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TREATMENT OF STRONG FERMENTATION WASTES BY ACTIVATED SLUDGE

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ABSTRACT

This paper reports a comprehensive wastewater pollution abatement program implemented at a plant producing pharmaceutical products by fermentation. The production is mainly devoted to tetracycline, oxytetracycline derivatives and to gentamicin sulfate, using different agricultural sources. The studies were undertaken in a context that covered all the principal components necessary for an industrial control program: wastewater characterization and pollution profile, treatability evaluation, description of the most suitable technology. Extensive studies were carried out to assess the treatability characteristics of process wastes as well as waste combinations. Pertinent kinetic constants were determined in lab-scale experiments. The availability of air regularly discharged from the processing plant made an aerobic process an economically attractive treatment system. A fraction of the cooling discharges was mixed with process wastes in the planning and design of the treatment flow scheme (a) to lower the BOD concentration below 2000 mgl^{-1}, and (b) to provide an equalization and buffering capacity for hydraulic and toxic shocks.

KEYWORDS

Pharmaceutical wastes; antibiotics; pollution profile; treatability; kinetic constants; activated sludge.

INTRODUCTION

Pharmaceutical wastes present major difficulties for proper handling and treatment. This is especially true for antibiotic production by fermentation (Howe, 1962):

(1) There is a number of different sources generating wastewaters.
(2) A major portion of the process wastes is very strong, with high BOD and COD, high dissolved solids, varying pH, high sulfates from acidification, etc.
(3) The wastewater flow pattern may exhibit irregularities and variations as the production is carried out on a batch basis and may change daily.
(4) The waste composition is greatly affected as the product changes.

These characteristics make it almost impossible to assign reasonably reliable values for wastewater parameters, simply on the basis of production category of the plant; it is now recognized that uniformly applicable pollution profiles, relating the magnitude of pollution figures to production by means of revelant parameters, can not be defined for the entire category of fermentation wastes (EPA, 1983). This necessitates detailed experimental evaluations for wastewaters generated from each individual pharmaceutical plant in order to define the most appropriate treatment technology.

The main objective of this paper is to illustrate the comprehensive wastewater pollution abatement program implemeted at Ansa, a plant in İzmit, Turkey, producing pharmaceutical products by fermentation. The paper summarizes all the principal phases taking part in the overall industrial pollution control program implemented: wastewater characterization and pollution profile, treatability characteristics of the wastes including the determination of the kinetic constants, and identification of the most suitable treatment technology. It also gives the particulars of the single-stage activated sludge system designed and constructed on the basis of the studies undertaken.

POLLUTION PROFILE

Ansa at Izmit, Turkey has the capacity to produce 120 tons per year of tetracycline and oxytetracycline derivatives and 1.5-2.0 tons per year of gentamicin sulfate by fermentation, using different agricultural sources and raw products as listed in Table 1. Tetracycline and oxytetracycline are alternately produced together with a continuous supply of gentamicin. All figures in Table 1 are given for full capacity and for tetracycline, oxytetracycline and gentamicin combined. During the study, the production rate of the plant was estimated to be 50 - 60 % of full capacity. The products mentioned above place the plant in the pharmaceutical raw materials (antibiotics) production by fermentation sub-category, within the pharmaceutical category, as far as polluting characteristics are concerned.

TABLE 1 Raw Materials Consumption for Antibiotics Production

Raw Materials	Usage(tons per year)
Carbohydrate sources starch,dextrin,sugars,vegetable oils	1500
Protein sources soy meal,soy flour,corn steep liquor gluten	300-400
Minerals ammonium sulfate,ferrous sulfate, manganese sulfate,cobalt chloride, calcium chloride,sodium ferrocyanide, sodium hydrogen sulfide, phosphates	25
Ammonia, 23 %	100-200
Acids, Bases NaOH, HCl,H_2SO_4, oxalic acid	600-700
Quarternary ammonium salts	100-125
Antifoams	30
Solvents (all regenerated) acetone,methanol,oxitol,n-butanol	500
Urea	150-200

The production mode currently adopted in the plant is illustrated in Fig. 1: basically it involves the production of a bacterial-based mycelium in the microbiology laboratory, its fermentation in two phases, solubilization of antibiotics by acidification and filtration. The whole process is carried out on a batch basis. For tetracycline and oxytetracycline, the filtrate is subjected to a recovery phase by extraction, followed by pH adjustment, filtration, precipitation, centrifugation, complex formation and crystallization prior to purification. Similarly, gentamicin is produced in batch fermentors followed by extraction, chromatographic resin adsorption, evaporation, filtration, crystallization or spray drying.

The production is normally pursued in 330 consecutive days per year. It is carried out in 3 shifts, 24 hours per day, 7 days per week. The maximum daily production capacity is 400 kg per day for tetracycline and oxytetracycline and 20 kg per 3 days (intermittent production) for gentamicin. The manpower use involves 135 workers, 25 personnel and 12 residences for personnel, representing a total daily capacity of 220 population equivalents per day.

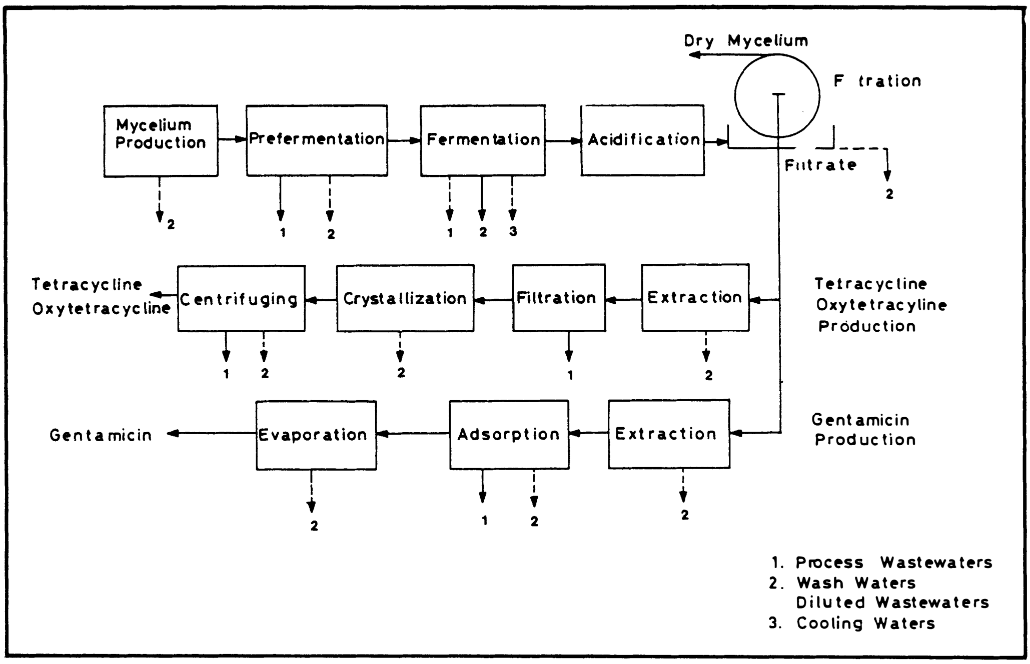

Fig. 1. Antibiotics production mode at Ansa plant

Wastewater Characteristics

A survey in the plant reveals 33 different sources of wastewater discharges grouped into 11 separate discharge pipe systems. A more detailed analysis shows that they may be regrouped as proposed by Howe (1962):

(a) wastewaters from fermentation processes (strong)
(b) wastewaters from extraction and purification processes (strong)
(c) wastewaters from recovery process(strong)
(d) floor and equipment washings (diluted)
(e) laboratory wastes, miscellaneous wastes (varied)
(f) sanitary wastes
(g) waste cooling water (uncontaminated).

In this context, it was estimated that further segregation of the wastewater streams into the following 3 general groups would be best suitable for subsequent characterization and treatability studies:

(1) Strong Process Wastes : Q = 120 m^3d^{-1}
Gentamicin filtration, tetra + oxytetracycline
filterpress and centrifuge discharges,pre-fermentation
wastes

(2) Other Diluted Wastes : Q = 160 m^3d^{-1}
Domestic-type wastewaters, laboratory wastes,
filter cloth washings,general cleaning

(3) Cooling Wastes: Q = 1000 m^3d^{-1}

Wastewater characteristics of these 3 groups were assessed on the basis of an extensive sampling and analysis program. The results of the analyses are listed in Table 2. As noted from this table, the selected process wastes are very strong in organic content, having a BOD_5 of 13500 mgl^{-1} and a COD of 34000 mgl^{-1}, corresponding to a BOD_5/COD ratio of lower than 1/2. Figures in this Table also yield a total BOD_5 load of 1680 kgd^{-1} and a COD load of 4180 kgd^{-1}, almost entirely from the waste streams identified as strong process wastes.These values are in good agreement with the literature reporting BOD_5's of 20000 mgl^{-1} for terramycin 8000 - 13000 mgl^{-1} for penicillin and 4000 - 7000 mgl^{-1} for aureomycin production (Ilhan _et al._ 1981).

TABLE 2 Characteristics of Major Wastewater Sources

Parameters	Process Wastes	Other Diluted Wastes	Cooling Waters
Flow, m^3d^{-1}	120	160	1000
pH	6.5-8.5	7.0-8.0	*
Alkalinity, mgl^{-1}	2000	-	
BOD_5 , mgl^{-1}	13500	400	*
COD , mgl^{-1}	34000	600	
SS, mgl^{-1}	1500	300	
TKN-N, mgl^{-1}	1500	40	
Total P, mgl^{-1}	70	10	
Sulfates, mgl^{-1}	3000	-	
Temperature, ^oC	ambient	ambient	30-40

* uncontaminated

TREATABILITY EVALUATIONS

The possibility of segregating very strong wastes inevitably suggest anaerobic processes as the most likely treatment systems. This idea was not pursued for Ansa, mainly for two reasons. (1) The preliminary anaerobic treatability studies indicated a number of serious adaptation and inhibition problems, possibly due to high sulfate levels and frequent changes in the products and wastewater properties. (2) The fact that a total of 360000 cubic metres per day of air, with a 17 - 19 oxygen content is regularly discharged from the plant as part of the routine production scheme, favored an aerobic process as an economically attractive treatment system. In this context, the emphasis was placed upon aerobic treatability experiments which were conducted in three groups (Ilhan et al., 1981):

(1) Batch Experiments
(2) Continuous Experiments
(3) Determination of Kinetic Constants.

In all experiments, the wastewater sample from strong process streams was used and diluted in an appropriate manner to levels compatible with aerobic treatment, with other wastewater sources.

Batch Experiments

Batch experiments were conducted in 10-litre glass containers, mixed and aerated with diffused air. The wastewater sample was seeded with activated sludge previously acclimated to the same waste, at the beginning of the experiment which was carried out for 10 consecutive days. The averages of the results obtained are given in Table 3, which indicates that the total COD could only be lowered to 890 mgl^{-1} from an initial concentration of 3175 mgl^{-1}, corresponding to a removal rate of 72 %. This rate was 82 % for soluble COD and 95 % for BOD_5, observed to drop to 103 mgl^{-1} after 10 days.

TABLE 3 Results of Batch Experiments

Time (days)	COD, mgl^{-1} (Total)	COD, mgl^{-1} (Dissolved)	BOD_5, mgl^{-1} (Dissolved)
0	3175	2900	2100
1	2740	2500	1962
2	2000	1250	550
3	1690	1075	326
4	1375	875	248
5	975	815	142
6	900	710	-
7	890	575	-
8	970	585	-
9	930	540	104
10	890	515	103

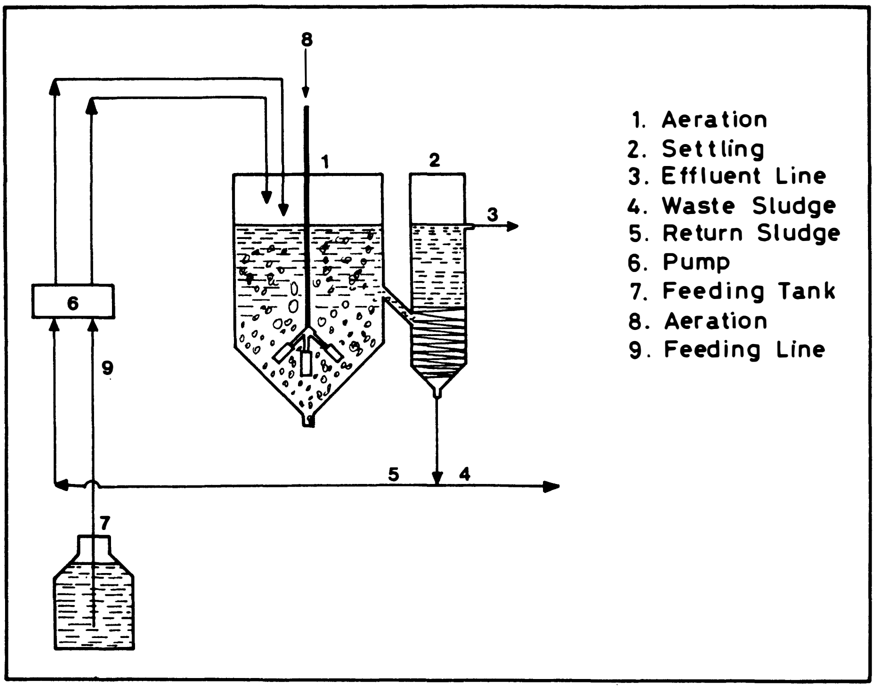

Fig. 2. Laboratory set-up for experimental evaluation

Continuous Experiments

Continuous experiments were run in 10-litre reactors with sludge recycle (Fig. 2) and in similar chemostats with no recycle. Data were recorded for at least a week after the steady state conditions were achieved in the reactors. In sludge recycle systems, the first run was adjusted to yield a hydraulic detention time, t= 5.2 h, with an average MLVSS concentration of 3000 mgl^{-1}; the influent feed was diluted to 1500 mgl^{-1} COD and at this level the system could only provide 57 % COD removal. In the second run, the hydraulic detention time was increased to 25.5 h and the feed COD to 3000 mgl^{-1}; at this operating condition it was possible to achieve a COD removal of around 80 % ; the effluent BOD_5 fluctuated around 127 - 176 mgl^{-1} corresponding to an average removal rate 90 %. Table 4 outlines the operating characteristics of this run.

The chemostat experiments were conducted at hydraulic detention times of 17.8 h, 19.8 h and 48.1 h, yielding BOD_5 removals of 55 %, 65 % and 90 % respectively. Table 5 gives the results of the chemostat experiment for t = 19.8 h. There, the BOD and COD removal rates are much less than those obtained with comparable sludge recycle experiments, due to markedly lower MLVSS concentrations that can be sustained in a chemostat at the operating conditions of the study.

Determination of Kinetic Constants

Although the previous experiments provide experimental proof that the effluent BOD_5 may be reduced to a level around 100 mgl^{-1} provided that adequate dilution and suitable operating conditions are secured, they do not reflect the full picture as far as the treatability of the strong wastes are concerned. The problem arises from the fact that strong process wastes do not maintain a uniform composition which is drastically affected when tetracycline and oxytetracycline are alternately produced together with gentamicin. The effect is not so much on the strength of the wastewater exhibiting approximately the same BOD and COD levels for the two alternating products, but it is on the treatability properties of the wastes generated. This effect is assessed by evaluating the kinetic constants for the two types of wastewaters.

TABLE 4 Results of Continuous Experiments with Sludge Recycle

Hydraulic Detention Time (h)	COD Influent (mgl^{-1})	COD Effluent (mgl^{-1})	COD Removal (%)	BOD_5 Influent (mgl^{-1})	BOD_5 Effluent (mgl^{-1})	BOD_5 Removal (%)	MLVSS (mgl^{-1})
25	2950	550	81.4				3610
25.3	3275	485	85.2	2075	135	93.5	3700
25.3	2950	468	84.1				3300
25.3	2825	480	83				3060
25	2825	460	83.7	1963	127	93.5	3030
26.8	3175	595	81.3	2040	136	93.3	3160
26.8	3425	655	80.9	1959	176	91.0	3090

TABLE 5 Results of Chemostat Experiments for t = 19.8 h

COD Influent (mgl^{-1})	COD Effluent (mgl^{-1})	COD Removal (%)	BOD_5 Influent (mgl^{-1})	BOD_5 Effluent (mgl^{-1})	BOD_5 Removal (%)	MLVSS (mgl^{-1})
2900	1250	56.9				
3150	1200	61.9				
2250	1130	49.8	1470	642	56.3	890
2100	860	59.0				750
2850	1140	60.0				880
3500	1050	70.0	1581	521	67.0	1040
3575	1730	51.7	1828	554	69.7	1070
3650	1600	56.2	1463	514	64.9	1060

Two sets of experiments were conducted to characterize process wastewaters during the periods of tetracycline and oxytetracycline production, using the same experimental setup as for sludge recycle systems. Each set included 4 different runs of continuous operation at steady state for hydraulic detention times of 0.5, 1.0, 1.5 and 2 days respectively. For oxytetracycline wastes the sludge age was maintained between 5.9 - 16.7 days, whereas for tetracycline wastes the above range was 5.6 - 13.6 days. The data collected during steady state were evaluated both individually and as an average of a given run in the standard linearized format to yield the pertinent kinetic constants as shown in Figs. 3 and 4. From the collected data the following kinetic constants were computed:

Oxytetracycline	Tetracycline
$Y = 0.26$ mg VSS mg^{-1} BOD_5	$Y = 0.58$ mg VSS mg^{-1} BOD_5
$k_d = 0.028\ d^{-1}$	$k_d = 0.088\ d^{-1}$
$k = 4.0\ d^{-1}$	$k = 0.50\ d^{-1}$
$k_s = 310\ mgl^{-1}$ BOD_5	$k_s = 50\ mgl^{-1}$ BOD_5

As evidenced by the constants tabulated above, the two alternating process wastes show substantially different properties affecting the mode of appropriate treatment. The yield value is much lower for oxytetracycline waste. The latter has also a very high maximum substrate utilization rate, k, but it takes a significantly large range of substrate concentration to reach this level as attested by a high half saturation constant, k_s . The tetracycline waste appears to be biodegradable at a much slower rate ($k = 0.5\ d^{-1}$) but it has an inherent instability as far as substrate removal rates to be employed in the treatment, since its k_s is comparatively too low.

RECOMMENDED TREATMENT SCHEME

In the planning and design of the treatment scheme it was noted that full segregation of the waste streams as indicated in Table 2 was not possible due to the complexity of the existing piping system, therefore the characterization as indicated in Table 6 was adopted. As the

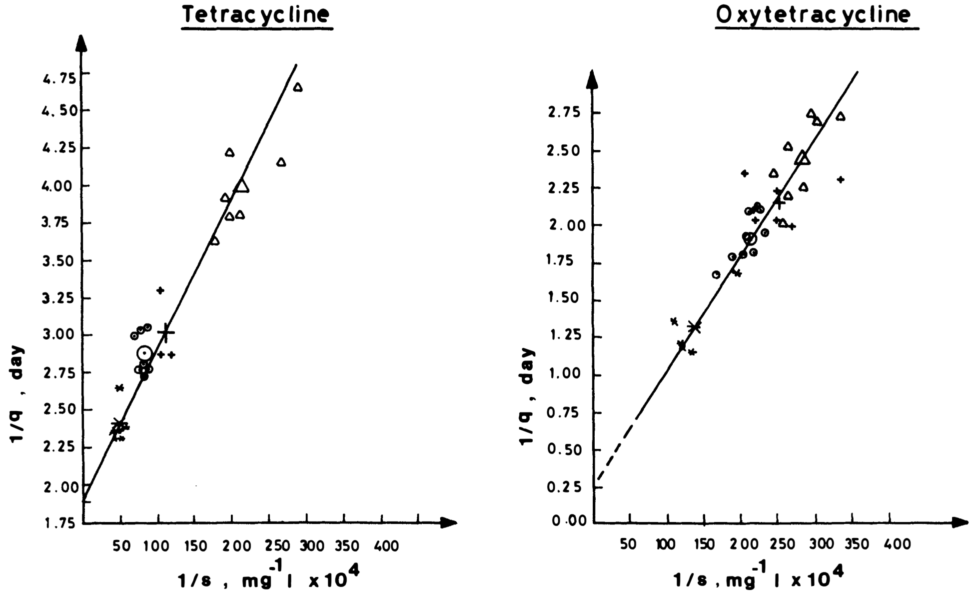

Fig. 3. Determination of k and k_s for tetracycline and oxytetracycline wastes

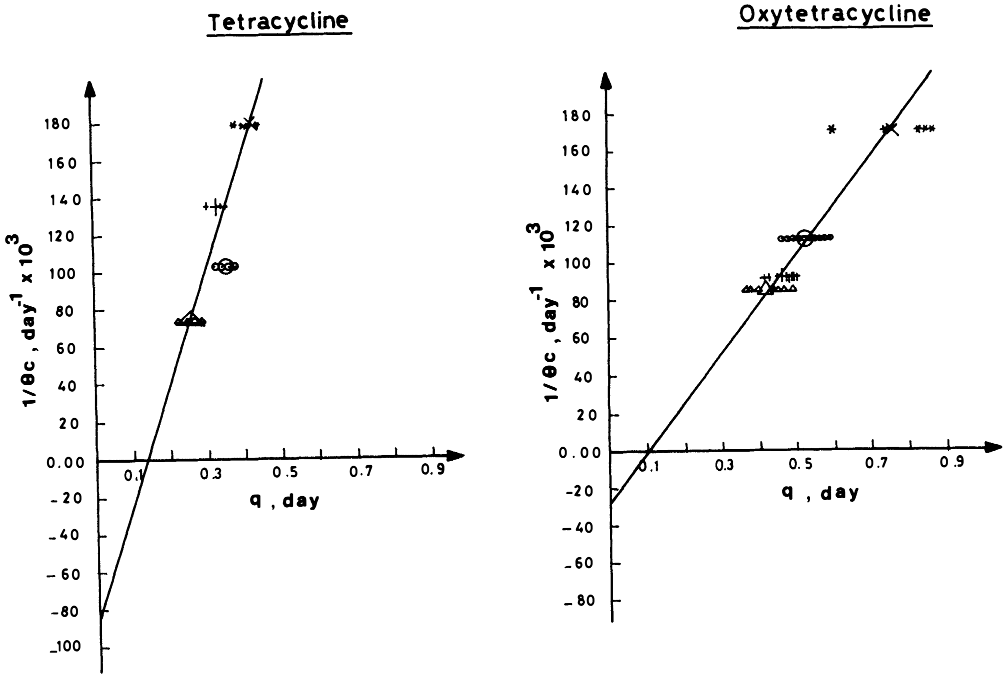

Fig. 4. Determination of Y and k_d for tetracycline and oxytetracycline wastes

TABLE 6 Wastewater Characterization Adopted for Design

	Flow Rate (m^3d^{-1})	BOD_5 (mgl^{-1})	BOD_5 (kgd^{-1})
Strong Wastes	200	8400	1680
Diluted Wastes	800	50	40
Total	1000	1720	1720

TABLE 7 Effluent Discharge Limits Applicable to Fermentation Wastes

Parameter	Monthly Avg.	Daily Max
pH	6-9	6-9
BOD_5, mgl^{-1}	200	500
TSS, mgl^{-1}	80	200

Table reflects, this approach dilutes the BOD_5 concentration to 1720 mgl^{-1}, a level compatible with aerobic treatment.The treatment system was designed to meet the effluent limits promulgated by the General Directorate for the Environment (Table 7). The proposed and implemented treatment system is shown in Fig. 5 (Şahin Kimya A.Ş., 1987). It basically involves separate equalization of the waste streams, pH adjustment and their combined treatment in a single-stage activated sludge unit where the aeration tank comprises four compartments in series. The aeration tank is designed for an hydraulic detention time of one day. Firstly, this aeration volume has proved adequate in terms of BOD_5 removal efficiency: in continuous experiments on combined wastes, an effluent BOD_5 of 126 - 176 mgl^{-1} was obtained with a t = 25.5 h; in kinetic constants experiments, t = 1.0 d yielded an effluent BOD_5 = 44 mgl^{-1} for oxytetracycline and 120 mgl^{-1} for tetracycline, values much lower than the allowable effluent limit. Secondly, in the light of the kinetic constants obtained, the hydraulic detention time of one day allows the operation of the system at a substrate removal rate of 0.5 d^{-1}, with a MLVSS concentration of 3200 mgl^{-1}, corresponding to a sludge age of 10 days. However, when the production is changed to tetracycline, it is no longer possible to maintain the substrate removal rate of 0.5 d^{-1}, because it is the maximum level achievable with this waste. It will be necessary to increase the MLVSS concentration. The higher yield value associated with this type of waste will favor this operation. At a MLVSS concentration of 3750 mgl^{-1}, a substrate removal rate of 0.4 d^{-1} coupled with a sludge age of 6.7 days will be adequate to maintain a BOD_5 level in the effluent consistently lower than the discharge limit. In fact, the experiments indicated that the activated sludge system could yield an effluent BOD_5 of 120 mgl^{-1} with a substrate removal rate of 0.31 d^{-1} and a MLVSS concentration of 4200 mgl^{-1}.

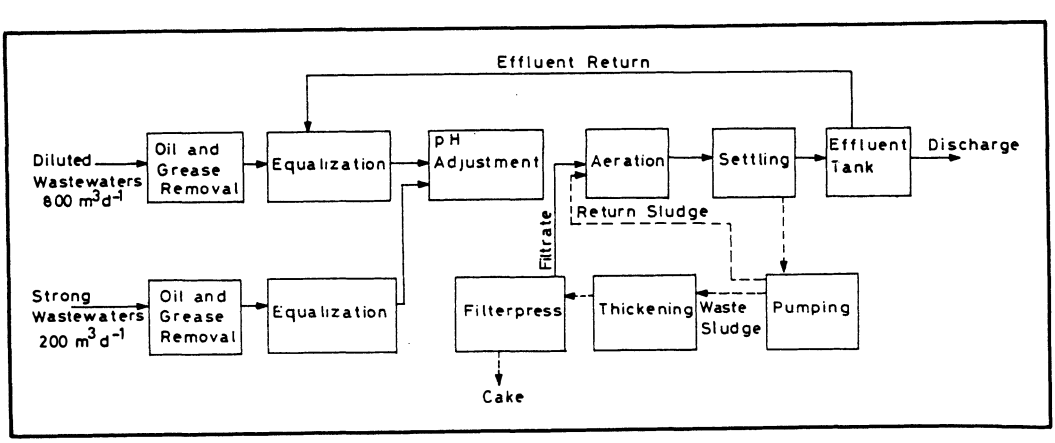

Fig. 5. Process flow diagram of the proposed treatment system

GENERAL EVALUATION

Antibiotic wastes are very complex in nature and require detailed experimental evaluation prior to a pollution control program. The study summarized at Ansa antibiotic plant identified 33 different wastewater sources which could be grouped into strong process wastes, diluted other wastes and cooling discharges. The aerobic treatment alternative, economically attractive because of the air exhaust in the plant, was only possible when combining and diluting the wastes to a BOD_5 of 1700 mgl^{-1} , a level compatible with this type of treatment.

Extensive studies were carried out to assess the treatability characteristics of process wastes as well as waste combinations. The striking feature of the plant was that tetracycline and oxytetracycline were produced alternately, generating wastewaters with completely different treatability characteristics, which was reflected in the set of kinetic constants determined in lab-scale experiments.

The collected data were the main asset in designing the proposed treatment system. The hydraulic detention time of one day adopted for the activated sludge system was justified by experimental results; but it required two different sets of operating conditions for tetracycline and oxytetracycline wastes: namely, oxytetracycline wastes required a substrate removal rate of 0.5 d^{-1} and a sludge age of 10 days. However the former had to be reduced to 0.4 d^{-1} for tetracycline since 0.5 d^{-1} was the maximum utilization rate for this substrate. This change also affected the sludge age of the operation since it was limited by the hydraulic residence time of the system and by the maximum MLVSS concentration that could be maintained in the aeration tank.

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