Pharmaceutical Waste Treatment and Disposal Practices

Part I: Treatment of Pharmaceutical Wastewater

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PRESENTATION OUTLINES

- Introduction
- Types of Waste
- Problems Involved in Pharmaceutical Wastewater Treatment
- Treatment Methods
- Case Studies
- Conclusions

INTRODUCTION

- Origin Of Pharmaceutical Wastewater
- Quantity Generated
- Typical Characteristics of Antibiotic Waste

ORIGIN OF PHARMACEUTICAL WASTE WATER (PWW)

- Spent liquors from fermentation processes (e.g. antibiotics, vitamins)
- Chemical waste
- Condenser waste from evaporation
- Floor and laboratory washing waste

QUANTITIES GENERATED

- In Ireland about 43 tons of BOD produced per day from Pharmaceutical Industry.
- In USA during 1983, about 3 million tons of hazardous waste produced in which 200,000 tons of sludge produced by pharmaceutical industry only.

Typical Characteristic of Antibiotic Waste

	Waste from production of			
Characteristic	**Penicillin**	**Terramycin**	**General antibiotic**	**Fermentation products**
BOD, ppm	8,000-13,000	20,000	1500-1900	4,500
S.S		10	500-1000	10,000
pH	2-4	9.3	1-11	6-7

Types of Waste

- Helogenated/non-helogenated solvents
- Organic chemical residues from still bottom
- Sludge & tars
- Heavy metals
- Test animal remains
- Return pharmaceuticals
- Low-level radioactive waste
- Contaminated filters, etc.

PROBLEMS INVOLVED IN PHARMACEUTICAL WASTEWATER TREATMENT

- Diverse characteristics of PWW. Different medicines produce different type of waste
- Variable amount of products
- Mixing of pharmaceutical waste with other type of waste
- Also, it may contain high BOD and highly variable pH

Treatment Methods

- Physical Treatment
- Chemical Treatment
- Thermal Treatment
- Biological Treatment

Physical treatment

- ***Reverse osmosis (RO):***
  - **Based on pressure application**
  - Removal of dissolved solids
  - Depends on concentration and pH
- ***Dialysis***:
  - Based on the chemical activity of the solute
  - Recovery of specific material from aqueous solution
  - depends on the molecular weigh and dialysis coefficient

- ***Electrodialysis***:
  - Based on application of an electric field
  - Used to separate ionized species
  - Operates over a wide range of pH
- ***Evaporation***:
  - Based on heat energy
  - Recovery of solvents
  - Produces high quality effluent
  - High cost

- ***Granular Activated Carbon Adsorption***:
  - Used for removal of organic contaminants (COD)
  - Survey showed that 1 out of 25 pharmaceutical plants use GAS to treat their wastewater
- ***Filtration***:
  - Used to remove particulate contaminants
- ***Sedimentation***:
  - Suspended particles are allowed to settle and supernatant removed.

- ***Flocculation***:
  - Gathering of fine particles as flocculates which allows them to settle
- ***Stream Stripping*** :
  - Difference in relative volatility between the organic chemicals and water are used to achieve a separation
  - Used for recovery of solvents (1 out of 4 pharmaceutical plants and Wastewater treatment 17 out of 91 pharmaceutical plants)

Chemical Treatment

- ***Ion-exchange***:
  - Reversible interchange of ions between a solid and a liquid phase
  - Used for the removal of trace metals, fluorides, nitrates, and manganese
- ***Neutralization***:
  - A process utilised to prevent excessively acidic or alkaline wastes discharge
  - 1 out of 2 pharmaceutical plants use neutralization to treat their wastewater

- ***Reduction***: treatment with sulphur dioxide to reduce the oxidants to less noxious materials
- ***Precipitin***: separation of solid from aqueous waste chemically
- ***Calcination***: heating of waste to a high temperature to oxidize organic matter

Thermal Treatment

- ***Incineration***: controlled heating processes to covert a waste to less bulky, less toxic or less noxious
- ***Pyrolysis***: thermal decomposition of waste at high temperature in the absence of oxygen

Fig 3.0

Biological Treatment

- Used to remove biodegradable organic matter
- Microorganisms converts organics into:
  - CO_2 and H_2O (aerobic)
  - CO_2, CH_4, and H_2O (anaerobic)
- 1 out of 3 pharmaceutical plants use biological processes

Biological Processes

- ***Activated sludge***:
  - process in which microorganisms are continuously circulated and contacted with organic waste in the presence of oxygen
- ***Aerated lagoons***:
  - a basin in which organic waste stabilised by a dispersed biological growth in the presence of oxygen

Common design criteria for single and two-stage activated sludge systems with nitrification capability

Parameter	Single Stage	Two-Stage
Suspended growth Food /Microorganism ratio (g BOD_5 /g MLVSS/d)	0.05-0.15	<0.15
Sludge retention time (days)	20-30	10-20
MLVSS (mg/L)	2,000 - 3,000	1,500 - 2,500
pH (standard units)	7.2 - 8.5	7.2 - 8.5

- ***Waste stabilisation ponds (Polishing ponds)***: large shallow basins store wastewater and purify under natural conditions in the presence of algae
- ***Trickling filters***: artificial beds of rocks or other porous media through which aqueous organic waste percolated and brought into contact with biological growth and oxygen
- ***Anaerobic digestion***: closed tanks operated in the absence of oxygen

Ranges of values being used in pharmaceutical wastewater treatment by trickling filters

Parameter	Range	Units
Flow Rate	0.03 - 2.18	MGD
Hydraulic Loading Rate	2.0 - 5.0	gpm/ft^2
Depth of Medium	6 - 72	inches

Fig 6.0

Table 6.0: Different Type of Pharmaceutical Wastewater Treatment Methods and Their Efficiencies

Types of treatment processes	Reduction in BOD, %
• Aerobic treatment – Activated sludge – Aerobic fixed growth systems.	56 – 96
• Anaerobic digestion with controlled aeration	80

(Table 6.0 continued)

• Anaerobic digestion	60 - 90
• Trickling filters	60 -98
• Biofiltration (consist of aerator, clarifier & filters)	>90
• Advanced Biological Treatment (provide, ammonia reduction & nitrification also)	90

Advantages of Biological Treatment for Pharmaceutical Wastewater

- Good treatment efficiency
- Addition of extra chemicals not required
- Less sludge production
- Relatively much more economical

AEROBIC TREATMENT

CASE STUDY I

Problem Description: A pharmaceutical and chemical company (producing drugs, diuretics, laboratory chemicals and others) discharging its waste in an evaporation pond. This was reported that this wastewater might pollute the river Nile water and groundwater resources in the near vicinity. Accordingly, the wastewater effluent must be treated to a sufficient degree to render it safe and comply with national regulatory standards

- Waste Characteristic
  - .relatively acidic
  - .high concentration of organic compounds
  - .high suspended solids and phenol up to 210 mg/l
- Objective

  It was required to bring the pollutants in wastewater up to permissible concentration to protect groundwater and environment

Table 13. Characteristics of Pharmaceutical Wastewater

Parameter	Range	Mean
pH	1.87-4.4	3.31
COD	1488-6818	3861
BOD	950-4050	2126
Phenol	116.7-210	165
Oil & grease	34.5-12332	273
TSS	56-656	276
TDS	1371-7314	4388

Methodology of Treatment

- Pharmaceutical wastewater treat by
  - Activated sludge processes (6 hr. aeration)
  - Activated sludge processes (20 hr. aeration)
  - Biological filters
  - Biological filters followed by activated sludge

Table 14. Efficiency of Pharmaceutical Wastewater Treatment (using activated sludge; aeration period 6hr)

Parameter	Treatment Efficiency	Average
COD	41.2-88.8	65
BOD	57.7-97.2	77.45
Oil & grease	37.5-74.9	56.2
TSS	59.2-86.4	72.8

(using activated sludge; aeration period 20hr)

Parameter	Treatment Efficiency	Average
COD	89-95	92
BOD	88-98	93
Oil & grease	90-93	91.5
TSS	87-98	92.5

Table 15. Efficiency of Pharmaceutical Wastewater Treatment

(using biological filter)

Parameter	Treatment Efficiency	Average
COD	43-88	65.5
BOD	58-87	72.5
Oil & grease	15-49	32
TSS	13-97	55

(using biological filter followed by activated sludge)

Parameter	Treatment Efficiency	Average
COD	90-96	93
BOD	81-96	88.5
Oil & grease	70-100	85
TSS	51-94	72.5

Recommendation of Study

Finally they recommended extended aeration activated sludge processes having the following design criteria to get the desired treatment standard (Act 48/82)

- Design flow = 14,000 m3/d
- Retention period in primary settling tanks = 3 hrs
- Retention period in aeration tanks = 20 hrs
- Sludge recycling ratio = 25%
- MLVSS in aeration tanks = 2000-3000 mg/l
- Retention period in final sedimentation tank = 3 hrs

CASE STUDY II

- **Problem Description:** A pharmaceutical industry engaged in the production of various type of allopathic medicines at Bombay. Treatment of this pharmaceutical waste using Oxidation Ditch Processes was under consideration (experimental set-up was already existed in the lab). Investigation carried out to improve the efficiency of processes

Specific Objectives of the Study

- Evaluate the effect of coagulants ($FeSO_4$, $FeCl_3$ & Alum) on SS and COD removal efficiency.
- Evaluate the performance of Oxidation Ditch processes at various organic loading
- Determine basic performance of biological treatment in terms of effluent quality & sludge property

Table 16. Characteristics of Pharmaceutical Wastewater

Parameter	Range	Mean
• COD	2000-3000	2700
• BOD	1200-1700	1500
• TSS	300-400	400
• Phenol	65-72	65
• Volatile acids	50-80	60
• Alkalinity	50-100	60
• pH	605-7.0	7.0

Conclusions of the study

- Physicochemical treatment is not necessary because the doses of coagulants required were high and the COD reduction was marginal
- Oxidation Ditch Process showed a removal efficiency in the range of 86 to 91% for COD removal and about 50% for phenol removal.
- Recommended design criteria :
  - solid retention times of 8 to 16 days
  - hydraulic residence time of about 1 to 3 days
  - removal rates of 0.19 to 0.24 day^{-1}

ANAEROBIC TREATMENT

- Anaerobic treatment of pharmaceutical waste is common in different countries because of
  - lack of biodegradability
  - toxic and
  - malodorous nature of pharmaceutical waste

Commonly Used Anaerobic Systems

- Upflow filters
- Membrane reactors
- Continuously-stirred reactors
- Fluidized bed reactors

CASE STUDY: Treatment of Herbal Pharmaceutical Wastewater (HPW) (Nandy and Kaul, 1991).

- **Problem Description:** Use of the Herbal pharmacy is common in several Asian countries. The waste generated during the production of herbal medicine usually contains high COD and low pH. The factory investigated produces about 700 herbal products.
- Objective of Study: to treat herbal PWW using anaerobic fixed film fixed bed reactor system

Table 9.0. Characteristics of Herbal Pharmaceutical Wastewater

Parameter	Range	Mean
• COD	5,000-60,000	32,500
• TSS	700-12,200	6,450
• Phenol	65-72	65
• Ammonia-N	40-320	180
• Lignin	450-6,500	3,475
• pH	4.2-4.5	4.35

Table 11.0. Reactor System Perform Data

Parameter	**Values (Range)**
Influent Conc.	5,000-60,000 mgCOD/l
HDT	0.54-5.0 day
OLR	1.0 - 36.0 Kg COD/m3
Removal Efficiency	54 - 97 %
Biogas Yield	0.33 - 6.0 m3 CH4/m3-d
Methane Content	62.0 - 66.5 %

Result/Conclusions of the Study

- They got about 90% of substrate removal efficiency
- Loading rate of 16 kg /m^3-d found optimum
- Increase in HRT results in increase of substrate removal efficiency. An optimum HRT of 2.5 days recommended

CASE STUDY IV: Study on anaerobic filters for the treatment of PWW, Sachs *et al*. (1982)

- **Background of the Study**: A number of studies show that anaerobic treatment of PWW gives better results (Nemerow 1978; Trubnick and Rudolf 1948)
- Young and McCarty (1968), compared the anaerobic filters with other existing biological processes and pointed out following distinct advantages

- The anaerobic filter is ideally suited for the treatment of soluble wastes.
- No effluent or solids recycle is required with the anaerobic filter because biological solids remain in the filter and are not lost with the effluent.
- The accumulation of high concentrations active solids in the filter permits the treatment of dilute wastes.
- Very low volumes of sludge produce.
- Effluent is essentially free of SS.

Objectives of Study

- Study the physical characteristics, chemical composition and variations of wastewater from chemically synthesised pharmaceutical production
- Apply that waste to the anaerobic filter and determine its treatability
- Compare this waste in terms of composition and treatability with others examined in previous studies
- Investigate possible waste toxicity
- Subject the filter to shock loading conditions to determine the effect on performance.

Methodology

- Waste from two pharmaceutical manufacturing facilities were used and studied to treat
- Anaerobic Filters were used to treat the waste
- Investigate the waste toxicity by using constant hydraulic and organic loading while varying the percentages of methanol and pharmaceutical waste in the feed; and
- Finally compared the treatment efficiency with other anaerobic treatment processes

Table 12. Characteristics of Pharmaceutical Wastewater

Parameter	Sample I	Sample II
COD	70,700	87,800
BOD	30,000	15,000
TS	42,120	28,218
DVS	24,510	15,240
Acidity	51,250	53,860
Alkalinity	0	0
pH	1.5	1.6

Results of the study

- Anaerobic filter giving 70 – 80% COD removal efficiency and 94% BOD_5 removal efficiency

- Anaerobic filters give 33% better performance as compared to aerobic extended aeration system

- Very low volumes of sludge produce

- Remove colour with higher efficiency

Conclusions of Presentation

- A number of physical, chemical and biological treatment processes are available to treat PWW
- Biological Treatment of PWW is difficult due to
  - Toxic effect to both aerobic and anaerobic microorganisms.
  - Less amenable to treatment

Conclusions of Presentation (continued)

- Treatment of PWW using anaerobic filter is much better because of
  - Rapid acclimatisation of bacteria
  - Faster treatment
  - Effluent quality as good or better than aerobic extended aeration system
  - Less sludge production
  - Methane generation gives additional benefit

Thank You