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REDUCTION IN ENVIRONMENTAL POLLUTION CAUSED BY WASTE WATERS FROM EDIBLE OIL REFINERIES, CONCEPT AND INVESTIGATIONS

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ABSTRACT

In the refining of edible oil highly concentrated flows of various waste waters, particularly acidic water, are produced. The mixing of these waste waters with other flows that are only slightly contaminated will be prohibited in West Germany in future. Moreover, the legislation will demand biological treatment of the waste waters extending beyond the chemicophysical wastewater purification hitherto employed. A concept is presented for a process for purifying the waste waters produced in the refining of edible oil whose essential innovative element is a two-stage aerobic biological treatment with a discontinuous activated sludge process in the first stage, and a submerged fixed bed reactor in the second stage. The combination of processes was tested in pilot trials, which show that maximum elimination of the relevant waste water constituents can be achieved in this way. COD inlet concentrations of around 3000 mg/l have been reduced to residual contents of approx. 200 mg/l, and fats and easily degradable carbon compounds (BOD_5) have been almost completely removed from the waste water. The biological treatment requires prior neutralisation and cooling of the wastewaters to 20 to 30°C, the controlled addition of nitrogen, and careful monitoring and control of the operation of the plant.

KEYWORDS

Process water; acid water; refining of edible oil; treatment system; discontinuous activated sludge process; submerged fixed bed reactor; COD removal.

INTRODUCTION

In future more stringent requirements will be imposed in West Germany on the treatment of the waste waters produced during the refining of edible oil and edible fat. In view of this development the West German Oil Mill Association is having investigations carried out to examine the combined effect of suitable technologies for reducing the quantities of waste water and pollutant levels produced and treating the residual waste waters to a higher standard than in the past. The following is a report on some of the results of pilot trials on a semi-industrial scale with original waste waters - particularly concerning the biological treatment of what is termed the acid water.

PRODUCTION PROCESSES

A simplified diagram of the process stages used in conventional refining of crude oil to produce edible oil is shown in Fig. 1. The purpose of the refining is to eliminate as far as possible the extraneous substances present in the crude oils used, such as seed particles, dirt, phosphatides (eg lecithin), carbohydrates, proteins, mucins, free fatty acids, dyes, waxes and substances which are imparting a characteristic taste or smell. In West Germany crude oil obtained mainly from seed fats is refined.

The essential operating stages are:

- Pre-cleaning (desludging) to remove mucins and phosphatides,
- Deacidification (neutralisation) to separate free fatty acids,
- Bleaching to remove undesirable dyes and
- Vaporising (deodorising) to drive out substances imparting an undersirable taste or smell.

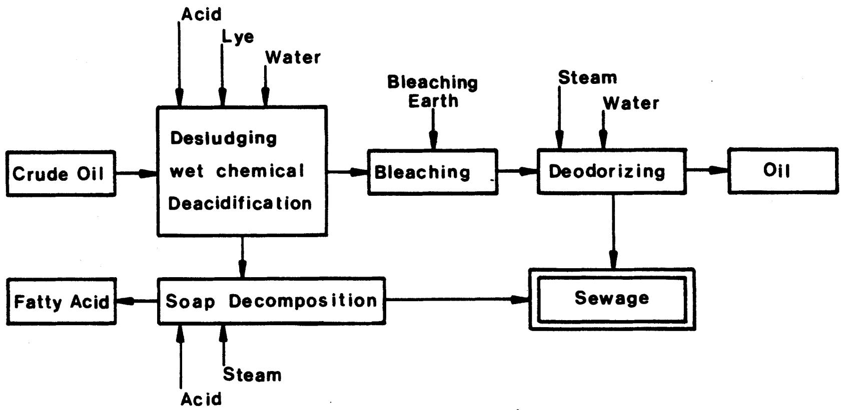

Fig. 1. Refining of edible oil

WASTE WATER

The quantity and contamination of the waste water from the refining of crude oil to produce edible oil and edible fat depend mainly on the temperature and hardness of the available cooling water, on the processing equipment used (continuous, discontinuous processes), process temperatures and pressures, on the raw material used and how often the type of oil is changed. In the conventional refining process the main flows of waste water arise during the wet chemical deacidification/soap decomposition, and during direct condensation of the vapours. Whilst the latter represents the highest waste water flow in the refinery, but only contains organic substances in low concentrations, the waste water flow from the wet deacidification/ soap decomposition displays much higher COD concentrations whilst representing only approx. 5% of the total waste water produced.

In crude oil refining without circulation of the water collected from the vapour condensation, total contaminated water production of 10 to 25 m^3/t of charge product must be assumed, the quantities of contaminated water indicated containing contaminated flushing and cleaning water. If circulation of the condensed water is provided, the specific quantity of contaminated water produced is reduced to below 10 m^3/t of raw material.

The waste waters contain the fractions of the undesirable extraneous products listed above which are not converted to usable by-products or solid waste. In addition the waste water contains substances which are formed during processing due to chemical reactions, or under the influence of heat, eg products of oxidation of fatty acids, polycyclic aromatic hydrocarbons and sodium sulphate or chloride.

Krause (1985) indicates the following values for the composition of the waste water as a whole from the refinery:

- deposited substances (after 0.5 h)	< 1 ml/l
- petrol ether extractable substances	< 150 mg/l
- COD	< 600 mg/l
- COD/BOD_5	1.5 - 2
- Temperature	< 35 °C
- pH value	5 - 9
- sulphate	300 - 1000 mg/l

(during decomposition of the soap stick with sulphuric acid)

The following concentrations may be found in the acid water (Sekoulov et al., 1988):

- COD 2000 - 10000 mg/l
- Sulphate 1000 - 20000 mg/l
- Fat 50 - 500 mg/l
- PO_4 -P 40 - 600 mg/l
- pH value 1 - 3

LEGAL REQUIREMENTS

The 4th Waste Water Administration Regulations of 17 March 1981, with the minimum requirements summarised in Table 1, currently apply to waste water discharged directly into surface waters, whose pollutants derive essentially from the oil seed preparation and the refining of edible fat and edible oil.

Table 1 Minimum requirements regarding the discharging of waste water according to the 4th Waste Water Administration Regulations

MINIMUM REQUIREMENTS ACCORDING TO ADMINISTRATIVE RULES									
ACTUAL VERSION (SINCE 1981)							EXPECTED VERSION (1990)		
	QUANTITY OF SEWAGE REFERED TO USED RAW MATERIAL m^3/t	SETTLEABLE SOLIDS mL/L	COD mg/L		EXTRACTABLE SUBSTANCES mg/L		QUANTITY OF SEWAGE REFERED TO USED RAW MATERIAL m^3/t	BOD mg/L	P mg/L
		RANDOM SAMPLE	AVERAGE SAMPLE					QUALIFIED RANDOM SAMPLE (HOMOGENIZED)	
			2h	24h	2h	24h		5 SAMPLES 2 min. INTERVAL	
CONDITIONING OF OIL BEARING SEEDS	<10	0.3	200	170	30	20	<0.5	25	2
EDIBLE OIL AND FAT REFINING	<10 10 - 25	0.3 0.3	250 200	230 170	50 30	40 20	<2	25	2

The specific water consumption and the quantity of substances that may be deposited are prescribed, together with the COD and the extractable substances in the deposited sample. The minimum requirements are based on chemico-physical treatment of waste water, but not biological treatment, according to the generally recognised rules of the art applicable when the regulation was issued.

In 1989 a revision of the Wastewater Administration Regulations will be passed in which minimum requirements presuppose the use of biological waste water treatment plant. In accordance with the applicable requirements for municipal waste waters, a restriction on the phosphorus content is also provided. Moreover, the permissible quantity of contaminated water, and hence the fresh water consumption during production, are drastically limited. Such a limitation of the quantities of waste water can only be achieved by consistent circulation of the water used for condensing the vapours, which is reconcentrated. The values currently being discussed as new minimum requirements imposed on the waste waters to be discharged into bodies of water, from edible oil refining, are also listed in Table 1.

In addition the requirements are tightened up on the 1981 version, in that the values in the homogenised, undeposited random sample must be adhered to. This necessitates maximum separation of the solids from the waste water.

TREATMENT CONCEPT

Methods to avoid or reduce the waste water pollutants have already been incorporated into the production process in order to minimise the losses of raw materials used or of usable intermediate and end products. Physical processes such as separation by centrifugal force and flotation to separate fat and oil from the water flows were introduced into the edible oil refining process some time ago. The changeover from wet chemical deacidifcation to distillative deacidification offers the best prospects for reducing the level of pollutants in the waste waters by means of internal methods. This obviates the need for the formation of soap stick and the decomposition process required hitherto to recover fatty acids, with inorganic acid, producing the highly concentrated acid water. However, the distillative deacidification is not yet regarded as usable for all oils.

In view of the fact that there will in future be hardly any dilution of the acid water, because of the circulation of the condensed water, a concept was developed for treating highly concentrated waste waters arising from refining of edible oil.

Due to the high COD values a multi-stage treatment system was chosen (Fig. 2). The wastewater supplied, in fluctuating quantities, cooled to 20 to 30 °C, is pretreated by internal installations (fat separator, flotation), and is initially fed to equalisation basins. The biological treatment takes place after a two-stage neutralisation, the 1st biological stage consisting of discontinuously operated, totally mixed reactors. The individual process phases are divided into: filling and mixing; aeration; sedimentation; decanting. This arrangement is particularly recommended in the case of highly contaminated waste waters. By incorporating anaerobic and aerobic phases special microorganisms are favoured and the formation of sludges tending to flotation are suppressed (Wilderer et al., 1985). In this first treatment stage there is a reduction in COD of about 80%, and for the residual reduction submerged fixed film

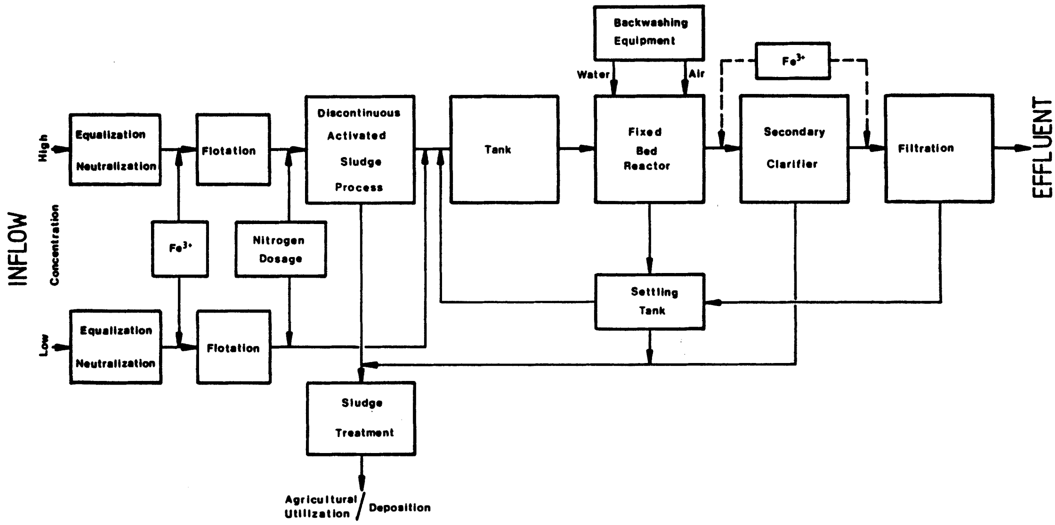

Fig. 2. Treatment system

reactors are provided as the 2nd biological stage. An equalising tank is arranged between the discontinuously operated first, and the continuously operated second, biological stages for the purpose of avoiding hydraulic shock loads. The fixed bed reactors consist of a tank with a constantly submerged packing through which a flow of air is forced from bottom to top with air in parallel with waste water. The microorganisms grow on the carrier materials and form a biofilm. Such submerged fixed bed reactors have proved ideal for waste waters of an unbalanced composition such as those found in the case under discussion. It is also an advantage for slowly growing microorganisms to be able to develop on the packings over a long period, these microorganisms being capable of converting special substances. The design and mode of operation of the reactors prevents the biomass from being washed out of the plant uncontrolled. This considerably increases the treatment capacity and results in higher operational reliability.
The excess sludge discharged continuously from the submerged fixed film reactor is separated in a post-treatment stage (settling basin or flotation). To prevent blockages the submerged fixed film reactor is regularly back-washed, and the sludge produced by this is separated in a waste water washing basin and fed to the sludge treatment phase just like the excess sludges from the first and second biological stage. A multi-layer filter is used to remove the remaining solids from the waste water, and the high phosphorus contents are eliminated by multipoint precipitation (before the 1st biological stage, after the 2nd biological stage, possibly in the filtration supply pipe).

If much lower COD supply concentrations occur permanently (due to internal measures) or temporarily, it is possible to dispense with the 1st biological stage, or bypass it.

STUDIES

Laboratory tests and pilot trials on a semi-industrial scale were carried out with the acid water from an edible oil refinery to ensure that the selected concept could be implemented and to obtain design parameters, interest centering on the two biological stages. No devices for P precipitation and residual solid sampling were used in the tests carried out.

Design and operation of the pilot plant

The design of the pilot plant is represented in diagramm form in Fig. 3, and Table 2 summarises the most important plant and operating data of the two biological stages.

After passing through 2 separators the acid water is pumped with the acid water pump (1) through the heat exchanger (2) into storage tank (9). The heat exchanger (2) cools the acid water, from a temperature of 50 to 80 °C, down to 20 to 28 °C, and this is followed by a two-stage neutralisation process which is controlled by a pH meter (3, 3a). Urea is added (8) for nitrogen enrichment of the acid water, and the storage tank (9) is aerated, with large bubbles of compressed air, by means of the ventilating device (10), for thorough mixing and to prevent the formation of hydrogen sulphide.

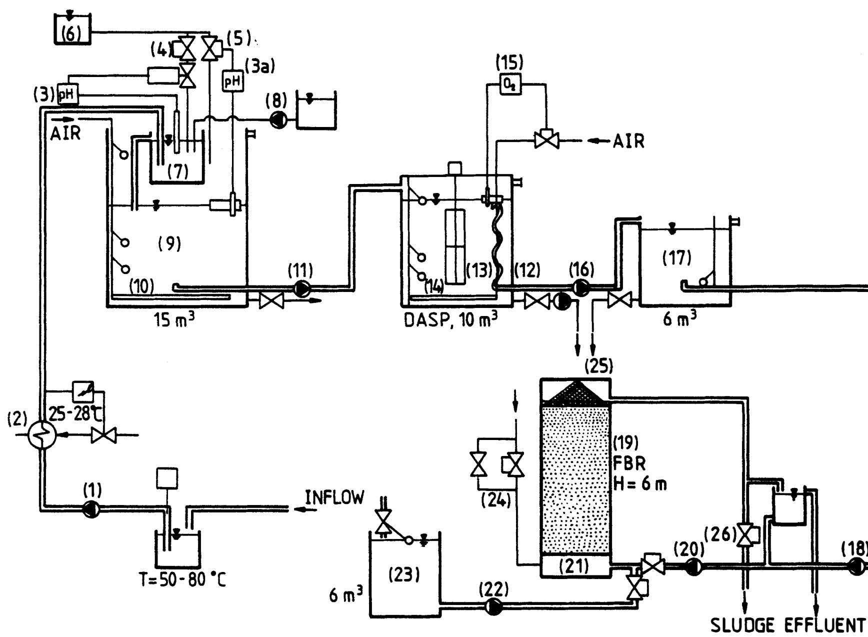

Fig. 3 Design and flow chart of the pilot plant

(1)Acid water pump (2)Heat exchanger (3),(3a)pH meter (4)Control valve (5)Solenoid valve (6)Lye tank (7)Mixing tank (8)Urea metering device (9)Storage tank (10)Ventilating device (11)Feed pump (12) DASP reactor (13)Agitator (14)Diaphragm fan (15)Control unit (16)Discharge pump (17)Intermediate tank (18)Feed pump (19)FBR (20) Recirculation pump (21)Water distribution device (22)Back-washing pump (23)Back-washing water tank (24)Solenoid valve (25)Screen (26) - (28)Solenoid valve.

The waste water is treated in batches by the discontinuous activated sludge process (DASP). The feed pump (11) conveys the waste water, at the beginning of the cycle, into the reactor (12) of the ASP, and the agitator (13) mixes the waste water with the activated sludge, thoroughly and uniformly. The oxygen supply required is provided by the injection of fine bubbles of compressed air by means of the diaphragm aerator (14), and is controlled by the oxygen meter and control unit (15). At the end of a cycle the pretreated waste water is fed with the discharge pump (16) into the intermediate tank (17).

The submerged fixed bed reactor (FBR) (19) filled with expanded clay is fed continuously from the intermediate tank by means of the feed pump (18), and a certain quantity of water can be circulated with the recirculation pump (20). The water flows upwards through the reactor, which is aerated, the water and air being supplied by the air and water distribution device (21). The reactor is back-washed by water and air washing devices, the water washing being provided by the back-washing pump (22), and the increased air demand for the air washing being provided by opening the solenoid valve (24). To ensure that the bulking clay is not discharged from the reactor during back-washing, a screen (25) is installed above the bulking clay filling, and the solenoid valve (26) is opened to discharge the sludge during back-washing. The plant is controlled and the measured values recorded by means of a central control unit.

Table 2a Pilot trials: plant and operating data DASP

cycle length	8 h (3 cycles/d)
reactor volume	8 m^3
sewage flow	4 m^3/cycle; 12 m^3/d; 1,5 (m^3/m^3 d)

Parameter		phase 1a 3.6.-24.6.87	phase 1b 25.6.-23.7.87	phase 2 24.7.-6.11.87
operation mode:				
filling	h	0.40	0.40	0.40
stirring	h	7.00	6.50	6.50
anaerobic	h	0.75	0.75	0.17
aerobic	h	6.25	5.75	6.33
sedimentation	h	1.00	1.50	1.50
decantation	h	0.50	0.50	0.50
	min	2.0		0 9
MLSS g/L	ø	3.5		2 3
	max	4.6		5 0
COD - space	min	0.93		1 50
loading	ø	3.49		4 80
kg/(m^3 d)	max	6.18		7 83
COD - sludge	min	0.26		0 62
loading	ø	1.11		2 04
kg/(kg d)	max	2.91		5 13

Table 2b Pilot trials: plant and operating data FBR

height	7.0 m	internal diameter	1.0 m
volume	4.71 m^2	packing material	expanded clay
grading	4-8 mm	ø diameter	5.5 mm
porosity	40 %	specific surface	680 m^2/m^3
packing density	690 kg/m^3	water volume	1,8 m^3
inflow on weekdays	500; 250 L/h	inflow on weekend	125 L/h
residence time (refered to empty reactor):			
on weekdays	9.45; 18.9 h	on weekend	37.8 h
inflow (refered to empty reactor):			
on weekdays	2.55; 1.27 $m^3/(m^3$ d)	on weekend	0.64 $m^3/(m^3$ d)
surface flow rate incl. recycle flow (refered to empty reactor):			
water	3 $m^3/(m^2$ h)	air	5 $m^3/(m^2$ h)

Parameter		phase 1a 3.6.-24.6.87	phase 1b 25.6.-23.7.87	phase 2 24.7.-6.11.87
COD - space	min	0.48		0.52
loading	ø	0.82		2.02
kg/(m^3 d)	max	1.21		3.92

The dry mass concentration in the DASP reactor in phase 2 was reduced to simulate higher loading of the submerged fixed film reactor.

Results

The characteristic data of the acid water produced in the feed pipe to the pilot plant is shown in Table 3.

Table 3 Acid water characteristics

Parameter	Average	Minimum	Maximum
COD mg/l	3300	2800	4100
Sulphate mg/l	9800	1200	20000
Fat mg/l	202	78	504
Phosphate mg/l	844	120	2000
pH		1.4	2.1
Temperature °C		50	80

The ratio of the COD in the original sample to that in the filtered (0.45 µm) sample was found to be about 1.30, and when related to the filtered samples the COD in the DASP reactor in phase 1 was reduced by an average of 86%. In phase 2, with a shorter anaerobic phase and a lower dry mass concentration, this value reduced to an average of 71%. This deliberately reduced output of the first biological stage could be absorbed in the second biological stage (submerged fixed film reactor), but in phase 2 no significant increase in the (filtered) COD discharge concentrations about 200 mg/l, achieved in otherwise trouble-free operation, was observed. The average total efficiency of both biological stages, over the whole test period, was approx. 93% (Table 4) as far as the filtered COD was concerned. Figs. 4 and 5 show the curve of the COD concentration in the inlet and outlet of the DASP reactor in phase 1, and in the inlet and outlet of the FBR reactor in phase 1+2. Fig. 6 provides a survey of the filtered (0.45 µm) and unfiltered COD concentrations in the inlet and outlet of the plant as a whole, but there was no clear dependence of the elimination rates on the spatial and sludge loads within the spans of these parameters observed (see Table 2). Preliminary tests showed that the treatment result that can be obtained is influenced by the type of acid water instead.

Table 4 Results of the pilot trials - average total efficiency of biological stages

Stage	COD,f Influent	COD,f Effluent	COD,f Removal	Residence Time empty reactor	COD,f space loading	COD,f sludge loading
	g/l	g/l	%	h	kg/(m³ d)	kg/(kg d)
I DASP	2754	567	79.4	8	0.93-7.83	0.26-5.13
II FBR	567	180	68.3	9.45/18.9	0.48-3.92	
I + II	2754	180	93.3			

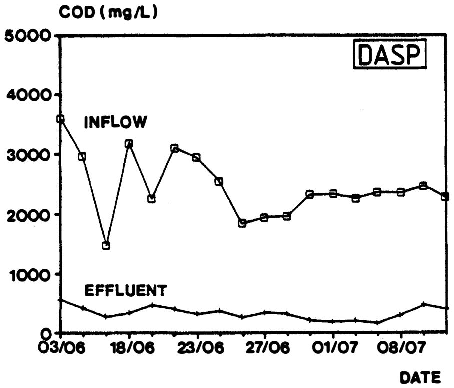

Fig. 4. DASP: COD concentration in phase 1

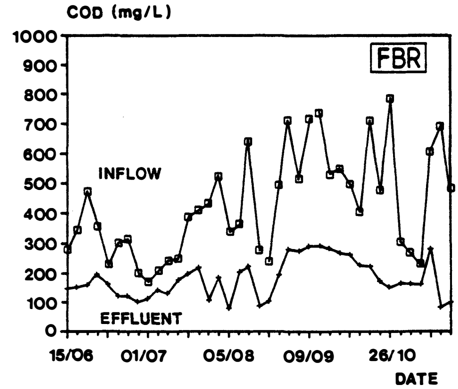

Fig. 5. FBR: COD concentration in phase 1+2

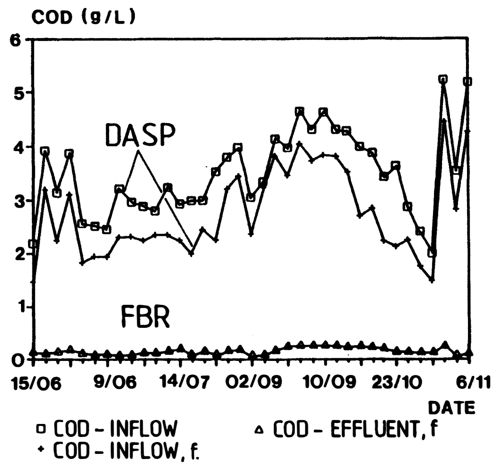

Fig. 6. COD concentrations in the inflow and effluent of the pilot plant

The specific excess sludge production was 0.17 kg dry mass per kg COD. The deposition of activated sludge was good throughout the test, and no bulking sludge formation was observed at any time.

The fat (average 202 mg/l) introduced into the plant with the acid water was fully eliminated with the process selected. The discharge concentrations were mainly below the detection limit and were due to a discharging mass of bacteria. This discharge of bacterial mass, in a large scale plant, is stopped by the downstream stages (flotation, filtration) in the plant process.

The addition of urea required to ensure an adequate supply of nitrogen for the microorganisms can be easily handled, but to avoid overdosing, regular examination of the nutrient ratio in the inlet, and monitoring of the nitrogen compounds in the outlet of the treatment plant are required.

During the tests there was considerable foaming in the DASP, and sometimes also in the outlet of the FBR. This is due on the one hand to the high fat content, and formation of soaps during the neutralisation of the waste water with soda lye, and on the other hand to the necessity for intense aeration to cover the high oxygen demand. Consequently there was sometimes undesirable flotation of the activated sludge. In a large scale plant suitable precautions must therefore be taken to overcome the problem of foaming.

CONCLUSION

The results of the tests carried out show that the future requirements regarding the discharge quality of the waste waters from an edible oil refinery can be met with the proposed concept (equalisation, two-stage neutralisation, flotation, discontinuous activated sludge process, submerged fixed bed reactor, flotation, filtration). If the operation of a large scale plant is optimised, treatment results going beyond those achieved in the pilot trials may be expected. The contents of fat and easily degradable carbon compounds (BOD_5) can be eliminated down to low residual concentrations, and the residual content of heavy degradable substances, represented by the outlet COD, is determined essentially by the crude oils used, and cannot be predicted on a generalised basis. Particular attention must be paid to the operating needs (constant wastewater supply, overcoming foaming, monitoring the nutrient ratios).
For dimensioning a large scale plant, the following design parameters are suggested:

COD space loading (DASP)	3.5 kg/(kg d)
COD space loading (FBR)	2.0 kg/(kg d)
Surface flow rates	2.5 m/h (Flotation)
	0.5 m/h (FBR, water)
	10 m/h (FBR, air)
	15 m/h (Filter)

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