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PHYSICO-CHEMICAL STUDIES OF EFFLUENTS AND EMISSIONS OF GHEE/EDIBLE OIL INDUSTRIES IN PAKISTAN

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Samples of the effluents from various Ghee / Edible Oil Industries were collected on fortnightly basis from July 1993 to June 1994 and of the emissions from January to April 1994. Parameters such as temperature, pH, conductivity, total dissolved solids (TDS), total suspended solids (TSS), total alkalinity / total acidity, total hardness, chemical oxygen demand (COD), chlorides, sulphates, phosphates, silica, calcium, magnesium, sodium, and iron were determined in the effluents. Trace metals like copper, manganese, nickel, and zinc were determined by atomic absorption spectroscopy, whereas SO_2, CO CO_2, hydrocarbons, hydrogen, nitrogen, oxygen and argon were examined in the flue gases by Gas Chromatography and other standard techniques such as Orsat Gas Analyzer and Dragger Detection Tubes. Remedial measures were suggested for the pollutants exceeding the National Environmental Quality Standards, (NEQS). Parameters like chlorine, ammonia, sulphides, arsenic,cadmium, chromium, cobalt, lead and tin were also analyzed in the effluents and were found to be nil or below the detection limit, while particulate matters, HCl, chlorine, HF, H_2S, mercaptans and NH_3 were found to be nil in the flue gases.

Key words: Edible oil, Atomic absorption spectroscopy, Vanaspati ghee

Introduction

Vanaspati ghee and cooking oil are the basic cooking ingredients used throughout Pakistan, but the preference vary from family to family. Some prefer the taste of the food cooked in ghee while others prefer cooking oil due to the health considerations. So the market is flooded with various kinds and brands of oils and shortenings.

Pakistan is facing chronic shortage of edible oil because of the much larger consumption than its production. Domestic edible oil production from all sources has grown at the rate of 2.56% annually over the last 24 years, whereas the consumption is increasing at an annual rate of 7.7%. Total requirement of the edible oil of the country is 1.6 million tonnes while only 0.4 million tonnes is produced within the country. The gap between in consumption and production is being bridged by importing edible oil, costing a substantial slice of resources (Arshad Mir and Uzma Qamar 1996).

Generally three basic steps are involved in ghee/edible oil processing, viz. neutralization and degumming, bleaching and deodorization and hydrogenation. In the neutralization and degumming step, high speed centrifuges along with mixers and plate heat exchangers are used for the removal of fatty acids and gum. Deodorization is being done at various steps by steaming. For the hydrogenation, hydrogen is produced by reforming of the natural gas over the nickel catalyst:

$$CH_4 + O_2 \xrightarrow{\text{Ni Catalyst}} CO_2 + 2H_2$$

Hydrogenation is the conversion of various unsaturated radicals of fatty acids into more highly or completely saturated glycerides by the addition of hydrogen in the presence of nickel catalyst.

$$(C_{17}H_{31}COO)_3C_3H_5 + 3H_2 \xrightarrow{\text{Ni Catalyst}} (C_{17}H_{33}COO)_3C_3H_5$$

Heat-180.9 BTU/LBS

The effluent of these industries contain nickel, normally less than 1 ppm but in case of any mis-operation the value may increase several folds. Nickel and its compounds may have harmful effects on industrial workers. Exposure to nickel dust and vapour may cause cancers of the lung and sinus, disorders of the respiratory system and dermatitis (Wurster 1940; Wisniak and Al brigh 1961; Alexander *et al* 1962; Shreve 1973 and Marshel 1973).

Methodology

Both effluent and emission samples of various ghee / edible oil industries were collected fortnightly, and were preserved

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and analysed according to standard methods (Vogel 1978; ASTM 1980). pH and conductivity were measured by pH and conductivity meters respectively, TDS and TSS were measured by gravimetric method, while alkalinity, hardness, calcium, magnesium, COD., chlorides, sulphates and phosphates were determined volumetrically. Sodium and iron were determined spectrophotometrically and trace metals were analysed by atomic absorption spectroscopy. The results were compared with the previous results (Anon 1988).

Gases were analysed by using gass chromatograph, Orsat gas analyser and sulfur analyser.

Results and Discussions

Comparison of fats in various types of edible oils and ghee is given in Fig (1). In addition to the parameters reported in the Tables 1 and 2, total acidity, chlorine, ammonia, sulphur, arsenic, cadmium, cobalt, chromium, lead, and tin were also determined. These results were either zero or beyond the detectable limits of the analytical procedures employed during the study (Anon 1983; 1988 and 1992).

Keeping in view the available facilities, it was planned to analyse different parameters in the effluents and emissions on regular fortnightly basis for at least one year. For each month, 3 -5 samples were collected and analysed and average of these are reported in Tables 1 and 2. Each parameter was checked in triplicate to give the reproducible results.

Table 1, present the effluent analysis of Mujahid Ghee Mill from July 1993 to June 1994. Most of the results are within the permissible NEQS limits, except pH, total suspended solids and nickel in some of the samples, which are beyond the limits and are dangerous for the on stream living organisms.

The pH is an important variable in water quality assessment, as it influences many biological and chemical processes within a water body and all processes associated with water body, water supply and treatment. At a given temperature, pH indicates the intensity of the acidic or basic character of a solution and is controlled by the dissolved chemical compound and biological processes within it. Comparison of pH of the effluents of two different mills is given in Table 4 (a).

The treatment of alkaline waste by neutralization is always beneficial and economical. The choice of an acidic reagent

Table 1

Effluent analysis (Mujahid Ghee & Oil Mills Hattar Industrial Estate Haripur)

Parameters	Unit	NEQS	July 1993 to June 1994											
			Jul. 93	Aug. 93	Sep. 93	Oct. 93	Nov. 93	Dec. 93	Jan 94	Feb. 94	Mar. 94	Apr. 94	May 94	Jun. 94
01 Temp.	°C	40	26	27	27	26	25	26	26	25	27	26	28	30
02 pH	-	6-9	8.3	9.5	7.5	6.8	8.9	8.4	8.4	9.2	7.9	8.3	8.0	9.5
03 cond	uu/cm	-	810	1300	2450	550	520	640	715	825	710	755	778	940
04 TDS	ppm	3500	438	450	1694	495	390	362	350	375	295	305	285	405
05 TSS	ppm	200	76	125	1345	130	245	422	51	65	47	95	35	110
06 TA	ppm	-	450	390	750	80	260	250	410	405	350	345	360	405
07 TH.	ppm	-	110	122	120	106	168	192	160	145	105	128	137	190
08 COD	ppm	150	14	13	12	24	16	15	15	13.5	18.2	4.5	7.8	6.5
09 Ca	ppm	-	40	21	42	28	42	51	49.5	45.5	34.5	39.5	42.3	58.2
10 Mg	ppm	-	18	19	18	20	16	16	10.8	10.5	8	9.1	14	18.5
11 Na	ppm	-	12	11	13	9	11	14	13	8	11	12.5	11	15
12 Fe	ppm	2.0	0.05	0.3	0.05	0.2	0.2	0.1	0.3	0.5	0.4	0.6	0.8	1.5
13 Cl	ppm	1000	30	60	300	175	18	21	40	90	59	49	52	105
14 SO_4	ppm	600	20	30	20	25	20	20	20	25	24	21	29	35
15 PO_4	ppm	-	0.2	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.15	0.1	0.2	0.3
16 SiO_2	ppm	-	18	14	13	12	24	15	10	12	11	13	15	20
17 Cu	ppm	1.0	0.01	BDL	BDL	0.0	BDL	BDL	0.05	0.05	0.1	0.05	0.08	0.15
18 Mn	ppm	1.5	0.01	BDL	BDL	0.0	BDL	BDL	0.04	0.05	0.04	0.04	0.05	0.08
19 Ni	ppm	1.0	5.0	BDL	BDL	1.7	BDL	BDL	1.7	1.5	2.0	1.75	1.9	2.5
20 Zn	ppm	5.0	0.5	BDL	BDL	0.35	BDL	BDL	0.2	0.04	0.15	0.25	0.2	0.35

BDL = Below Detection Limit.

for neutralization of an alkaline wastewater is generally between sulphuric acid and hydrochloric acid. (Ross 1968; Patterson and Minear 1971). Sulphuric acid is usually selected due to its low cost, while hydrochloric acid has the advantage of soluble reaction end products. However, chlorides resulting from hydrochloric acid neutralization may cause the waste to exceed chloride level in effluent (Knowlton 1954; Zievers *et al* 1968).

Total dissolved and suspended solids correspond to filterable and non-filterable residue. The type and concentration of suspended matter controls the turbidity and transparency of the water. Comparison of TSS (total suspended solids) in the effluents of two different oil mills is given in Table 4 (b). Suspended matter consists of silt, clay, fine particles of organic and inorganic matter. These fine suspended particles in the effluent may kill fish and other water life if discharged as such. Suspended solids are usually removed by settling and decantation process, which is the most economical way of removal.

Comparison of Ni in the effluents of two different Oil mills is given in Table 4 (c). Nickel is usually removed from the wastewater as insoluble Nickel hydroxide, by the addition of lime. The precipitation is more effective at a high pH. Treatment for such a low level of nickel 1-7 ppm is not feasible, but can be applied for the concentrated samples.

Table 2 represents the effluent analysis of the Chinyot Oil Mill from July 1993 to June 1994. The results are almost within the permissible limits, which is a healthy sign. If the effluents are treated/controlled regularly, it will set an example to other similar industries.

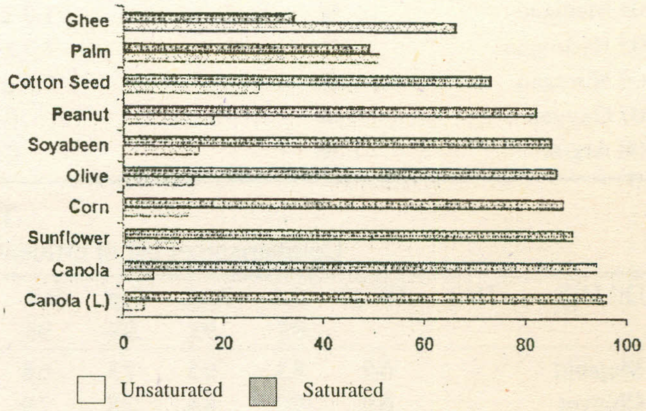

Fig 1. Comparison of saturated and unsaturated fats in different vegetable oils.

Table 2

Effluent analysis (Chinyot Oil Mills Hattar Industrial Estate Haripur)

			July 1993 to June 1994											
Parameters	Unit	NEQS	Jul. 39	Aug. 93	Sep 93	Oct. 93	Nov. 93	Dec. 93	Jan 94	Feb. 94	Mar 94	Apr. 94	May 94	Jun. 94
01 Temp.	°C	40	30	29	25	26	22	23	26	25	31	28	30	32
02 pH	-	6.9	9.0	8.5	7.8	7.9	7.7.	8.0	7.5	8.0	8.0	7.9	7.5	7.8
03 Cond.	uu/cm	427	370	450	415	425	375	800	395	750	415	450	350	
04 TDS	ppm	3500	352	320	395	391	399	385	415	250	458	390	370	375
05 TSS	ppm	200	40	25	35	36	37	41	51	20	49	25	30	31
06 TA	ppm	-	415	320	265	267	260	315	305	310	415	285	280	285
07 TH.	ppm	-	245	219	200	208	220	205	245	215	238	225	230	218
08 COD	ppm	150	4.2	3.9	3.5	3.5	3.6	3.8	3.2	4.1	4.2	3.9	3.5	3.8
09 Ca	ppm	-	55.2	49.3	45.0	46.8	49.5	46.1	55.1	48.8	53.6	50.6	51.8	49.1
10 Mg	ppm	-	18	16	15	15	16.8	15.4	18.4	16.2	17.9	17	17.3	16.5
11 Na	ppm	-	9.0	8.0	9.0	9.0	10.0	8.0	10.0	9.0	8.0	8.0	9.0	0.45
12 Fe	ppm	2.0	0.35	0.2	0.45	0.4	0.35	0.7	1.0	0.025	1.28	1.1	0.9	0.45
13 Cl	ppm	1000	31	29	35	32	29	28	80	29	75	35	25	28
14 SO_4	ppm	600	51	38	50	45	47	39	45	25	42	35	25	28
15 PO_4	ppm	-	0.15	0.2	0.1	0.15	0.2	0.1	0.1	0.15	0.1	0.1	0.2	0.15
16 SiO_2	ppm	-	19	14	15	16	15	13	25	15	22	18	17	9
17 Cu	ppm	1.0	0.03	0.14	0.11	0.12	0.14	0.11	0.05	0.04	0.1	0.05	0.07	0.02
18 Mn	ppm	1.5	0.15	0.14	0.11	0.12	0.01	40.11	0.14	0.14	0.15	0.11	0.12	0.14
19 Ni	ppm	1.0	0.25	0.7	0.67	0.65	0.45	0.55	0.7	0.45	0.85	0.3	0.5	0.45
20 Zn	ppm	5.0	0.45	0.39	0.47	0.4	0.35	0.5	0.6	0.55	0.6	0.06	0.42	0.3

Table 3
Flue Gas Analysis (Mujahid Ghee and Chinyot Oil Mills)

Parameters	Unit	NEQS	Chinyot Oil Mill		Mujahid Ghee Mill	
			January 94	February 94	March 94	April 94
01 Sulphur Dioxide	mg/m^3	600	200 ± 9.5	175 ± 7.6	150 ± 7.2	195 ± 8.2
02 Carbon Monoxide	mg/m^3	800	500 ± 24	615 ± 31	560 ± 4.65	519 ± 4.92
03 Carbon Dioxide	%	-	96.8 ± 4.75	95.75 ± 4.65	96.2 ± 4.65	96.45 ± 0.05
04 Methane	%	-	1.0 ± 0.04	0.9 ± 0.04	1.1 ± 0.05	1.0 ± 0.05
05 Hydrogen	%	-	1.7 ± 0.07	1.4 ± 0.07	1.5 ± 0.07	1.3 ± 0.06
06 Nitrogen	%	-	0.5 ± 0.02	1.6 ± 0.07	0.8 ± 0.03	1.0 ± 0.04
07 Oxygen	%	-	0.0	0.2 ± 0.01	0.2 0.01	0.1 ± 0.007
08 Argon	%	-	0.0	0.1 ± 0.007	0.15 ± 0.06	0.1 ± 0.06

Table 4
Comparison of pH of effluents from two different oil Mills. (a)

Oil Mill	Unit	NEQS	Jul. 93	Aug. 93	Sep 93	Oct. 93	Nov. 93	Dec. 93	Jan 94	Feb. 94	Mar 94	Apr. 94	May 94	Jun. 94
Mujahid	-	6-9	8.3	9.5	7.5	6.8	8.9	8.4	8.4	9.2	7.9	8.3	8.0	9.5
Chinyot	-	6-9	9.0	8.5	7.8	7.9	7.7	8.0	7.5	8.0	8.0	7.9	7.5	7.8

Comparison of TSS in Effluent from two different Oil mills. (b)

Oil Mill	Unit	NEQS	Jul. 93	Aug. 93	Sep. 93	Oct. 93	Nov. 93	Dec. 93	Jan 94	Feb. 94	Mar 94	Apr. 94	May 94	Jun. 94
Mujahid	ppm	200	76	125	1345	130	245	422	51	65	47	95	35	110
Chinyot	ppm	200	40	25	35	36	37	41	51	20	49	25	30	31

Comparison of Ni in Effluent from two different Oil mills. (c)

Oil Mill	Unit	NEQS	Jul. 93	Aug. 93	Sep 93	Oct. 93	Nov. 93	Dec. 93	Jan 94	Feb. 94	Mar 94	Apr. 94	May 94	Jun. 94
Mujahid	ppm	1.0	5.0	BDL	BDL	1.7	BDL	BDL	1.7	1.5	2.0	1.75	1.9	2.5
Chinyot	ppm	1.0	0.25	0.7	0.67	0.65	0.45	0.55	0.7	0.45	0.85	0.3	0.5	0.45

Table 3 shows the flue gas analysis of both Mujahid Ghee and Chinyot Oil Mills. Particulate Matters, HC1, HF, Cl_2 H_2S, mercaptans (organic sulfur), ethane, propane, butane, and pentane are almost nil or beyond the detectable limits of the instrument used during this study. Most of the parameters are within the permissible NEQS limits, except for CO_2 which is very much on the higher side >95%. Although CO_2 is a relatively insignificant non-pollutant species in the atmosphere, it is of serious environmental concern and ultimately CO_2 leads to Green House Effect and Global Warming (DE 1992).

It may be concluded from the physico-chemical analysis effluents and emissions that the edible oil industries investigated during the study are not causing any significant pollution, however, regular monitoring of the effluents and emissions is necessary to keep the situation under control.

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