Original Research

Characterization and Biological Treatability of Edible Oil Wastewaters

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Received: 27 July 2008
Accepted: 30 January 2009

Abstract

This study investigates the conventional characterization and biological treatability of two different wastewaters that originated from corn oil and sunflower oil refining processes. Our aims for characterization of wastewaters included: total and soluble chemical oxygen demand, total and soluble biological oxygen demand, suspended solid, oil and grease, pH, total kjeldahl nitrogen, ammonia nitrogen, total phosphor, phosphate, color and sulfate analyses. In corn oil wastewaters, total COD is portioned as 80% soluble COD, 20% particular COD, 3.4% total soluble inert COD, 0.5% total particular inert COD, whereas in sunflower oil wastewaters soluble COD, particular COD, total soluble inert COD, total particular inert COD are found as 81.7%, 18.3%, 1.9%, and 5.1%, respectively. In our characterization studies, BOD_5/COD ratio were 0.15 and 0.2 for corn oil and sunflower oil wastewaters, respectively. These results indicate that wastewaters are not suitable for biological treatment. But investigation of COD fractions has pointed out that wastewaters contain mostly biodegradable organic substances.

Keywords: biodegradability, characterization, edible oil, wastewater, inert COD

Introduction

Refining crude vegetable oils generates large amounts of wastewater [1]. In the edible oil industry, wastewaters mainly come from the degumming, deacidification and deodorization and neutralization steps [2]. In the neutralization step, sodium salts of free fatty acid (soap stocks) are produced whose splitting through the use of H_2SO_4 generates highly acidic and oily wastewaters [3]. Its characteristics depend largely on the type of oil processed and on the process implemented that are high in COD, oil and grease, sulphate and phosphate content, resulting in both high inorganic as well as organic loading of the relevant wastewater treatment works.

Previously, effluent from the vegetable oil industry used to be discharged directly into soil or groundwater. But, due to the emergence of environmental consciousness, the Pollution Control Boards have become stricter and imposed stringent norms [4]. So studies on treatment of oily wastewaters have gained increasing importance. The studies have shown that fatty materials within waste streams from food industries are readily biodegradable and it therefore follows that these effluents are amenable to biological treatment [5]. Mkhize et. al., observed that 75% influent COD reduction and more than 90% removal of oils and suspended solids have been achieved by using an anaerobic/aerobic sequencing batch reactor [6]. 95% of BOD in wastewaters from a soybean food producing plant is removed by using an activated sludge process [7].

Characterization of wastewaters is important as it is very useful for control and development of treatment processes [8]. Total organic carbon (TOC), biological oxygen demand and chemical oxygen demand are the most common parameters used for measurements of organic

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materials in characterization studies. TOC is widely used for determination of organic content, but it does not give information about the oxidation steps of organic compounds. On the other hand, electron release potentials of carbonaceous substrate cannot be defined by using BOD [9]. As a result, COD has replaced BOD as a basis for organic matter measurements [10]. The traditional approach in biological treatment systems assumes that the influent COD has a homogeneous character and the effluent COD is composed of the remaining fraction of influent COD. Therefore, practically the effluent COD may be completely treated by increasing the residence time. However, recent studies have shown that increasing the sludge age does not lead to a higher COD removal but it raises the effluent COD levels [11]. This fact can be explained by the existence of the COD fractions such as initially inert particulate COD, initially inert soluble COD, particulate residual metabolic products, and soluble residual metabolic products [12].

In this study biological treatability of wastewaters coming from sunflower and corn oil production were investigated by determining COD fractions. Characterization studies were also done in order to define wastewater properties.

Material and Experimental Procedures

Seasonal samples for characterization studies were taken from the influent of a treatment plant consisting of chemical treatment and the conventional activated sludge process. All analyses were made as defined by Standard Methods [13]. In order to determine the COD fractions, composite samples were taken from effluent of chemical treatment as influent wastewater contains high organic load having inhibition characteristics.

In the literature various respirometric methods have been defined to determine COD fractions [14-16]. These methods generally involve experimental procedures using batch reactors and are designed to determine residual particulate products generated by metabolic activities during the treatment processes [17].

Orhon and Artan have developed a direct experimental method for observing soluble and inert particulate COD fractions [9]. In this method two aerated batch reactors were used. One of the reactors was filled with unfiltered wastewater (C_T) and the other was filled with filtered wastewater (S_T).

The initial situation of the first reactor filled with unfiltered wastewater can be expressed as:

$$C_{T0} = S_{S0} + S_I + X_{S0} + X_I \tag{2.1}$$

While the second reactor is started up with filtered wastewater:

$$S_{T0} = S_{S0} + S_I \tag{2.2}$$

At the end of the experiment C_{S0} (sum of S_{s0} and X_{s0}) is completely consumed and X_H is accepted as zero then equations (2.3) and (2.4) are observed for the fist reactor; whereas (2.5) and (2.6) are for the second one:

$$C_{TI} = S_I + X_I + S_{PI} + X_{PI} \tag{2.3}$$

$$S_{TI} = S_I + S_{PI} \tag{2.4}$$

$$C_{T2} = S_{P2} + S_I + X_{P2} \tag{2.5}$$

$$S_{T2} = S_{P2} + S_I \tag{2.6}$$

If X_P and S_P are considered as fractions of C_{S0} with a kinetic approach:

$$X_{PI} = Y_{xp} C_{S0} \tag{2.7}$$

$$S_{PI} = Y_{sp} C_{S0} \tag{2.8}$$

and,

$$X_{P2} = Y_{xp} S_{S0} \tag{2.9}$$

$$S_{P2} = Y_{sp} S_{S0} \tag{2.10}$$

The difference of C_{TI} and S_{TI} is calculated from equations (2.3) and (2.4):

$$C_{TI} - S_{TI} = X_{PI} + X_I \tag{2.11}$$

From equations (2.1) and (2.3):

$$\Delta C_{TI} = C_{S0} - S_{PI} - X_{PI} \tag{2.12}$$

is determined.

Difference of C_{T2} and S_{T2} is calculated from equations (2.5) and (2.6):

$$C_{T2} - S_{T2} = X_{P2} \tag{2.13}$$

$$\Delta C_{T2} = S_{T0} - C_{T2} \tag{2.14}$$

$$\Delta C_{T2} = S_{S0} - S_{P2} - X_{P2} \tag{2.15}$$

Considering the ratio between equation (2.7) and (2.9), the following expression can be written:

$$X_{P1} = X_{P2} \frac{\Delta C_{T1}}{\Delta C_{T2}} \tag{2.16}$$

The above equations may be manipulated to derive the following expressions for the experimental assessment of S_I and X_I:

$$S_I = S_{T1} - \frac{S_{T1} - S_{T2}}{1 - \dfrac{\Delta C_{T2}}{\Delta C_{T1}}} \tag{2.17}$$

$$X_I = C_{T1} - S_{T1} - X_{P2} \frac{\Delta C_{T1}}{\Delta C_{T2}} \tag{2.18}$$

Table 1. Characterization of sunflower and corn oil wastewaters.

Parameter	Sunflower oil				Corn oil			
	min.	max.	mean	std. dev.	min.	max.	mean	std. dev.
pH	3.53	4.50	4.01	0.49	2.72	2.85	2.79	0.07
Total COD (mg/L)	8345	9700	9215	756.06	11580	15450	12880	2225.70
Soluble COD (mg/L)	5195	5560	6385	182.85	5140	6700	5680	884.70
Total BOD_5 (mg/L)	1500	1900	1850	327.87	1250	2278	1932	591.22
Soluble BOD_5 (mg/L)	1450	1800	1550	217.90	1100	1207	1135	61.78
SS (mg/L)	1516	1985	1733	236.45	1058	2990	2850	1077.30
TKN (mg/L)	458	625	517.60	93.17	1125	1458	1261	174.68
NH_3 (mg/L)	18	51	29.60	18.50	38	62	48	12.49
Total P (mg/L)	52	420	177.30	210.19	275	775	583	269.60
Oil-gress (mg/L)	533	760.20	664.30	117.60	307.80	498.60	375	107.18
Sulfate (mg/L)	10800	11750	11416	534.10	11900	12300	12006	257.16
Color (Pt-Co)	224	272	242	21.60	868	1700	1161	467.12

In this study we have used the direct method described above. Batch reactors of 3 L volumetric capacity were prepared by using filtered and unfiltered wastewaters. In order to decrease the organic load and experiment period sunflower and corn oil wastewaters were diluted to have initial COD of 1495 and 1750 mg/L, respectively. For dilution 1 L of wastewater was complemented to reactor volume (3L) with distilled water. By this way, experiments were carried out in more controlled conditions. Standard methods were used during all experiments. 2 mg/L dissolved oxygen concentration was supplied in reactors. Total and soluble COD parameters were monitored for periods long enough to prove the consumption of all biodegradable substrate and complete mineralization of biomass [18]. Experiments were completed when C_T and S_T concentrations reached their constant threshold levels. Each reactor was fed with acclimated microorganisms by adjusting VSS as 10-50 mg/L.

Results and Discussion

Characterization results for sunflower and corn oil wastewaters are given in Table 1. Considering COD values given in Table 1, it is stated that wastewaters of this sector have high organic loads. Although corn oil wastewaters contain more total COD compared with sunflower wastewaters, soluble COD values are close to each other. This can be explained as higher amounts of total COD in corn oil wastewaters coming from suspended solids. Pollutants in these influents generally exhibit biodegradable characteristics. But in this study, it is shown that BOD_5 concentrations are low despite high COD values. This result shows that wastewater contains hidden BOD that cannot be determined in five days.

Sulfate contents of wastewaters are also high due to usage of sulfuric acid during degradation of soap stock in the neutralization process. In this step, extraction effluent consisting of fatty acid (RCOOH) and $NaSO_4$ forms during degradation of soap stock in the form of RCOONa. This process generates acidic wastewaters. Lower pH value of corn oil wastewaters is related to higher concept fatty acid in raw corn oil. The formation of more soap stock increases the amount of acid used for acid oil production.

Vegetable raw oils contain phospholipids. Furthermore, in the degumming step of the rafineration process phosphoric acid is widely used for removal of phospholipids and lipoproteins. These cause high phosphor concept in wastewaters.

In literature, color is an ignored parameter for these wastewaters. But as a result of high organic load, excess levels of color may be notable. Obtained results show that average value of color for corn oil and sunflower wastewaters are 1161 and 242 Pt-Co, respectively. Higher values of color for corn oil wastewaters can be explained with higher organic load of raw oil content in corn oil.

BOD_5/COD and COD/N/P ratios calculated with mean concentrations are 0.15, 0.2; and 22/3/1, 52/3/1 for corn oil and sunflower oil wastewaters. According to these values, there is no demand for nitrogen and phosphorus for the microbial activity in treatment process. However, the low ratio of BOD_5/COD shows that the biological treatment alone is not enough to obtain satisfying removal efficiency.

The results of inert COD experiments for sunflower oil wastewaters are given in Table 2. Total and soluble COD fractions for raw and filtered samples of the studied wastewater are illustrated in Figs. 1a, b.

Diluted raw and filtered samples taken from chemical treatment effluent have initial total COD of 1,495 and

Table 2. Total and soluble COD fractions of sunflower oil wastewaters.

Time	Reactor 1 Fed with raw wastewater (COD, mg/L)		Reactor 2 Fed with filtered wastewater (COD, mg/L)	
	C_T	S_T	C_T	S_T
Start of experiment	1,495	1,222	1,222	1,222
End of experiment	234	110	139	98.4
Duration, h	528	528	528	528

Table 3 Total and soluble COD fractions of corn oil wastewaters.

Time	Reactor 1 Fed with raw wastewater (COD,mg/L)		Reactor 2 Fed with filtered wastewater (COD,mg/L)	
	C_T	S_T	C_T	S_T
Start of experiment	1,750	1,400	1,400	1,400
End of experiment	132.2	100.9	110.6	92.6
Duration, h	672	672	672	672

1,222 mg/L for sunflower oil wastewaters. After an experimental period of 528 hours, total COD became stable at 234 and 139 mg/L (Table 2). Investigating Figs. 1 a, b, it is seen that COD removal efficiency is higher in the first five days.

The results of inert COD experiments for corn oil wastewaters are given in Table 3. Total and soluble COD fractions for raw and filtered samples of the studied wastewater are illustrated in Figs. 2 a, b.

At the start of experiments for the diluted samples of corn oil wastewaters, total COD and soluble COD were measured as 1,750 and 1,400 mg/L, respectively, in Reactor 1. At the end of the experimental period (672 hours) C_T and S_T reached constant threshold values of 132.2 and 100.9 mg/L. In Reactor 2, fed with filtered wastewater, C_T and S_T values decreased to 110.6 and 92.6 mg/L from 1,400 mg/L in 672 hours (Table 3). Similar to sunflower oil wastewaters, rapid removal is obtained in early periods (Fig. 2 a, b).

Calculated COD fractions of sunflower and corn oil wastewaters according to the direct method developed by Orhon and Artan 1994 are given in Table 4. Related ratios are shown in Table 5 observed by using the values in Table 4.

During determination of COD fractions, C_T values of 1495 and 1750 mg/L, measured in diluted chemical treatment effluents, were used for sunflower and corn oil wastewaters. Total COD of sunflower and corn oil wastewaters having biodegradable fractions of 93% and 96%, consisting of 79.9% and 76.6% readily biodegradable COD; 13.1% and 19.5% slowly biodegradable COD. As seen from Table 4, calculated Y_{SP} and Y_{XP} fractions are low. This can be explained with the younger age of the sludge. As known from literature, higher sludge ages cause higher amounts of inert microbial products [16].

A comparison between the COD fractions obtained in this study and the COD fractions of different wastewaters given in literature are shown in Table 6. The soluble

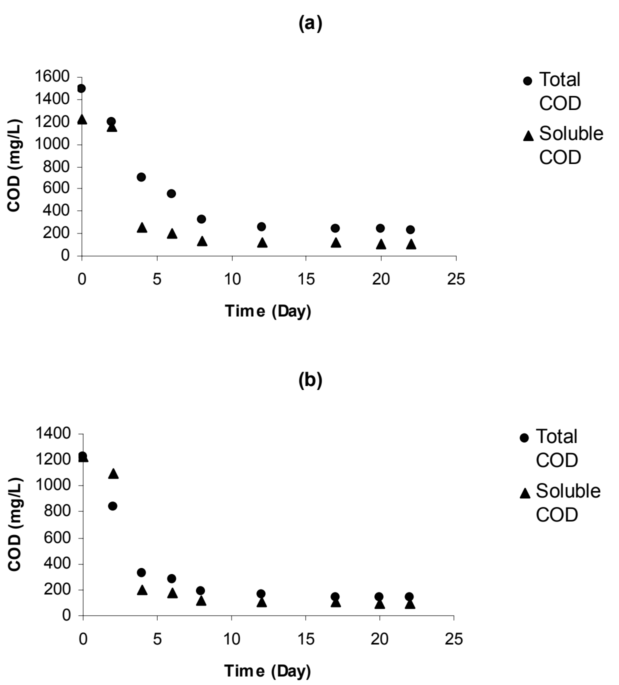

Fig. 1. Total and soluble COD fractions of raw (a) and filtered (b) sunflower oil wastewaters.

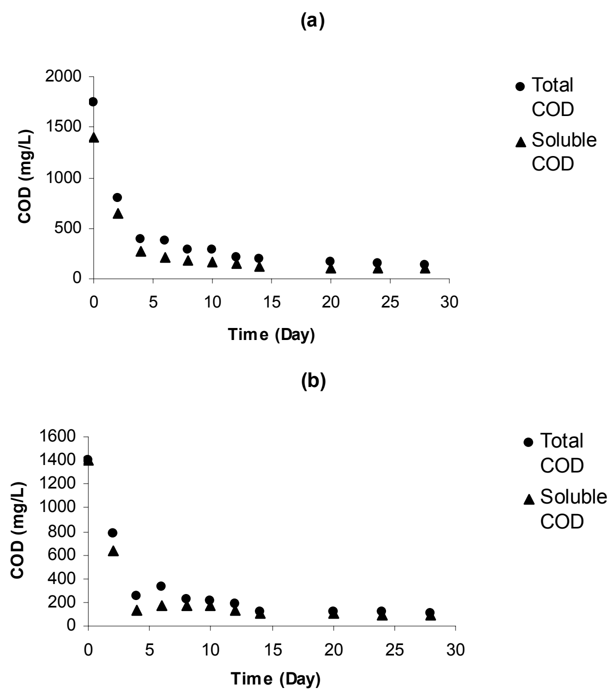

Fig. 2. Total and soluble COD fractions of raw (a) and filtered (b) corn oil wastewaters.

COD/total COD ratios (S_T/C_T) are calculated as 0.817 and 0.800 for this study. These ratios exhibit similarity to the values of previously studied wastewaters of other sectors. Total COD values in diluted samples of corn oil and sunflower wastewaters are measured as 1,750 and 1,495 mg/L whereas inert particular CODs are 8.72 and 76.73 mg/L; inert soluble CODs are 60.01 and 27.82 mg/L. As a result, compared with literature while X_I/C_T ratios show similarity, S_I/C_T ratios are lower than the results of previous studies (Table 6).

Table 4. Calculated COD fractions of sunflower and corn oil wastewaters.

Calculated COD fraction (mg/L)	Sampling oil	
	Sunflower oil	Corn oil
C_T	1,495	1,750
X_T	273	350
S_T	1,222	1,400
X_I	76.73	8.72
S_I	27.82	60.01
X_P	47.20	22.58
S_P	83.60	40.89
C_S	1,390.45	1,681.27
S_S	1,194.18	1,339.99
X_S	196.27	341.28
Y_{SP}	0.060	0.024
Y_{XP}	0.034	0.013

Conclusion

In conventional characterization studies, the total COD values were determined as 9215±756 mg/L (8,345 to 9,700) and 12,880±2,225 mg/L (11,580 to15,450) for sunflower and corn oil wastewaters, respectively. It is observed that despite the high organic load in these wastewaters, the formation of inert COD and inert microbial products are poor. It states that studied wastewater is highly biodegradable. With respect to C_S/C_T ratios, it is seen that total readily biodegradable COD for each wastewater is considerably high (for corn oil 0.96 mg/L and for sunflower oil 0.93 mg/L). Total COD of these wastewaters are mostly consisting of biodegradable COD (96% and 93%). Although corn oil wastewaters contain more organic load, the biodegradability characteristics of each wastewater show similarity. At the end of experimental studies approximately 80% of COD content can be removed in five days. So, it is concluded that a reaction period of five days is enough to obtain satisfying removal efficiency for the wastewaters with similar characteristics. Low BOD and COD ratios show the necessity of physical and chemical treatment before biological treatment for the wastewaters of edible oil sector. Phosphor, nitrogen and color parameters of wastewaters coming from this sector are rather high. But in the National Water Pollution Control Act there is no limit for these parameters of the edible oil sector. Excess values of nitrogen and phosphor cause eutrophication in surface waters. Color prevents diffusion of sunlight and atmospheric gases to the water. So regulations should be created regarding discharge limits of these parameters. At the end of this study, it is thought that obtained COD fractions could be useful in planning treatment processes for similar types of wastewaters.

Table 5. Calculated COD ratios.

Sampling oil	X_I/C_T	S_I/C_T	C_S/C_T	$\mathbf{S_S/C_T}$	$\mathbf{X_S/C_T}$	$\mathbf{S_T/C_T}$	$\mathbf{X_T/C_T}$
Sunflower oil	0.051	0.019	0.930	0.799	0.131	0.817	0.183
Corn oil	0.005	0.034	0.960	0.766	0.195	0.800	0.200

Table 6. Comparison of COD fractions with literature.

Wastewater Type	S_T/C_T	S_S/C_T	S_S/S_T	S_I/C_T	X_S/C_T	X_I/C_T	References
Textile	0.71	0.14	0.19	0.04	0.29	-	[20]
Dairy	0.76	0.28	0.37	-	0.16	0.08	[19]
Meat	0.438	0.146	0.33	0.011	0.44	0.117	
Domestic water (Spain)	-	0.18	-	0.09	0.33	0.25	[21]
Domestic water (South Africa)	-	0.28	-	0.08	0.6	0.64	[14]
Domestic water (Turkey)	0.31	0.28	0.89	0.03	0.15	0.54	[22]
Corn oil	0.800	0.766	0.957	0.034	0.195	0.005	this study
Sunflower oil	0.817	0.799	0.977	0.019	0.131	0.051	

Abbreviations

COD: Chemical oxygen demand (mg/L),
BOD: Biological oxygen demand (mg/L),
SS: Suspended solids (mg/L),
VSS: Volatile suspended solids (mg/L),
TKN: Total kjedhal nitrogen (mg/L),
C_T: Total COD of wastewater (mg/L),
C_S: Total biodegradable COD of wastewater (mg/L),
S_I: Soluble inert COD of wastewater (mg/L),
S_S: Readily biodegradable COD of wastewater (mg/L),
S_T: Total soluble COD of wastewater (mg/L),
X_I: Particulate inert COD of wastewater (mg/L),
X_S: Slowly biodegradable COD of wastewater (mg/L),
X_T: Total particulate COD of wastewater (mg/L),
X_P: Particulate inert microbial products of wastewater (mg COD/L),
S_P: Soluble inert microbial products of wastewater (mg COD/L),
Y_{SP}: Ratio between the soluble residual products and initial COD,
Y_{XP}: Ratio between the particulate residual products and initial COD.

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