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COMPARATIVE EVALUATION OF TREATMENT ALTERNATIVES FOR WASTEWATERS FROM AN EDIBLE OIL REFINING INDUSTRY

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ABSTRACT

The aim of this study was to investigate the treatment alternatives for high-strength acid waters from an edible oil refinery and to determine an appropriate treatment system. The study was conducted in three stages: waste characterization, treatability studies and wastewater treatment system design. Based on preliminary lab-scale flotation experiments a full-scale Dissolved Air Flotation (DAF) plant was constructed. The removal of fatty materials (FM) was more than 80% without using any chemical reagent in the DAF unit. Physico-chemical treatability studies were conducted by using $FeCl_3$, $Al_2(SO_4)_3$ and $Ca(OH)_2$ as coagulants. Aerobic treatability experiments were carried out by means of an insitu pilot-scale activated sludge (AS) unit with a volume of 240 l. A BOD_5 removal of 85% and FM removal of 95% were achieved for the organic loading rate (OLR) of 0.45 kg BOD_5kg VSS.d. The biological sludge had an excellent settling property with a sludge volume index (SVI) of 55 to 74 ml/g. Anaerobic sulphate removal kinetics was also investigated as a comparable alternative to physico-chemical treatment both in a pilot upflow anaerobic sludge blanket reactor (UASBR) and anaerobic filter (AF). Anaerobic treatability experiments showed that the linearized second-order substrate removal kinetics could be used to explain the anaerobic sulphate removal from acid waters of edible oil refineries. The maximum sulphate removal efficiency of the AF was about 60% for a hydraulic retention time of two days.

KEYWORDS

Activated sludge process; anaerobic sulphate removal; acid waters; dissolved air flotation; edible oil; Monod kinetics; physico-chemical treatment; second order kinetics.

INTRODUCTION

The process of edible oil refining includes neutralization of free fatty acids, removal of gummy materials, deodorization and color removal stages. The first three stages of refining are carried out in the same reactor as a batch process that produces a sopstock from which fatty acids are recovered by the process of acid splitting. Acid splitting is conducted by the addition of sulphuric acid to the sopstock,which causes the free fatty acids to be separated from the medium. The resulting effluent, that is highly acidic with an average pH of 1.7 and sulphate content of 4000 mg/l, constitutes the main source of process wastewaters.

The objective of this paper is to investigate the treatment alternatives for process wastewaters from an edible oil refining industry for the design of a treatment plant that would produce an effluent to satisfy the discharge standards to the municipal sewer system. The lack of satisfactory design criteria showed that a multilateral treatability study, including physico-chemical, aerobic and anaerobic biological phases, would be useful. This paper covers the results of treatability studies, that were carried out for about one and a half years, on wastewaters from a private edible oil industry and evaluation of the treatment kinetics both for aerobic and anaerobic processes.

MATERIAL AND METHODS

An intensive monitoring program was run for the first two months. Composite wastewater samples were collected from the main discharge channel of acid waters to determine effluent characteristics. Daily and hourly flow rate variation were monitored for two weeks by means of a triangular weir installed in the main sewer.

Physico-chemical analyses and treatability studies were carried out according to Standard methods (1985).

Aerobic biological treatability studies were conducted in a pilot on-site activated sludge unit. The pilot plant consisted of two compartments, an aeration tank with a volume of 240 l and a settling compartment of 52 l(Fig.1). Diffused air was used to maintain a sufficient dissolved oxygen level in the aeration chamber. The plant was designed to provide total internal recycle of settled activated sludge. The effluent from the DAF unit was diverted via a submersible pump to a constant head level tank and neutralized by adding caustic soda in a mechanically mixed neutralization tank, then fed into the pilot activated sludge (AS) unit.

The seed sludge was supplied from a local package activated sludge plant treating municipal wastewaters. Acclimatization period took about three weeks with a hydraulic retention time of 5 days,which was gradually decreased to 1 day. Mixed liquid volatile suspended solids concentration (MLVSS) was maintained in the range of 2.6-4.1 g/l depending on the influent BOD_5 content of the wastewater.The parameters including pH, BOD_5, COD, TSS, TFM and MLVSS were measured daily but other parameters were determined three times per week.

Anaerobic treatability studies for acid waters were carried out in a pilot UASBR and an AF. A pilot plant was operated as an UASBR at first and then it was converted to the AF by filling the plexiglass column with synthetic packing material. The pilot reactor had an empty volume of 49 l, and DAF effluent, following pH correction in the neutralization tank, was fed continuously by means of a peristaltic pump (Fig.1). The reactor inside temperature was controlled to between 30-35°C by heating the bottom half of the column by means of a thermostat-controlled water bath. Sludge containing 65 gSS/l from a local septic tank was screened through a 50 mm sieve and used as the seed for the UASBR. An initial organic loading rate (OLR) of 0.1 $kgCOD/m^3.d$ was applied to the reactor and the start-up period ended after 15 days of operation and then the OLR was gradually increased by increasing the feed rate simultaneously. The major operating parameters were temperature, pH, TFM, SS, COD and $SO_4^=$.

RESULTS AND DISCUSSION

Effluent Characterization

Effluent characterization includes flow rate measurements and determination of polluting parameters. Hourly flow rate fluctuations were measured for about two weeks. Evaluations on flow rate variations showed that maximum and minimum values did not differ too much from the average. Daily averages are illustrated in Fig.2. It is seen from this figure that average flow for a ten-day period is almost 7.1 l/s. Maximum and minimum values in that period are 10 and 5 l/s are respectively.

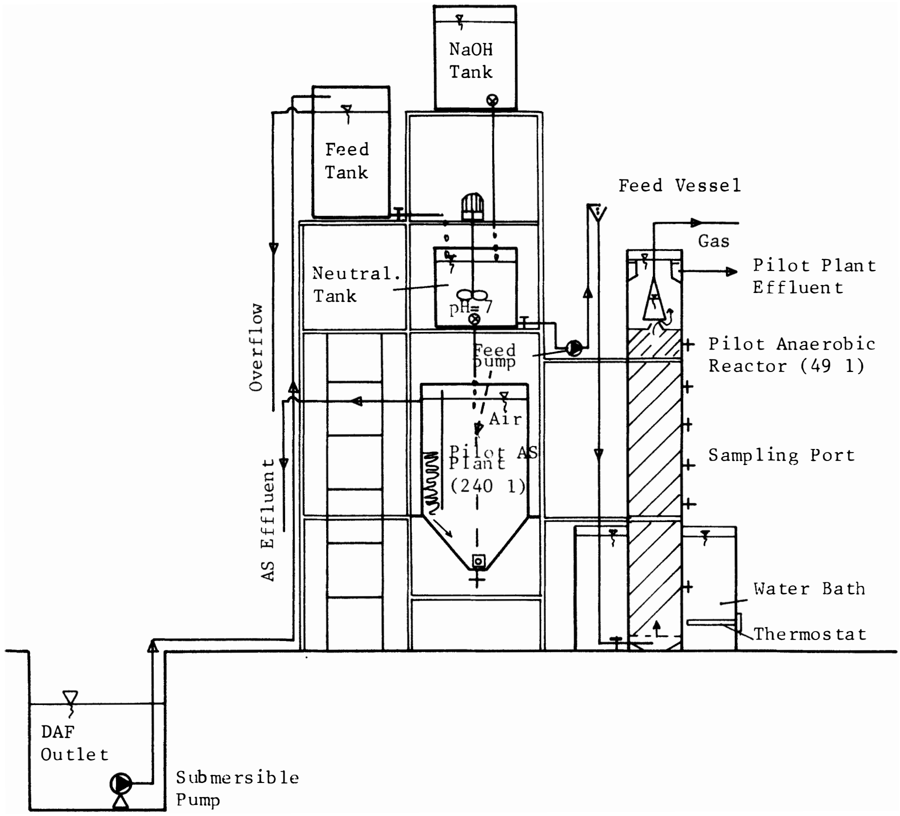

Fig.1. Pilot plants.

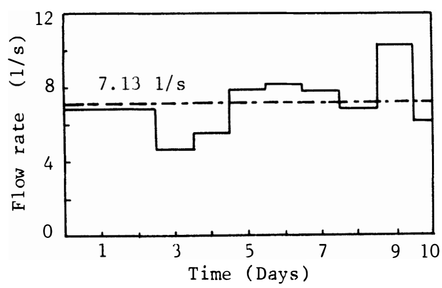

Fig.2. Daily flowrate variations.

Acid water contains materials such as fatty acids, neutral oil, protein, glycerol , and glycerides. This waste is harmful to concrete even after neutralization. The volume of acid water is approximately 0.5 to 0.6 m^3 per tonne of edible oil produced. Polluting parameters which are based on waste characterization are given in Table 1 together with municipal sewer standards.

Treatment of Acid Waters From Edible Oil Refineries

Conventional treatment of acid water involves a combination of physical, chemical and biological processes with substantial mechanical equipment required for the dewatering of sludges. Comparative evaluation of performances

TABLE 1 Wastewater Characteristics and Istanbul Municipal Sewer System Discharge Standards

Parameter	Range	Average	Sewer system standards
pH	1.4-2.0	1.7	5.5-10.0
Temperature (°C)	45-60	50	40
BOD_5 (mg/l)	1500-2500	2200	250
COD (mg/l)	2500-5400	3500	800
Oil-Grease(mg/l)	100-1500	500	50
TSS (mg/l)	150-400	240	350
Nitrogen (mg/l)	60-85	70	30
Phosphorus(mg/l)	250-450	350	8
$SO_4^=$ (mg/l)		4000	1000
Ni (mg/l)	2-5	3	10

of various treatment alternatives that were investigated in this study has been presented in the subsequent sections.

Physico-Chemical Treatment

For many years the removal of separable fatty matters (SFM) was achieved in so called "fat traps". The gravity fat trap which is usually installed as standard equipment on all process effluent streams is the simplest form of physical treatment. Such a gravity fat trap cannot reduce emulsified fatty matters under 500 mg/l, which is very high to discharge to municipal sewerage system. Dissolved air flotation (DAF) techniques are, however, much more widely applied to fatty effluents. Laboratory-scale flotation studies resulted in a fatty material removal as high as 80 %, and as a result a full-scale DAF unit was constructed. The DAF unit is rectangular in shape with the dimensions: length = 12.5 m, width = 2.5 m, height = 1.5 m; and has a detention time of 6.6 hours.

Since the process wastewaters from edible oil refinery are acidic and extremely corrosive to the equipment, cooling water withdrawn from the sea was used as a recirculation water and saturated with air. The flowrate of the recirculated stream constitutes 20 % of total flow.

Pollutant parameters in the DAF outlet were monitored and it was observed that concentrations were too high to satisfy municipal sewer discharge standards. Results are given in Table 2 together with pilot-scale activated sludge unit performance data. The DAF unit provides a fatty material recovery of 65 kg/kg.d which is a valuable by-product that can be used for soap production.

TABLE 2 DAF and Pilot Activated Sludge Systems Treatment Results

Parameter	DAF inlet	DAF outlet	AS system performance
T(°C)	45-60	10-12	
BOD_5 (mg/l)	2200	1400	85 %
COD (mg/l)	3500	2500	72 %
Oil-grease(mg/l	500	100	95 %
TSS (mg/l)	240	240	80 %

Since the FM is highly dispersed and emulsified, with the droplet size of the fatty matter less than 20 μm, gravity separation techniques are largely ineffective and additional treatment must be applied to reduce the FM content. Destabilization of the emulsified system is achieved by charge neutralization adjusting the pH or adding an opposite charge ion into the waste. It is a well known practice that alum, ferric chloride, lime and polyelectrolytes are effective coagulant aids in reducing the suspended solids and organic matter content of wastewaters.

Ferric cloride was found to be the most effective coagulant during physico-chemical treatability studies, resulting in a BOD_5 and COD removal of about 36 percent. Physico-chemical treatment provides a considerable reduction in organic loading, but the discharge standards are still not met. Dart (1974) and Grant (1981) have reported that 60 to 64 % BOD_5 and 88 to 91 % TFM removals are possible by 1500 mg/l lime addition after adjusting pH to 10 with NaOH. Treatability studies with lime in this study did not give such high BOD_5 and TFM removals, and low treatment efficiencies with lime were thought to be related to the quality of the lime used in the experiments.

Aerobic Biological Treatment

Since effluent from the DAF unit did not meet discharge standards, acid water was decided to be further treated by an activated sludge system. A pilot on-site AS unit was installed and biological treatability studies were conducted in this system.

Pilot AS plant was operated for three months under field conditions by simulating extended aeration system. Hydraulic retention times were varied in the range of 10 to 24 h. The pilot AS plant was subjected to unintentional concentration shock loadings from time to time but effluent BOD_5 values of the system remained stable, even in such unsuitable conditions (Fig.3). BOD_5:N:P ratios were about 100:4.4:23 which indicates that N can be the growth limiting nutrient while P is in excess in the medium. Average values of parameters for the AS plant are given in Table 2.

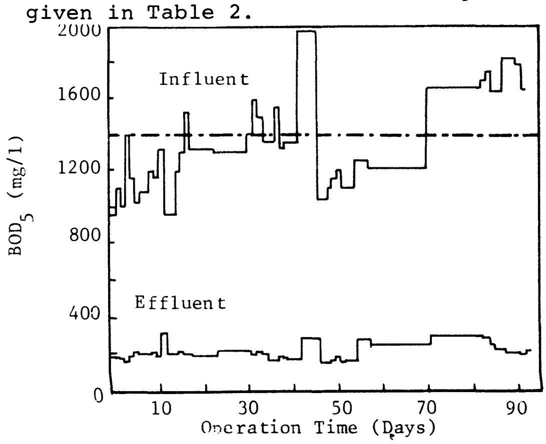

Fig.3. Influent and effluent BOD_5 profiles for the pilot AS system.

The pilot AS system was operated at about 10°C, although the mean temperature of the raw effluent was 50°C, since the season was winter and the system was open to the atmosphere. However substrate removal efficiencies in the pilot-plant were satisfactory to all unfavorable conditions and it is expected that the efficiency would be more than 85 % when a full-scale AS plant is put into the service.

Kinetic Evaluation of the AS Treatment Data. The theory and principles governing the kinetics of substrate removal, formation of biomass, in suspended growth systems are fully explained in the related literature such as Lawrence and McCarty(1970) and Grady and Lim (1981). Using Monod (1950) kinetics, the following final expressions can be obtained for effluent substrate concentrations from completely mixed activated sludge reactors (Öztürk et al, 1989):

$$\frac{S_o - S}{X.\theta} = \frac{1}{Y} \cdot \frac{1}{\theta_c} + \frac{b}{Y} \qquad (1)$$

and

$$\frac{1}{\mu} = \frac{K_s}{\mu_m} \cdot \frac{1}{S} + \frac{1}{\mu_m} \qquad (2)$$

where S_o is the influent substrate concentration (mg/l), S is the effluent substrate concentration (mg/l), X is the MLVSS concentration in the AS aeration tank (mg/l), θ is hydraulic retention time (d), θ_c is sludge retention time (d), Y is growth yield coefficient (gVSS/gBOD$_5$), b is cell decay rate coefficient (1/d), μ is the specific biomass growth rate (1/d), μ_m is the maximum specific biomass growth rate (1/d) and K_s is the half-velocity constant (mg/l). Eqs.1 and 2 provide the means for evaluation of kinetic constants from the steady state operational results of the pilot AS system. The straight lines generated by these two equations give the kinetic constants which are summarized in Table 3, for the acid water from edible oil refining industry. The values for

TABLE 3 Summary of Kinetic Constants.

Waste	μ_m (1/d)	K_s (mg/l)	b (1/d)	Y (-)	basis for Y	SVI (ml/g)	Reference
Edible Oil (Sunflower)	0.36	350	0.075	0.28	VSS/BOD	55-74	This study
Edible Oil (Soybean)	12.0	355	0.144	0.74	TSS/BOD	310	Jorden et al(1971)
Edible Oil	-	-	0.11	0.5	VSS/BOD	-	Adams et al(1975)
Domestic Waste	5-6	100	0.06	0.6	VSS/BOD	-	Metcalf and Eddy (1979)

the same industry given by Jorden et al (1971), Adams et al (1975) and typical values for domestic wastes are also included for comparison.

As is shown in Table 3, once suitable environmental conditions were established for biomass growth, edible oil wastes seem to be quite degradable. Cell yield obtained in this study for AS system is smaller than the values given in the literature. It is likely that the difference depends on the evaluation basis for Y. Furthermore, the treatability experiments in this study were conducted under winter conditions, therefore low temperature has affected the maximum growth rate coefficient. Critical nitrogen content of the waste, that decreases cell growth, might be another factor. Since the original temperature of wastewater before DAF entrance was extremely high, about 50^{o}C, a temperature over 20^{o}C, even under winter conditions, is expected in the full-scale aeration basin, which would alter kinetic coefficients significantly.

Results from full-scale DAF and pilot AS systems revealed that a BOD$_5$ removal efficiency of more than 85 % could be achieved even under winter conditions and the variation in the sludge retention time (θ_c) from 10 to 30 days significantly influences system performance in the range of 88 to 93 % according to Equation 1.

Anaerobic Biological Treatment

The sulphate concentration of acid water from the investigated edible oil industry was about 4000 mg/l and no significant reduction in sulphate was achieved in the AS system. Lime treatment of acid water does not bring about a substantial reduction in sulphate when its concentration is less than 1500 mg/l. The most practical alternative to decrease the sulphate content of the effluent from the AS unit is to dilute it with cooling waters. If the amount of the cooling water is small, the least expensive way of reducing sulphate concentration may be to replace sulphuric acid for splitting the soap stock with hydrochloric acid.

In recent years, anaerobic sulphate removal has been considered an attractive alternative for sulphate reduction from high-sulphate-bearing wastes. In the anaerobic digestion of high-strength industrial wastes containing high levels of sulphate, the two major processes of concern are sulphate reduction and methane production, the latter being inhibited by the former. In anaerobic sulphate reduction, organic matter is diverted from methane production to sulphide generation. Sulphur-reducing bacteria (SRB) such as Desulfovibrio and Desulfotomaculum utilize sulphate as an electron acceptor with hydrogen sulphide being the end product of the process. The kinetics of competition for the available electron donors between SRB and methane producing bacteria have received considerable attention (Abram and Nedwell, 1978; Archer, 1983).

Investigation of the feasibility of anaerobic treatment for sulphate reduction for the treatment of acid water was one of the main objectives of this study. For this purpose, pilot-scale anaerobic treatability studies were conducted. Pilot-plant experiments were carried out in two stages of 6 weeks and 4 weeks respectively. In the first stage, the pilot plant was operated as an UASBR. Steady state treatability results for the UASBR are shown in Table 4 together with operating results of the AF.

TABLE 4 Average Steady State Performance Data For UASBR and AF

Process	Period (weeks)	Flow (l/d)	HRT (d)	OLR ($kgCOD/m^3.d$)	Inf.COD (mg/l)	Inf.$SO_4^=$ (mg/l)	COD_{rem} (%)	$SO_4^=$ rem. (%)
UASBR	0-2	24.5	2	1.7	3400	3400	35	35
	3-4	24.5	2	1.7	3400	3590	41	42
	5-6	49.0	1	3.6	3590	3590	39	40
AF	7-8	24.5	2	1.8	3580	3320	42	45
	9-10	24.5	2	1.8	3620	3510	56	57

In the first stage maximum sulphate reductions were about 42 % and 40 % for HRT's of 2 and 1 day, respectively. Temperature differences between upper and bottom parts of the reactor caused a significant loss of biomass from the system and for that reason the reactor was converted to an anaerobic filter by filling with synthetic packing. The synthetic packing was made of nodose plastic rings with a specific surface area of 95 m^2/m^3.

The second stage of the experiments was carried out in the AF unit. Hydraulic retention time was kept as constant at 2 days and a maximum sulphate reduction of 57 % was achieved in this stage (Table 3). The biomass loss was controlled by the packing material and the system performance was also significantly increased in the AF unit in comparison to that of the UASBR unit.

Anaerobic Sulphate Removal Kinetics. Sulphate-reducing bacteria (SRB) derive energy for synthesis and maintenance from the metabolism of organic matter, and use sulphate as their terminal electron acceptor. The reduction of sulphates in this process may be expressed by the following equation (Abram and Nedwell,1978)

$$8H^+ + 8\bar{e} + SO_4^= \xrightarrow{SRB} S^= + 4H_2O. \quad (3)$$

Thus, the reduction of one mole of $SO_4^=$ (96g) corresponds to the oxidation of eight equivalents of organic matter, or about 64 g COD. The theoretical COD:$SO_4^=$ ratio required for the reduction of sulphate is thus 0.67:1. However, this excludes the removal of COD for cell growth and the effects of COD removal by other microorganisms such as methanogenic bacteria operating within the same system, which would tend to result in a higher COD:SO_4 ratio (Anderson et al, 1986).

Considering the n-th order substrate ($SO_4^=$) removal kinetics, anaerobic sulphate removal process can be expressed by the following equation (Grau et al,1975).

$$-\frac{ds}{dt} = k_{n(s)} X_o \left(\frac{S}{S_o}\right)^n \quad (4)$$

where $k_n(s)$ is the n-th order substrate removal kinetic constant (1/d) and X_o is average biomass concentration in the reactor (mg/l). Integrating equation(4)for n=2 yields the following second-order substrate removal kinetic expression:

$$S = \frac{S_o^2}{S_o + k_{2(s)} \cdot X_o \cdot \theta} \tag{5}$$

The second-order equation can be rearranged to give:

$$\frac{\theta \cdot S_o}{S_o - S} = \theta + \frac{S_o}{K_{2(s)} \cdot X_o} \tag{6}$$

and in general it is linearized in the following form:

$$\frac{\theta \cdot S_o}{S_o - S} = a + b\theta . \tag{7}$$

The second-order kinetics constant then becomes:

$$k_{2(s)} = \frac{1}{a} \cdot \frac{S}{X_o} . \tag{8}$$

The coefficient b in equation (7) is close to one and generally it reflects the impossibility of attaining a zero value of COD in the reactor effluent.

The results presented in Table 3 and the data given by Anderson et al (1986) for acid water from a similar edible oil refinery were plotted in Fig.4. Figure 4 shows that the experimental data fit sufficiently well to the proposed process kinetics and the effluent $SO_4^=$ concentration can be expressed by the following linear equation:

$$\frac{S_o \cdot \theta}{S_o - S} = 1.79\ \theta + 1.04 . \tag{9}$$

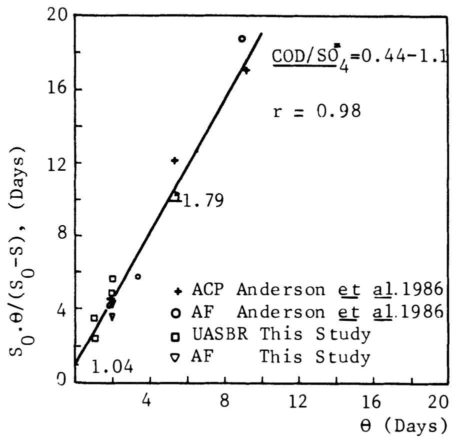

Fig.4. Linearized second-order kinetic of anaerobic sulphate removal for acid water from edible oil refineries

The second-order substrate removal rate constant was also calculated for the related data as $k_{2(s)} = 0.095/d$. Anaerobic sulphate removal has a significant relation with the COD to $SO_4^=$ ratio (Gao et al, 1988). A more detailed information about anaerobic sulphate-removal kinetics will be given in a separate paper due in time. Results obtained in the pilot anaerobic treatability study have clearly shown that a 60 percent sulphate reduction could easily be achieved in anaerobic filters and that COD removal rates of as high as 60 % were also possible simultaneously.

PROCESS DESIGN

The chemical treatment which is followed by the extended aeration AS system was designed to meet effluent discharge standards to the city sewerage system (Fig.5). Based on the findings of the treatability studies it was concluded that the AS system with a 24 h HRT and 30 d SRT following chemical treatment would satisfy discharge standards. Treatment cost of acid water from the related industry was predicted as about 0.08 US dollars per m^3 of process water. Pilot-plant experiments clearly showed that anaerobic filter treatment of acid waters could be a feasible alternative to chemical treatment.

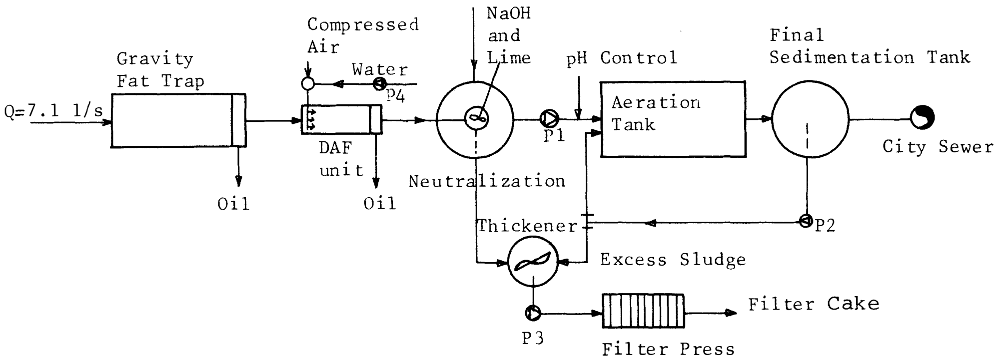

Fig.5.Schematic flow diagram of the proposed treatment system.

CONCLUSION

The treatment alternatives for process wastewaters from an edible oil refining industry were investigated. Ferric chloride was found to be the most effective coagulant during physico-chemical treatability studies, resulting in a BOD_5 and COD removal of about 36 percent. Results from full-scale DAF and pilot AS system revealed that a BOD_5 removal efficiency of more than 85% could be achieved even under winter conditions. Results obtained from the pilot anaerobic treatability study have clearly shown that a 60 percent sulphate reduction could easily be accomplished in anaerobic filters. A COD removal ratio as high as 60% was also possible simultaneously. It can be concluded from the results of treatability studies that anaerobic treatment of acid waters could also be a feasible alternative to chemical treatment.

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