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LOW COST WASTE TREATMENT METHODS FOR TREATING PHARMACEUTICAL WASTES

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INTRODUCTION

One of the industrial wastes of serious consequence from the point of view of water pollution in India is the waste water from pharmaceutical industry. A large number of pharmaceutical units are there in India discharging waste waters containing various organic and inorganic pollutants.

While considerable work has been carried out in other countries on the treatment of pharmaceutical wastes (ref. 1,2), no work has been carried out in India (ref. 3,4). With this in view the studies presented in this communication were carried out. An in-plant survey was carried out in a pharmaceutical factory producing Calcium sennocide, diosgenin, Mebendozole benzyl ether, cycloester and sennocide tablets. The treatability of the waste waters from this industry using low cost waste treatment methods was studied. Results obtained are presented in this communication.

PROCESS DETAILS

There are six units in the factory studied producing different products as described below.

Calcium sennocide unit

The basic raw materials used are senna leaves and ethyl alcohol. An extract of the senna leaves is prepared using alcohol and sennocides are precipitated from the extract as calcium sennocides with calcium chloride solution. The mother liquor is distilled and distillate recovered. The remaining mother liquor amounting to 100 lpd is discharged as waste water.

Diosgenin unit

Dioscorea roots are treated with hydrochloric acid and the mixture is filtered. The filtrate containing acid is neutralised with lime and discharged into the drain. From the solid retained on the filter, diosgenin is extracted with petroleum solvent. The spent cake is used as fertiliser while the petroleum solvent is recovered. The diosgenin extract is concentrated and used.

Mebendozole unit

In the mebendozole unit 3,4-diaminobenzophenone is converted using thiourea and acetic acid into mebendozole. In a month about 10 batches are processed. About 2400 litres of waste water per batch containing unreacted methyl chloroformate, acetic acid and dimethyl sulphate is discharged.

Benzyl ether unit

In the first step a mixture containing acetyl methyl salicylate, aluminum chloride, ethylene dichloride and dimethyl sulphate is reacted with benzyl bromided and the intermediate obtained is precipitated using 40 litres of hydrochloric acid. The quantity of waste water generated during this step is about 1200 litres per batch including wash water. In a month 20 batches are processed in this way. Hence the total quantity of waste water discharged is 24000 litres per month or 80 lpd. In the second step the prcipitated intermediate obtained with benzyl bromide and dimethyl sulphide to produce benzyl ether. In a month six batches are processed using second step and discharging 6000 litres of waste water per month.

Cycloester unit

In the first step, diethyl oxalate is treated with methanol and sodium and converted into an intermediate which is further treated in second step with sulphuric acid to produce cycloester precipitate. The precipitate is filtered and the filtrate is discharged as waste water. The quantity of waste water discharged from first and second steps are 7200 litres and 30000 litres per month respectively.

Sennocide tablet unit

Calcium sennocide is made into tablets About 15 million tablets are produced per month. As this is dry process there is no liquid effluent from this operation.

TABLE 1

CHEMICAL CHARACTERISTICS OF WASTE WATER FROM DIFFERENT UNITS IN THE FACTORY
(All results except pH are expressed in mg/l)

Unit	pH	COD	BOD	Chlorides (Cl)
1. Calcium sennocide	4.6	501120	205800	16600
2. Diosgenin	10.5	92016	45080	1600
3. Mebendozole	0.5	122750	65750	1550
4. Cycloester				
(a) First step	2.2	48168	20150	325
(b) Second step	0.5	156780	80900	4100
5. Benzyl ether				
(a) First step	6.5	171071	80350	120
(b) Second step	3.2	-	-	190

NATURE AND CHARACTERISTICS OF WASTE WATER

Water is used in the process for extractions and washing of various units of the plant. Floor washings also contribute to the waste flow. Raw water of about 45 cum/day is obtained from a bore well. About 20 cum/day is used in the process and the rest for gardening, laboratory, canteen, boiler feed etc.

Waste water is discharged from the processes where calcium sennocide, diosgenin, mebendozole, benzyl ether and cycloester are produced. Waste water is also discharged from water treatment plant, boiler house, laboratory and canteen. Equipment and floor washing waters are discharged as waste water. The total quantity of waste water discharged is about 30 cum/day. Waste water from calcium sennocide unit, diosgenin unit, cycloester unit, water softening plant, boiler house, equipment and floor washings are discharged daily but intermittently. Effluent from mebendozole unit is discharged once in three days. The waste water from benzyl ether unit is discharged once in 36 hours in the first step and once in 120 hours in the second step.

Samples of waste water were collected on different days and analysed as per procedures given in Standard Methods. Results obtained are shown in Table 1.

Combined waste water is obtained after proportional mixing of various section -al wastes based on flow and analysed. Results obtained are shown in Table 2.

LABORATORY STUDIES ON TREATMENT

Equalisation and preaeration

As the nature of discharges from various operations are intermittent, it is felt necessary to equalise the effluent flow. Effluents from different sections as well as from canteen are equalised for 5 days and the characteristics of equalised effluent was studied. The equalised waste showed a pH of 4.0, BOD of 95000 mg/l, COD of 100000 mg/l and suspended solids of 2000 mg/l.

As the equalised effluent still contained volatile substances like benzyl ether, alcohol, petroleum solvent it is felt necessary to preaerate the effluent. The equalised effluent is preaerated using diffused aeration with an aquarium aerator for different aeration periods. Samples were analysed at different aeration periods. It is found that aeration for 2 hours resulted in a BOD reduction of 30% and BOD of the aerated effluent was 66500 mg/l.

Neutralisation and settling

The equalised and preaerated effluent is then neutralised with sodium bicarbonate to a pH of 7.0 and settled for 3 hours. Samples were drawn from the settling unit and analysed. The neutralised and settled effluent had a BOD of 46550 mg/l.

TABLE 2

CHARACTERISTICS OF COMBINED WASTE WATER FROM THE INDUSTRY
(All results except pH are expressed in mg/l)

Characteristics	1	2
pH	3.6	3.4
Acidity ($CaCO_3$)	35	50
COD	219520	320000
BOD	120000	130000
Suspended Solids	2000	1200
Nitrogen (N)	5700	4080
Phosphorous (P)	1300	1200

TABLE 3

PERFORMANCE OF ANAEROBIC LAGOON IN THE TREATMENT OF NEUTRALISED AND EQUALISED WASTE WATER

Raw waste characteristics : BOD : 46550 mg/l pH : 7.0

Parameters	Detention Time in days				
	70	60	50	40	30
pH	8.2	7.9	7.2	7.0	6.7
Volatile acids as CH_3COOH mg/l	2000	2100	2500	3100	4700
BOD mg/l	3724	4655	9310	13965	23275
% reduction in BOD	92	90	85	70	50
BOD Load (kg/cum/day)	0.33	0.39	0.47	0.58	0.78

TABLE 4

PERFORMANCE OF SECONDARY ANAEROBIC LAGOON USING EFFLUENT FROM PRIMARY LAGOON

Influent characteristics : BOD : 4655 mg/l pH : 7.9

Parameters	Detention Time in days			
	50	40	30	20
pH	8.6	8.4	8.2	8.1
Volatile acids as CH_3COOH mg/l	1400	1690	1950	2800
BOD mg/l	1496	1512	2794	3700
% reduction in BOD	68.5	67.5	40	20.5
BOD Load (kg/cum/day)	0.09	0.12	0.15	0.23

Biological treatment of waste water

Anaerobic lagoon : Since the effluent after neutralisation and settling has a BOD of about 46550 mg/l, it is felt necessary to treat the effluent biologically to remove the biodegradable organics. Experiments were carried out to study the possibility of treating the waste water in anaerobic lagoon. Laboratory lagoon with a capacity of 5 litres was used with 1.65 litres of seed sludge made upto 5 litres with waste water. The lagoon was initially operated at 70 days and 60 days detention time. Detention time was then gradually reduced to 40 and 30 days. Performance data of the lagoon is shown in Table 3.

With gradual decrease in detention time from 70 days to 30 days the pH of the waste water in the lagoon reduced from 8.2 to 6.7. The BOD removal varied from 50% at a loading of 0.78 kg/cum/day to 92% at a loading of 0.33 kg/cum/day. At 60 days detention time and a loading of 0.39 kg/cum/day, the BOD removal was 90%.

From the results in Table 3, it can be seen that the effluent from the lagoon at a detention time of 60 days showed a BOD of about 4655 mg/l. It was felt necessary to treat the effluent by a secondary lagoon. The effluent from the primary lagoon was further treated in a secondary lagoon. Detention time was varied from 50 days to 20 days. The results of performance of secondary lagoon are given in Table 4.

The BOD removal in secondary lagoon varied from 20.5% at a loading of 0.23 kg/cum/day to 68.5% at a loading of 0.09 kg/cum/day. It would appear that 40 days detention time in secondary lagoon would be sufficient to bring down the BOD to 1512 mg/l. The waste water has to further treated in an aerobic system to bring down the BOD to 30 mg/l.

Extended Aeration : The system was initially started with sewage and as the sludge built upto 4000 mg/l, the substrate was replaced by dilute effluent from the secondary lagoon of 40 days detention. The concentration of the effluent was increased in several steps and finally undiluted effluent was fed. This was to acclimatise the sludge to the new waste water. When stabilised conditions of operation was evidenced by the presence of active bacterial culture together with ciliate protozoa, experiments were started. The effluents were drawn after fixed time of aeration, and analysed. The

TABLE 5

PERFORMANCE OF EXTENDED AERATION SYSTEM USING WASTE WATER AFTER SECONDARY ANAEROBIC LAGOON

MLSS : 4000 mg/l

Detention Time in days	BOD mg/l	% reduction
0	1512	-
1	302	80
2	100	93.3
2.5	45	97
3	30	98

results are presented in Table 5.

From the table, it can be seen that the BOD of the waste water is reduced to 30 mg/l after aeration for 3 days.

CONCLUSIONS

1. An in-plant survey was carried out in a typical pharmaceutical unit producing calcium sennocide, diosgenin, mebendozole, benzyl ether, cycloester and sennocide tablets discharging a waste water of 30 cum/day.

2. The combined waste water from the factory had a pH of 3.4 - 3.6 and a BOD of 120000 to 130000 mg/l.

3. Equalisation of the combined waste water for 5 days reduced the BOD to 95000 mg/l which is further reduced to 66500 mg/l by preaeration for 2 hours.

4. When the equalised and preaerated combined waste water is neutralised to a pH of 7.0 and settled for 3 hours BOD reduced to 46550 mg/l.

5. Treatment of the preaerated combined effluent in two anaerobic lagoons in series with a detention time of 60 and 40 days respectively reduced the BOD to 1512 mg/l.

6. When the lagoon treated effluent is further treated in an extended aeration unit with a detention time of 3 days the BOD could be brought down to about 30 mg/l.

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