| | | - | - | - | Same as raw sewage except more organisms present. |
| | | - | - | - | Same as raw sewage except more organisms present. |
| Settled Sewage | Supernatant | 1/10 ³ | 660 | 660,000 | Large rods in chains, gram - positive. |
| | | 1/10 ⁴ | 1080 | 10,000,000 | Large rods in pairs, gram - positive. |
| | | 1/10 ⁵ | 2700 | 270,000,000 | Small spheres, in pairs and chains, gram - negative. |
| | Sludge | - | - | - | Large and small spheres in pairs and chains, gram - positive. |
| | | - | - | - | Small spheres and rods in chains and separate, gram - negative. |
| | | - | - | - | Same as settled sewage except fewer organisms present. |
| Settled Sewage (Settled with a solvent) | Supernatant | 1/10 | 34 | 340. | Same as settled sewage except fewer organisms present. |
| | | 1/10 ² | 1800 | 180,000 | Same as settled sewage except fewer organisms present. |
| | | 1/10 ³ | 240 | 240,000 | Same as settled sewage except fewer organisms present. |
| | Sludge | - | - | - | Same as settled sewage except more organisms present. |
| | | - | - | - | Same as settled sewage except more organisms present. |
| | | - | - | - | Same as settled sewage except more organisms present. |
| Settled Trickling Filter Effluent | Supernatant | 1/10 | 13,500 | 135,000 | - - - |
| | | 1/10 ² | 4320 | 432,000 | |
| | | 1/10 ³ | 102 | 102,000 | |

IX. RESULTS (SCREENING INVESTIGATION)

Comparison of Different Solvents on Different Wastes

The purpose of this solvent screening investigation was to determine if one particular chlorinated solvent produced better extraction than others. The purpose for investigating different wastes was to determine if the chlorinated solvent process produced better extraction on some wastes than on others.

The results from the solvent screening investigation are presented in Table 5. The results showed that the solvent mixture of 80 per cent chloroform and 20 per cent butanol in conjunction with 200 mg/l. of lime produced on an average better extraction than the other solvents investigated. Trichloroethane appeared to produce fairly good extraction of the waste samples settled with it. Dichlorisopropyl ether accomplished reasonably good extraction of settled sewage. The results also showed that solvent extraction was not effective on effluent from the aeration tank of an activated sludge treatment plant. The lime dosage of 200 mg/l. increased the residue that settled from the waste samples without the aid of a solvent. Two-hundred mg/l. of lime was effective in increasing the amount of residue extracted from

Table 5: Comparison of different solvents for treatment of various wastes by extraction.

| Description of Sample | S O L V E N T | | | | | | | | | | | | | | | | | | Blanks Samples with no solvents added | | | | | | | | |
|---|---|------|------|-----------------------|------|------|-----------------------------------|------|------|----------------------|------|------|------------------|------|------|------------------|------|------|---------------------------------------|------|-----|------|--|--|-----|--|--|
| | Ethylene Dichloride | | | Carbon Tetra-chloride | | | 80-20% Mixture Chloroform-Butanol | | | Chlorobenzene (mono) | | | Trichloro-ethane | | | Dichlorisopropyl | | | | | | | | | | | |
| | Residue Settled out in 1.5 hours Settling (mg/l.) | | | | | | | | | | | | | | | | | | Tot. | | | Vol. | | | Ash | | |
| | Tot. | Vol. | Ash. | Tot. | Vol. | Ash. | Tot. | Vol. | Ash. | Tot. | Vol. | Ash. | Tot. | Vol. | Ash. | Tot. | Vol. | Ash. | | | | | | | | | |
| Raw Sewage | 163 | 131 | 32 | 155 | 107 | 48 | 163 | 141 | 22 | 200 | 164 | 36 | - | - | - | - | - | - | 141 | 85 | 56 | | | | | | |
| Raw Sewage+200 mg/l. Ca(OH) ₂ | 322 | 149 | 173 | 343 | 165 | 178 | 506 | 313 | 193 | 395 | 179 | 216 | - | - | - | - | - | - | 354 | 147 | 207 | | | | | | |
| Raw Sewage+200 mg/l. H ₂ SO ₄ | 150 | 128 | 22 | 234 | 185 | 46 | 129 | 108 | 21 | 180 | 150 | 30 | - | - | - | - | - | - | 195 | 93 | 102 | | | | | | |
| Settled Sewage | 56 | 36 | 20 | 58 | 42 | 16 | 81 | 57 | 24 | 58 | 41 | 17 | - | - | - | 115 | 33 | 82 | 53 | 35 | 18 | | | | | | |
| Settled Sewage+200 mg/l. Ca(OH) ₂ | 228 | 62 | 166 | 285 | 69 | 216 | 270 | 104 | 166 | 266 | 63 | 203 | - | - | - | 387 | 76 | 311 | 252 | 63 | 189 | | | | | | |
| Settled Sewage+200 mg/l. H ₂ SO ₄ | 81 | 54 | 26 | 79 | 56 | 23 | 84 | 60 | 24 | 67 | 51 | 16 | - | - | - | 69 | 27 | 42 | 58 | 35 | 23 | | | | | | |
| Trickling Filter Effluent | 19 | 11 | 8 | 31 | 13 | 18 | 22 | 9 | 13 | 25 | 11 | 14 | - | - | - | - | - | - | 26 | 11 | 15 | | | | | | |
| T. F. Effluent+200 mg/l. Ca(OH) ₂ | 170 | 13 | 157 | 234 | 41 | 193 | 391 | 51 | 340 | 276 | 46 | 230 | - | - | - | - | - | - | 216 | 27 | 189 | | | | | | |
| T. F. Effluent+200 mg/l. H ₂ SO ₄ | 18 | 7 | 11 | 38 | 17 | 21 | 36 | 18 | 18 | 43 | 19 | 24 | - | - | - | - | - | - | 36 | 18 | 18 | | | | | | |
| Settled Trickling Filter Eff. | 44 | 23 | 21 | 24 | 19 | 5 | 35 | 19 | 16 | - | - | - | 52 | 28 | 24 | - | - | - | 41 | 23 | 18 | | | | | | |
| S.T.F. Eff.+200 mg/l. Ca(OH) ₂ | 159 | 32 | 127 | 291 | 99 | 192 | 303 | 140 | 163 | - | - | - | 276 | 124 | 152 | - | - | - | 195 | 50 | 145 | | | | | | |
| S.T.F. Eff.+200 mg/l. H ₂ SO ₄ | 38 | 21 | 17 | 35 | 18 | 17 | 36 | 15 | 21 | - | - | - | 52 | 22 | 30 | - | - | - | 44 | 20 | 24 | | | | | | |
| Activated Sludge (MLSS) | 2952 | 1989 | 963 | 2601 | 1887 | 714 | 2559 | 1846 | 713 | - | - | - | 2883 | 2254 | 629 | - | - | - | 2648 | 1925 | 763 | | | | | | |
| MLSS + 200 mg/l. Ca(OH) ₂ | 2402 | 1591 | 811 | 2725 | 1667 | 1058 | 2832 | 1818 | 1014 | - | - | - | 2875 | 2056 | 819 | - | - | - | 2570 | 1727 | 843 | | | | | | |
| MLSS + 200 mg/l. H ₂ SO ₄ | 1849 | 1280 | 569 | 2329 | 1805 | 524 | 2268 | 1774 | 494 | - | - | - | 2580 | 2048 | 532 | - | - | - | 2651 | 1817 | 834 | | | | | | |
| Sewage Lagoon Effluent | 34 | 16 | 18 | 38 | 19 | 19 | 35 | 16 | 19 | - | - | - | 48 | 26 | 22 | - | - | - | 35 | 16 | 19 | | | | | | |
| S.L. Eff. + 200 mg/l. Ca(OH) ₂ | 201 | 36 | 165 | 210 | 61 | 149 | 236 | 52 | 184 | - | - | - | 419 | 104 | 315 | - | - | - | 213 | 47 | 166 | | | | | | |
| S.L. Eff. + 200 mg/l. H ₂ SO ₄ | 56 | 28 | 28 | 46 | 18 | 28 | 46 | 19 | 27 | - | - | - | 54 | 24 | 30 | - | - | - | 44 | 17 | 25 | | | | | | |

some of the waste samples. The acid dosage of 200 mg/l. did not appear to increase the amount of residue settled from the waste sample except in minute quantities for several samples.

The results showed that the chlorinated solvent extraction process was more effective on wastes that contained low concentrations of suspended solids than it was on wastes that contained high concentrations of suspended solids. The results also showed that mixing butanol with a chlorinated solvent appeared to improve the solvents extraction efficiency. The relatively good extraction results of trichloroethane and dichlorisopropyl ether tend to indicate that chlorinated solvents with low vapor pressures produce better solids removal from waste liquids than chlorinated solvents with high vapor pressures.

Effect of Per Cent Butanol in Trichloroethane-
Butane Mixture, on Extraction Performance

The results from the screening investigation indicated that a mixture consisting of a chlorinated solvent and butanol would produce better extraction than the solvent would alone. An investigation was made to determine the amount of butanol mixed with the solvent that would effect optimum extraction efficiency.

The modifications made in the general procedure described under Analytical Methods were as follows.

1. The waste used was settled sewage dosed with 200 mg/l. of lime.

2. The solvents used were the following mixtures (by weight) of trichloroethane and butanol, (1) 95 per cent trichloroethane, five per cent butanol, (2) 90 per cent trichloroethane, 10 per cent butanol, (3) 80 per cent trichloroethane, 20 per cent butanol, (4) 70 per cent trichloroethane, 30 per cent butanol.

3. Settling time was two hours.

4. Volume of sample used was one liter.

The results from the trichloroethane-butanol mixture investigation are presented in Table 6. These results indicated that increasing the amount of butanol in the trichloroethane-butanol mixture increased the solids removal produced by the mixture, until the amount of butanol exceeded 20 per cent of the total mixture. When the amount of butanol in the mixture was increased to 30 per cent the solids removal decreased.

The results showed that the amount of butanol in a butanol-solvent mixture does effect the extraction performance of the mixture. The results also showed that a mixture of approximately 80 per cent trichloroethane and 20 per cent

Table 6: Effect of per cent butanol in trichloroethane-butanol mixture, on extraction performance.

| Notation | % Trichloroethane in mixture (Bu. Wt.) | % Butanol in mixture (Bu. Wt.) | Suspended Solids (mg/l.) | | Residue Settled Out (mg/l.) | |
|------------------------|--|--------------------------------|--------------------------|-------|-----------------------------|-------|
| | | | Tot. | Vola. | Tot. | Vola. |
| Blank ^a | - | - | 51 | 24 | 306 | 62 |
| Sample ^b | 95 | 5 | 43 | 25 | 323 | 96 |
| Sample | 90 | 10 | 42 | 24 | 365 | 96 |
| Sample | 80 | 20 | 33 | 20 | 375 | 115 |
| Sample | 70 | 30 | 38 | 23 | 355 | 25 |
| S. Sewage ^c | - | - | 67 | 30 | - | - |

- a) Blank was settled sewage dosed with 200 mg/l. of lime, mixed, and settled for 2 hours.
- b) Samples were settled sewage dosed with 200 mg/l. of lime, plus 5 per cent of the solvent mixture indicated, mixed and settled for 2 hours.
- c) S. Sewage, was settled sewage.

butanol (by weight) was the most effective mixture for removing solids from settled sewage.

X. GENERAL DISCUSSION

The chlorinated solvent process for sewage and waste treatment was investigated because it was known that chlorinated solvents cause coagulation of bacteria and proteins contained in liquids. The coagulated material gathers at the interface between the solvent and the aqueous phase. It was conceived that since sewage and other wastes contain suspended microorganisms and proteins that a chlorinated solvent process might be effective for removal of these materials.

The variables selected for investigation were pH, temperature, type of waste, and solvent system. The basis for the selection of variables was established experience in other solvent extraction processes.

In the residue analysis used in this investigation some of the residue that settled out was very unstable in that it would go back into suspension with the slightest disturbance. A small portion of such residue would occasionally be siphoned off with the supernatant. The residue comparison was a good criterion of process efficiency if the entire amount of residue was transferred to the evaporation dish and if no other residue losses occurred in the remainder of the analysis. The suspended solids test was also made for the purpose of determining the amount of material removed by the solvent extraction

process. However, with small quantities of suspended solids the results may not be dependable due to error in weighing or slippage through the filter mat. With the small quantities that were measured in the suspended solids test it was difficult to obtain consistent results on repeated samples.

Another fact that caused considerable variation in the results was the variable composition of the waste samples. Unless all of the waste samples are obtained at one time, subsequent samples may differ materially in composition from the original sample. This is especially true with sewage because of varying flows, varying loads, and infiltration of surface waters during heavy rains. Because of the procedures employed samples were picked up at different times or else stored in the refrigerator until the analyses with each waste was completed. Refrigeration was probably the better method for having consistent sample composition for all analyses. However, refrigeration may have caused some changes in the waste samples. It is possible that greases and fats, that were emulsifying in the waste samples, were condensed on the container walls during refrigeration. Greases and fats on the container walls may not have been removed with waste samples transferred to the mixing and settling chambers for analyses.

The results from the settled sewage investigation showed that chloroform produced reasonably good suspended solids

removal. However, it should be noted that the suspended solids removal indicated by the results was not entirely due to the effect of chloroform, because some solids would have settled from the waste without the addition of the chloroform. The samples designated as blanks in the suspended solids analyses were not resettled with the extracted samples. The suspended solids blanks were analysed to determine the amount of suspended solids in the waste initially so that the total suspended solids removal could be evaluated.

From observation of the results it is quite obvious that they were variable. The sample range for the suspended solids tests on unextracted settled sewage was 107 mg/l., the sample mean was 85.9 mg/l., and the standard deviation was 32.5 mg/l. For extracted settled sewage the range of the suspended solids test results was 31 mg/l., the sample mean was 13 mg/l., and the standard deviation was 9.4 mg/l. The suspended solids sample range was 71 per cent higher for unextracted settled sewage than for extracted settled sewage. The suspended solids mean was 85 per cent higher for unextracted than for extracted settled sewage, and the standard deviation was 71 per cent higher for unextracted than for extracted settled sewage. The variability of the suspended solids results is partly due to variations in sample composition of different samples picked up at different times. Analytical techniques possibly caused

some variations in the results, too. Although the results were variable the trend indicated that chloroform aided suspended solids removal from settled sewage.

In the residue analysis on settled sewage the sample range for chloroform extraction was 68 mg/l., the mean was 69.8 mg/l., and the standard deviation was 27.6 mg/l. The unextracted residue sample range was 21 mg/l., the mean was 52.5 mg/l., and the standard deviation was 14.8 mg/l. The sample range was 224 per cent higher for extracted than unextracted residue sample results. The sample mean was 33 per cent higher for extracted than unextracted residue sample results, and the standard deviation was 87 per cent higher for extracted than for unextracted residue results. It is obvious that the results were quite variable, but this was primarily attributable to the variability of the waste samples. Comparison of the means of the residue determinations showed that chloroform extraction improved the settleability of the material in settled sewage.

The C.O.D. results from settled sewage not extracted had a sample range of 119 mg/l., a mean of 257 mg/l., and a standard deviation of 45.6 mg/l. The settled sewage samples that were chloroform extracted had a C.O.D. sample range of 1372 mg/l., a mean of 715 mg/l., and a standard deviation of 577 mg/l. Expressed in percentages the C.O.D. sample range for extracted

settled sewage was 1050 per cent higher than for unextracted, the sample mean was 178 per cent higher for the extracted than the unextracted, and the standard deviation was 1165 per cent higher for extracted than for unextracted samples. The high values for the C.O.D. samples that were extracted was caused by incomplete removal of dissolved chloroform from the samples before making the C.O.D. analyses. The variations in composition of the different settled sewage samples also produced some fluctuations in the C.O.D. results.

The B.O.D. sample results for unextracted settled sewage had a sample range of 75 mg/l., a mean of 109.4 mg/l., and a standard deviation of 25.5 mg/l. The extracted settled sewage results had a sample range of 92 mg/l., a mean of 56.5 mg/l., and a standard deviation of 32.5 mg/l. Expressed in percentages the B.O.D. sample range was 23 per cent higher for the extracted than for the unextracted results, the sample mean was 49 per cent lower for the extracted than the unextracted results, and the standard deviation was 28 per cent higher for the extracted than for the unextracted results. Because of the methods used in the B.O.D. analysis and the variable composition of the settled sewage samples, the B.O.D. results were expected to have some variability. However, the sample ranges and standard deviations of the extracted and unextracted samples in the B.O.D. tests were in closer agreement than in other tests. This close agreement between the sample ranges and standard

deviations of the B.O.D. results indicated that the B.O.D. test was probably a better test for evaluating the chloroform extraction efficiency than the other tests used. Comparison of the mean B.O.D. of the extracted sample with the mean B.O.D. of the unextracted samples showed that the chloroform is effective in reducing the B.O.D. of settled sewage by 52.9 mg/l. or 49 per cent. Although chloroform extraction produced B.O.D. reduction of settled sewage, the reduction was not sufficient to provide complete treatment.

The results from treatment of the settled trickling filter effluent more or less verify the results from the settled sewage analyses, in that both wastes appeared to be partially treated by chloroform extraction.

Since the initial results from the extraction process appeared to be unfruitful, some investigation was made of variables affecting the process to determine if changes in any particular variable would improve or hinder the extraction efficiency. Although no specific experiments were made to investigate settling time, the different settling times used through the investigation indicated that extraction produced by the solvent was essentially complete after the first hour of settling.

Chloroform appeared to be more effective when the waste sample temperature was 20° C than at other temperatures investigated. Because chloroform extraction was most effective at a temperature near 20° C and the normal temperature of the samples

was near 20° C, sample temperature was not considered detrimental to extraction efficiency.

The investigation of the effect of sample pH indicated that unless the pH is modified to an unreasonable extreme (near 12.0), it has little effect on extraction efficiency. However, there were several instances in the screening investigation when the 200 mg/l. lime dosage appeared to improve the extraction efficiency, but this was not the general trend.

The bacteriological investigation showed that chlorinated solvents produced a substantial removal of bacteria from settled sewage, but the removal was not as great as anticipated.

The results from the solvent and waste screening investigation showed that chlorobenzene, trichloroethane, and dichloroisopropyl ether produced better results than the other solvents used. Because these solvents have lower vapor pressures than the other solvents, it is possible that chlorinated solvents with low vapor pressures are the best solvents for an extraction process. The screening investigation also showed that mixing a certain percentage of butanol with some solvents increased the extraction efficiency of the solvent.

In summary, the process appeared to be most effective for settled sewage treatment, but the results were not sufficient to warrant consideration as a complete treatment process. The extraction process was less effective on other wastes. The

microorganism removal was significant but not as complete as would be desired for an effective process.

It is possible that the performance or value of the process was not indicated by the analyses made. No analyses were made on wastes containing high concentrations of fats or greases. Domestic wastes do not always contain high concentrations of greases, fats, and waxes; but occasionally these materials cause treatment problems. Dichlorisopropyl ether, a chlorinated solvent, is cited as being an excellent extractant of these materials (2).

Future investigation using chlorinated solvents for the removal of specific materials such as greases, fats, or waxes from wastes containing high concentrations of these materials may prove more fruitful for the process. Also solvent extraction of sewage and other wastes using chlorinated solvents with very low vapor pressures may be successful.

XI. CONCLUSIONS

This investigation has led to the following conclusions:

1. A chlorinated solvent extraction process is more effective on settled domestic sewage than other wastes.
2. Temperature and pH of waste samples appear to have little effect on the extraction efficiency of chlorinated solvent extraction processes.
3. Chlorinated solvents with low vapor pressures appear to effect better extraction than chlorinated solvents with high vapor pressures.
4. The B.O.D. and residue analyses are the best analyses for evaluating the effectiveness of the chlorinated solvent extraction process.
5. Mixing butanol with some chlorinated solvents improves extraction performance.
6. The chlorinated solvents failed to produce relatively complete removal of bacteria from the wastes.
7. The chlorinated solvent extraction process is not highly recommended as a waste treatment process unless more favorable results are obtained from further investigations with the process.

XII. SUMMARY

The object of this investigation was to evaluate chlorinated solvent processes for the removal of microorganisms, proteins, and other substances from sewage and other wastes.

The use of a chlorinated solvent extraction process for sewage and waste treatment was conceived because chlorinated solvents cause coagulation of bacteria and proteins, and this coagulated mass gathers at the interface between the solvent and the aqueous phase. Since sewage and other wastes contain dispersed bacteria and proteins the solvent should be beneficial in removing these materials.

The investigation showed that the process was of limited effectiveness as a waste treatment operation. Wastes with high concentrations of solids were less effectively treated than waste with low solids concentrations. Of the wastes tested, settled domestic sewage appeared to be most suited for the solvent extraction process. The process didn't produce complete removal of the microorganisms. The variables, temperature and pH, had little or not effect on the process; and chlorinated solvents with low vapor pressures appeared to be most effectual for waste extraction.

More research is needed before the chlorinated solvent extraction process can be completely evaluated as a sewage and waste treatment process.

XIII. ACKNOWLEDGEMENTS

The entire graduate program undertaken by the author was supported by a Public Health Traineeship Program Award from the Public Health Service, United States Department of Health, Education and Welfare. For this award the author expresses his appreciation.

The author also wishes to express his appreciation to Dr. Harry R. Bungay, thesis advisor, for his suggestion of this thesis topic and guidance during the research investigation; to Dr. William A. Parsons, major course professor, for his help, encouragement and many suggestions pertinent to the preparation of this manuscript; and to Mrs. Walter Johnston for her excellent typing assistance.

XIV. LITERATURE CITED

1. American Public Health Association, American Water Works Association, Federation of Sewage and Industrial Wastes Association; Standard Methods for the Examination of Water Sewage, and Industrial Wastes; Tenth Edition; American Public Health Association, Inc.; 1790 Broadway, New York, New York; 1955.
2. Carbide and Carbon Chemicals Company, a Division of Union Carbide and Carbon Corporation; Organic Chlorine Compounds, Bulletin No. F4769B, Copyright, 1955, by Union Carbide and Carbon Corporation.
3. Davison, R.R.; Smith, W.H., Jr.; and Hood, D.W.; "Structure and Amine-Water Solubility in Desalination by Solvent Extraction", Journal of Chemical and Engineering Data, Vol. 5, No. 4.; pages 420-423; October, 1960.
4. Gurnham, C. Fred; Principles of Industrial Waste Treatment; John Wiley and Sons, Inc.; New York, New York; pages 250, 251 and 310; 1955.
5. Hennigan, John J.; Nemerow, Nelson L.; "B.O.D. Analysis by Solvent Extraction", Engineering Bulletin of Purdue University, Proceeding of the Fourteenth Industrial Waste Conference; May 5, 6 and 7, 1959; Engineering Extension Series, Series No. 104, Vol XLIV, No. 5, pages 68-76; September, 1960.
6. Pelczar, Michael J., Jr.; and Reid, Roger D.; Microbiology; McGraw-Hill Book Company, Inc.; New York, Toronto, London; page 536; 1958.
7. Rudolfs, Willem; "Solvents Effect on Digestion" (Abstract); Sewage Works Journal; Volume 17, page 402; 1945.
8. Sevag, M. G.; "Separation of Biologically Valuable Components from Plant and Animal Substance", (Abstract), Chemical Abstracts; Volume 34, Column 3448a, 1934.
9. United States Department of Health, Education and Welfare; Advance Waste Treatment Research-I Summary Report for June, 1960 - December, 1961; United States Public Health Service, Robert A. Taft Sanitary Engineering Center; Cincinnati, Ohio.

XV. VITA

The author was born in Pittsylvania County, Virginia on May 31, 1937. In June, 1957, he graduated from Halifax County High School in South Boston, Virginia. In September, 1957, he entered the Danville Branch of Virginia Polytechnic Institute at Danville, Virginia. After two years of study at the Danville Branch of V.P.I., the author entered the parent institution at Blacksburg and received a B.S. degree in Civil Engineering in June, 1961.

Upon receipt of a Public Health Service Traineeship in June, 1961, the author enrolled in the Sanitary Engineering graduate program of Virginia Polytechnic Institute. Since September, 1961, the author has been pursuing the fulfillment of the requirements for the degree of master of science in Sanitary Engineering.

Herbert M. Dawson

ABSTRACT

Removal of Microorganisms and Proteins from Sewage and Industrial Waste with Chlorinated Solvents

Very few sewage and industrial waste treatment effluents are free from microorganisms and proteins. Such discharges require further treatment by the receiving stream and consequently lower stream quality. The object of this investigation was to evaluate chlorinated solvent processes for the removal of microorganisms, proteins, and other substances from sewage and other wastes.

Six different chlorinated solvents were added to different waste samples in the ratio (by volume) of five per cent solvent and 95 per cent waste, mixed and allowed to settle for a specified period of time. The efficiency of the solvent extraction process was evaluated in terms of reduction of suspended solids, biochemical oxygen demand, and by increased weight of residue separable by sedimentation. The results showed that the process produced the following effects on settled sewage. Suspended solids were reduced by 85 per cent, the weight of residue separable by sedimentation was increased 33 per cent, and the biochemical oxygen demand was reduced 49 per cent.

The process was less effective for treatment of raw sewage, trickling filter effluent, sewage lagoon effluent, or for separation of activated sludge.

The variables investigated were temperature, pH and the solvent waste system. Temperature and pH appeared to have negligible effect on the extraction efficiency. The solvents employed were; chloroform, ethylene dichloride, chlorobenzene, carbon tetrachloride, trichloroethane, and dichlorisopropyl ether. Solvents with low vapor pressures and wastes with low concentrations of suspended solids appeared to be the most efficient system. The addition of 20 per cent of butanol (by weight) to trichloroethane appeared to increase the extraction efficiency of trichloroethane.

Bacterial counts made indicated that the solvent extraction process was affecting better than 90 per cent removal of microorganisms from the waste samples.

More research will be needed to completely evaluate chlorinated solvent processes for the removal of microorganisms, proteins, and other substances from sewage and other wastes.