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A CASE STUDY ON SUNFLOWER SEED OIL INDUSTRIES WASTE CHARACTERIZATION, CLASSIFICATION AND TREATMENT

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ABSTRACT

The sunflower seed oil industry is one of the most important industrial sectors. As a part of the agro-industry, sunflower seed oil production makes a significant contribution to environmental pollution in Turkey. A lot of research studies are known to be performed on the characterization and treatment of olive oil production wastes in Turkey, but the nature, amount, waste loads and treatment of the wastewaters produced by sunflower seed oil industries have not been studied to a great extent.

In this study, a typical sunflower seed oil refinery in the city of İzmir was selected as representative of this sector. Method of production is evaluated and the refinery is investigated for the characterization of its wastewaters. During the first part of the test program, quality of combined and separate raw effluents was investigated. Possible physical-chemical treatment alternatives were studied using bench-scale laboratory models. Based on these studies, the most practicable and efficient combination of treatment operations and processes were pointed out. Waste segregation possibilities for minimization of wastewater quantities are investigated. In these investigations treated effluent quality has been evaluated with respect to the discharge parameters set by the present Turkish environmental legislation.

KEYWORDS

Sunflower seed oil refinery effluents; wastewater characterization; emulsion breaking; acid cracking; chemical coagulation.

INTRODUCTION

Turkey produces above 1 million tons of sunflower seed according to 1985 projections of the State Statistics Institute. Approximately 300 000 tons of raw and 110 000 tons of refined edible oil have been produced in the same year. (DIE, 1985; DPT, 1985).

The raw sunflower seed oil can be obtained by using one of the following methods: mechanical press method, press-extraction method and direct extraction method. All the three methods are in use in Turkey for the production of raw sunflower seed oil. Press-extraction method is the most widely used method in Turkey, but most of the sunflower seed oil is produced in primitive presses having a total press capacity of 150 000 tons, working only a few months during the year. They have small capital investments, but are not efficient in production. More modern edible oil plants use up-to-date extraction processes for the production of sunflower seed oil, too. Three such plants are operating in Trace and there are two more in the Marmara Region (TÜBİTAK, 1984).

Effluents of sunflower seed oil refineries originate from neutralization, winterization, condensation processes and cooling operations. At the neutralization stage impurities in the raw oil are settled with caustic soda and the settled material is removed. Thus, wastewaters originating from the neutralization process are the most polluted ones produced during the refining of oil. Temperatures of these effluents are between 50 and 70°C. Amount of wastewater generated at this stage is 10-20 % of the oil charged into the neutralization boiler. Other wastewaters produced from refineries are wash waters, which do not have as high pollution loads as the neutralization process wastewaters. Effluents of the winterization process are obtained during the cleaning of press filters and discharging of boiler waters. Refining of raw oil consists of a series of operations utilizing pressurized steam; thus condensation and cooling waters are also produced as wastewaters. Amounts of such waters are too high, but their pollutant concentrations are weak. Total amount of effluents is 32 - 46 % of soap production on a weight basis. As in the soap production caustic soda is used; soap production wastewaters contain high alkalinity, high turbidity, and suspended solids, as well as high COD and BOD_5 values.

OIL AND GREASE REMOVAL METHODS

Control of oil and grease is a stringent requirement of municipal authorities responsible for permitting connection of industrial wastewaters into the sewer system. Oil and grease tend to clog the sewer pipes and pumps and create difficulties in the municipal wastewater plants. Thus oil and grease limits are to be considered along with other indicator parameters such as BOD, pH, total suspended solids in sewer discharge standards. Industries are asked to remove oil and greasy material from their wastewaters in order to utilize the economic and other advantages of pretreatment and joint treatment. In domestic wastewaters, oil and grease concentrations may range from 30 - 50 mg/1, whereas wastewaters from communities with industrial contributors usually have higher concentrations (Tsugita and Ellis, 1981).

Free oil and grease which is not emulsified, presents no serious problem with respect to its removal from water because it will tend to float and agglomerate. The surface layer of oil and grease can then be mechanically skimmed off the surface. Emulsified oil, however, stays in suspension causing severe separation problems. That is why oil and grease treatment may be categorized into two stages: first-stage treatment can be utilized to separate free flotable oil and grease from water. At this stage, the treatment process involves gravity separation of the greasy material, which is equally effective in removing greases and non-emulsified oils. The simplest form of this first-stage treatment is the grease interceptor or grease trap. The typical process for oil and grease removal, particularly in situations where emulsification exists, is a gravity separator followed by a second-stage unit using one of the several methods for breaking the oil and grease emulsion that passes through the first-stage unit. In the second stage physical, chemical electrical and biological methods exist for breaking oil and grease emulsions. Chemical methods are presently in wide use, in conjunction with physical removal methods. Emulsions can be broken by chemicals that will balance or reverse the surface tension on each side of the interfacial film, neutralize stabilizing electrical charges, or precipitate emulsifying agents. Common chemicals that have been utilized to break emulsions or coagulate the colloidal particles include alum, ferrous sulfate, ferric sulfate or chloride, sodium hydroxide, calcium chloride, sulfuric acid, lime, soda, borax, sodium sulfate and commercial organic treating chemicals. After chemical additions freed oil and grease is concentrated and removed by a suitable physical process such as dissolved air flotation. Coagulation utilizing aluminum or iron salts has been effective for de-emulsifying oily wastes, but the precipitated sludges are difficult to dewater and the volume of sludge generated and requiring ultimate disposal creates an additional problem (Eckenfelder, 1980).

Physical methods used to break emulsions include heating, centrifugation and filtration. Centrifugation breaks oil emulsions by separating the oil and water phases by centrifugal force. Such centrifugation procedures are best applied to oily sludges or small volumes of oily wastewaters. Filtration has also been used with some success, as have high-rate sand and diatomaceous earth filters (Tsugita and Ellis, 1981).

CHARACTERISTICS OF WASTEWATERS ORIGINATING FROM SUNFLOWER SEED OIL PRODUCTION IN TURKEY

In this study a typical sunflower seed oil refinery in the city of İzmir was selected to represent the edible vegetable oil industries. In the plant, 5000 tons of sunflower seed oil and 2000 tons of soap were produced in 1987. Raw oil is supplied from Trakya Region. Refined sunflower seed oil is sold to the inner and southern regions of Anatolia. Refining processes which are used in the plant are neutralization, drying, decolorization, boiling, deodorization, cooling and winterization. A mixture of municipal and ground water is used at the rate of 40 m^3/day, of which 30 m^3/day is discharged as wastewater. The sources of wastewaters are mainly neutralization and soap production processes.

In the city of İzmir, sewer discharge limits apply to industries located within the Metropolitan area. Therefore wastewaters of this edible oil refinery must be pretreated for oil and grease removal. Before selection of a pretreatment process scheme,a study for characterization and treatability of the edible oil refinery wastewaters must be performed.Wastewater characteristics of this selected sunflower seed oil factory were examined by the DEÜ, Department of Environmental Engineering during years 1986 and 1987. Experimental results are submitted in Table 1 (DEÜ, 1986, 1987).

TABLE 1 Wastewater Characterization of the Sunflower Seed Oil Factory

WW sample	pH	BOD (mg/l)	COD (mg/l)	Oil-grease (mg/l)	Suspended solids (mg/l)
Soap prod. (18.3.1986)	11.5	33000	71000	6455	9070
Soap prod. (8.4.1986)	12.6	70000	100800	31690	13450
Refining (16.5.1986)	12	-	29920	15045	-
Composited	12.4	-	39360	35400	-

In another study, the same properties of wastewaters originating from different processes of the same factory were studied. The results are summarized in Table 2(Oktay, 1986).Different samples taken at different dates are numbered as I and II.

TABLE 2 Wastewater Characteristics of Sunflower Seed Oil Refinery Processes

WW sample	Temp. (C)	Oil-grease (mg/l)	BOD (mg/l)	COD (mg/l)	SS (mg/l)	pH
Neutralization process wastewaters						
I	65	145520	155800	275000	-	13.8
II	60	132700	143600	270800	-	13.7
First wash waters following neutralization						
I	50	3540	4760	9280	-	13.3
II	55	3720	4870	9630	-	13.5
Second wash waters following neutralization						
I	56	3320	3750	8780	-	12.6
II	55	3250	3700	8690	-	12.5
Winterization process wastewaters						
I	70	350	525	980	-	11
II	75	525	840	1430	-	12
Condensation process wastewaters						
I	35	40	60	35	-	7
Soap production wastewaters						
I	55	420	65000	120000	13550	13.4
II	65	740	77500	140000	12500	13.9

In a third program aiming at the wastewater characterization of this refinery, wastewater samples from different production stages were collected at different dates and analyzed. Table 3 shows the results of this last study.

During the experimental studies COD, BOD_5, Oil and Grease and Suspended Solids determinations were carried out according to the techniques given in American Standard Methods (APHA, 1981).

TABLE 3 Wastewater Characterization of the Sunflower Seed Oil Factory Located in İzmir

WW sample	pH	Oil-grease (mg/l)	COD (mg/l)	SS. (mg/l)
	Refining process wastewaters			
I (4.11.1988)	11.0	597	7840	-
II (19.12.1988)	11.3	230	1040	-
III (3.5.1989)	10.0	1012	3360	433
	Soap production wastewaters			
I (4.11.1988)	12.5	166	19200	-
II (19.12.1988)	12.0	380	18640	-
III (3.5.1989)	11.3	564	48000	1766
	Combined wastewater			
I (17.10.1988)	13.0	2900	13600	240
II (3.5.1989)	12.0	688	5440	845

MODEL STUDIES ON TREATABILITY OF WASTEWATERS

Physical-chemical treatment studies were carried out on composite samples obtained by combining effluents from several processes of the refinery on the first run and on combined wastewaters from soap and refinery processes. These studies were conducted by two groups of researchers in the scope of dissertation thesis works (Oktay, 1986; Yıldırım and Sancar,1988). A laboratory bench-scale test model was used in both of the studies, however, coagulants and coagulant aids used in the jar tests were different in both cases. In the first study, many coagulants and polyelectrolytes were tested for the treatment of composited wastewaters of the sunflower seed oil factory. After determining the optimal test conditions, coagulation efficiencies have been found by adding appropriate doses of $FeSO_4$ and $FeSO_4$ and A-470 type anionic polyelectrolyte at pH 6.5. Results obtained by these chemicals are given in Table 4.

TABLE 4 Jar Test Results With $FeSO_4$ and $FeSO_4$+Anionic Polyelectrolyte

Coagulant dose (g/l)	Oil-grease Eff. conc. (mg/l)	Oil-grease Removal eff. (%)	Chemical Oxygen Demand (COD) Eff. conc. (mg/l)	Chemical Oxygen Demand (COD) Removal eff. (%)
	Ferro sulfate ($FeSO_4$)			
0	31500	-	115000	-
0.5	11340	65	51750	59
1.0	9130	71	47150	65
1.5	7870	75	35650	69
2.0	7250	77	27600	76
3.0	9750	69	41400	64
	Ferro sulfate+anionic polyelectrolyte			
1.0 g/l +2 mg/l	9450	70	39100	66
1.5 g/l +2 mg/l	8500	73	33350	71
1.5 g/l +3 mg/l	8200	74	31050	73
2 g/l +3 mg/l	7250	77	28750	75
2g/l +4 mg/l	8800	72	35650	69

When alum was used as a coagulant, the optimum pH range was found to be between 6.5 to 7.0. Lime and alum were added until the pH reached 7.0. Results of this experiment are presented in Table 5.

Chemical coagulation with lime was also tried in these effluents. Again, pH of the wastewater sample was reduced to pH= 2.0 by adding concentrated H_2SO_4 and then lime. During the test, 90 % pure reactive lime ($Ca(OH)_2$) was used as coagulant. Lime and cationic polyelectrolyte addition alternative was also tried. The results are given in Table 6.

TABLE 5 Jar Test Results With Alum and Alum+Cationic PE (K-570)

	Oil-grease		Chemical Oxygen Demand (COD)	
Coagulant dose (g/l)	Eff. conc. (mg/l)	Removal eff. (%)	Eff. conc. (mg/l)	Removal eff. (%)
Alum ($Al_2(SO_4)_3.18\ H_2O$)				
0	41000	-	144000	-
0.5	12700	69	43100	70
1.0	11100	73	34600	76
2.0	6200	85	18800	87
3.0	1700	96	4000	97
4.0	1800	96	4800	96
5.0	2250	94	10000	92
Alum+Polyelectrolyte				
0	41000	-	144000	-
2 g/l +3 mg/l	6450	85	28900	80
3 g/l +3 mg/l	2400	94	7100	95
3 g/l +4 mg/l	3300	92	11500	92

For the treatment of wastewaters of sunflower seed oil factory which were examined in this study, acid cracking for de-emulsification plus chemical coagulation methods have been used. First, the pH of the oily wastewaters was lowered to pH= 2.0 with the help of concentrated sulfuric acid. After breaking the oil and grease emulsion, freed oil and grease were removed by phase separation and then chemical coagulation method was applied. By using the jar test apparatus, coagulant and polyelectrolyte doses have been determined.

TABLE 6 Jar Test Results Obtained with Lime and Lime+Cationic Polyelectrolyte(K-570)

	Oil-grease		Chemical Oxygen Demand (COD)	
Coagulant dose (g/l)	Eff. conc. (mg/l)	Removal eff. (%)	Eff. conc. (mg/l)	Removal eff. (%)
Lime ($Ca(OH)_2$)				
0	29700	-	98000	-
3.0	14800	50	46050	53
4.0	10400	65	35300	64
5.0	3250	89	9750	90
6.0	1800	94	5100	95
7.0	2950	90	10800	89
Lime + nonionic polyelectrolyte				
0	29700	-	98000	-
5 g/l +2 mg/l	5900	80	18600	81
5 g/l +3 mg/l	4200	86	15600	84
5 g/l +4 mg/l	4800	84	16000	84
6 g/l +2 mg/l	3300	89	7800	92
6 g/l +3 mg/l	3000	90	10000	89
6 g/l +4 mg/l	2900	90	10800	89

In this series of experimental studies, the characteristics of the effluents of a sunflower seed oil factory were re-examined as presented in Table 5.

In performing the treatability study in this program acid cracking for de-emulsification of oil and grease was conducted as a separate process. At this stage, pH of the effluents was reduced to 2.0 and the freed oil and grease was removed by phase separation. The results of acid cracking method are given in Table 9. Coagulation with lime and polyelectrolyte was tried after the pH of the supernatant was adjusted to pH= 6.0, pH= 7.0 and pH= 8.0 at different series. At each series, selected doses were applied in separate beakers and anionic-type polyelectrolyte was added.

In the first series of tests, composited effluents from several processes from the oil refinery were treated. Chemical coagulation process consists of 2 minutes of rapid mixing with lime solution, then 45 minutes of slow mixing, with 60 min for settling. When $FeSO_4$ was used as coagulant, efficiencies of 76 % for COD and 77 % for oil and grease with 2 g/l $FeSO_4$ were found (Table 4). If alum was used on the other hand, efficiencies obtained were 96 % oil and grease removal and 96 % COD removal (Table 5). Results with lime and lime+nonionic polyelectrolyte are given in Table 6. Best efficiencies were 95 % for COD and 94 % for oil and grease.

In the second part of the treatability studies, efficiencies obtained after sulfuric acid addition to break emulsions and subsequent phase separation are found to be higher. These results are given in Table 7. For this alternative process removal efficiencies obtained for oil and grease were 86-96 % and for COD 52-57 %. When this first-stage treatment is followed by chemical coagulation utilizing lime or aluminum salts this process is shown to be more effective for the wastewaters, especially if lime and anionic polyelectrolyte (Praestol 2430) were used for pH adjustment and effectiveness of coagulation increases (Table 8).

TABLE 7. Test Results of Acid Cracking Method

		Oil-grease		Chemical Oxygen Demand (COD)	
Wastewater Sample	pH	Eff. conc. (mg/l)	Removal eff. (%)	Effluent conc. (mg/l)	Removal eff. (%)
Combined ww (17.10.1988)					
Raw ww	13	2900	-	13600	-
oil skimmed	2	360	86	6400	53
Refinery process ww (4.11.1988)					
Raw ww	11	597	-	7840	-
oil skimmed	2	24	96	3360	57
Soap production ww (4.11.1988)					
Raw ww	12.5	166	-	19200	-
oil skimmed	2	18	89	9300	52

TABLE 8. Results of Chemical Coagulation Carried out with Lime and Polyelectrolyte After the Removal of Oil and Grease from the Composited Sample (17.10.1988)

	Oil-grease		Chemical Oxygen Demand (COD)	
Chemical addition (mg/l)	Eff. conc. (mg/l)	Removal eff. (%)	Eff. conc. (mg/l)	Removal eff. (%)
0 (Raw ww.)	2900		13600	
pH= 6.0				
6 mg/l PE			1920	86
10 mg/l PE	200	93	1760	87
12 mg/l PE			1440	89
14 mg/l PE			1600	88
100 mg/l Alum+ 10 mg/l PE	870	80	2680	80

Results obtained at the second part of the study are given in Tables 7,8,9. In this series of studies, refinery and soap production effluents are treated separately. Test results indicate that acid cracking and oil separation is to be followed by lime + polyelectrolyte coagulation. Then, sludge volumes to be formed from the treatment of refinery wastewaters will not be as high as the amount of sludges to be obtained from the treatment of soap production wastewaters.

TABLE 9. Experimental Results of Acid Cracking + Chemical Coagulation Tests

	Oil-grease			Chemical Oxygen Demand (COD)	
Wastewater sample	pH	Eff. conc. (mg/l)	Removal eff. (%)	Eff. conc. (mg/l)	Removal eff. (%)
Refinery process wastewater (12.4.1989)					
Raw ww	12	4840	-	6400	-
oil skimmed	2	80	98	-	-
+lime added	6	60	-	488	-
oil skimmed +lime added	10	30	99.4	400	93.4
oil skimmed +3.0 mg/lPE	6	30	99.4	432	93.3
Refinery process wastewater (3.5.1989)					
Raw ww	10	1012	-	3360	-
oil skimmed	2	800	21.0	2000	40.5
oil skimmed +lime added	7.6	100	90.1	400	88.0
oil skimmed +lime added	10.7	-	-	350	89.6
Soap production wastewater (3.5.1989)					
Raw ww	11.8	564	-	48000	
oil skimmed	2	460	18.4	25600	46.7
oil skimmed +lime added	7	-	-	17600	63.0
oil skimmed +lime added	10.6	250	55.7	16000	66.7
Combined ww. (3.5.1989)					
Raw. ww.	12	688	-	5440	-
oil skimmed	2	570	17.7	4640	14.7
oil skimmed +lime added	7.3	-	-	4350	20.0
oil skimmed + lime added	10.1	-	-	4200	22.8

DISCUSSION OF RESULTS

According to the Turkish Water Pollution Control Regulation passed in 1988, the discharge limits into the sewerage system are given on the basis of guidelines for municipalities that want to have such provisions to be: pH 6.5-10.0, suspended solids 500 mg/l, oil and grease 250 mg/l, tar and petroleum oils 50 mg/l, chemical oxygen demand 4000 mg/l, sulfate 1000 mg/l.

Sunflower seed oil effluents investigated in this study are oily, turbid, alkaline and yellowish-brown in color. Most important pollutants in samples are oil and grease, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) which are present in excessive amounts. The wastewater qualities obtained from the pretreatment studies that were carried out show that the pretreatment standards for the discharge into the sewerage system have been met in most of the cases. Chemical treatment alternative without using acid cracking was not so effective as acid cracking plus chemical coagulation methods. Although many chemicals can be successfully used in the de-emulsifying process, sulfuric acid was found to be the most efficient. Acid cracking skimmings containing oily materials may be recovered and returned to the process in order to be used as acid oil or for production of soap. This may reduce the amount of sludge to be formed in the treatment plant.

For acid cracking of refinery process wastewaters, the required acid was 0.4 l/m^3 wastewater. Sulfuric acid was concentrated (98 % pure, BDH). Amount of acid required for combined effluents of refinery and soap production was found to be 2.0 l/m^3 ww.For the adjustment of the pH from 2 to 7, amounts of required lime (90 % pure) were found to be 0.6 kg/m^3 ww for refinery process wastewater and 0.6 kg/m^3 ww for combined wastewaters.

CONCLUSION

In the city of İzmir, sewerage system construction project is underway and the responsible authority (İZSU) declared that it will accept industrial wastewaters into the sewerage system provided that the pretreated water quality will be in compliance with the local discharge limits.
Effluent quality after these pretreatment stages was acceptable for discharging into the sewerage system; but insufficient for discharge into the receiving waters. Thus, this edible oil refinery may discharge its treated wastewaters into IZSU sewer system, because the proposed pretreatment scheme of acid cracking (acidification and phase separation) followed by lime coagulation, gives out a sufficiently good quality effluent for the sewerage system.

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