

## Anaerobic treatment of the mixture of automotive industry and molasses wastewater for different organic loading rates in an upflow anaerobic sludge blanket (UASB) reactor

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### ABSTRACT

In the present study, the anaerobic treatability of automotive industry wastewater by using molasses, which is a sugar industry waste, as a co-substrate was investigated. The anaerobic treatment of automotive industry wastewater was examined at mesophilic temperature (37°C) in a UASB reactor. The performance of the upflow sludge blanket reactor (UASB) was evaluated in terms of pH, chemical oxygen demand (COD), alkalinity and volatile fatty acid (VFA) parameters at 2–2.5 and 3.5 gCOD/L·d organic loading rates. The chemical oxygen demand (COD) removal rates for the UASB reactor were found to be 56–83%, 64–83% and 73–80%, respectively. The biogas yields were 0.34–0.50 L biogas/g COD removal, 0.33–0.46 L biogas/g COD removal and 0.31–0.46 L biogas/g COD removal, respectively. The application of the data obtained from the UASB reactor to the modified Stover-Kincannon and Monod kinetic models was performed, the  $U_{max}$ ,  $K_p$ ,  $K_s$  and  $U_{max}$  constants were determined, and it was concluded that the best model is the Stover-Kincannon model. Anaerobic sludge samples were taken after completing the experiments in the UASB reactor and prior to the start of the experiments. After drying the sludge taken and bringing it to small sizes, the SEM, and FTIR analyses were conducted.

**Keywords:** Upflow anaerobic sludge blanket reactor; Organic loading rate; Automotive industry wastewater; Biogas production; Molasses

### 1. Introduction

The sugar industry takes an important place in our country because of its effects on human needs and health as well as its contribution to the national economy. It is a field of industry that can be defined as a production system, in which products such as raw sugar, white sugar, powdered sugar, brown candy, white candy, liquid sugar, food and manufacturing syrup, sugar syrup, artificial honey, molasses, and spirit are obtained. These products are manufactured from sugar beet and sugar cane as a result of a series of procedures.

If attention is not paid to the production process of the sugar industry, it may have a serious impact on the environment due to the organic pollution it causes. Serious problems may arise in surface waters if appropriate treatment techniques are not used in sugar factories where molasses is used as a raw material. It is absolutely necessary to treat molasses wastes with a high organic matter content by appropriate methods before releasing them to the receiving environment. It is possible to use anaerobic treatment and the biogas produced during this treatment as a sustainable source of energy in wastewaters with a high organic matter content. For this purpose, it is thought that the treatment of molasses wastes in anaerobic systems

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will provide considerable potential benefits in terms of the environmental pollution control and the development of sustainable sources of energy. Molasses is used as a substrate [1–8] and as a co-substrate [9,10] in treatment since it has a high organic matter content and is utilized as a source of carbon.

In the study conducted by Jagadevan et al. [11] Fe<sup>2+</sup>, they investigated the feasibility of employing sequential Fenton-biological oxidation for the treatment of recalcitrant components of MWF wastewater. The removal of synthetic metal processing wastewaters by means of 2 synthetic polymers was examined by Connolly et al. [12]. Rodriguez-Verde [13] studied the treatment of metalworking wastewaters by using pig manure as a co-substrate in anaerobic digestion. Perez et al. [14] reported the effect of organic loading rate on the removal efficiency of COD and TOC anaerobic thermophilic fluidized bed reactor (AFBR) in the treatment of cutting-oil wastewater under different hydraulic retention time (HRT) conditions. Carvalhina et al. [15] used a mechanically stirred anaerobic sequencing batch biofilm reactor in the treatment of soluble metalworking fluids to remove organic matter and produce methane.

In recent years, the technologies of membrane separation, such as microfiltration, nanofiltration, ultrafiltration and reverse osmosis, have been investigated to treat oil emulsions due to the process efficiency and high quality of exit water [16,17]. Physical methods are mostly used for the removal of waste oil/water emissions in the automotive industry [18–26].

Oil/water emissions in the automotive industry are commonly used to prolong tool life, to prevent corrosion, to cool and lubricate machines in the process, and to increase their efficiency. The chemical structure and toxicology of oil/water emission liquids are considerably complicated. The contact of these liquids with skin and their inhalation with air cause adverse impacts on human health [16]. The separation of the water phase from the oil phase constitutes the basis of the methods used in the treatment of waste oil/water emissions, following which the independent treatment of every phase is performed. Hybrid processes (biological and physical processes) can also be used as well as biological treatment with different treatment techniques to treat waste oil/water emissions. However, there is little information on the treatment of oily wastewaters.

In the present study, the treatment of the mixture of waste oil/water emissions that are automotive industry wastewaters and molasses that is a sugar industry waste in an anaerobic reactor was investigated. An upflow anaerobic sludge blanket (UASB) reactor was utilized in the present study as an anaerobic reactor. The evaluation of system performance was performed by feeding to the reactor at different organic loading rates.

## 2. Material and methods

### 2.1. Material

#### 2.1.1. Wastewater, Co-substrate characteristics and granulated anaerobic sludge

The mixture of molasses that is a sugar industry waste and waste oil/water emission liquids that are used during

the production of a piece of metal and formed in the automotive industry was used in the present study. Although automotive industry wastewaters contain high organic matter, molasses was used as a co-substrate since it is difficult biodegradable wastewater due to the COD: BOD ratio higher than 3.

The wastewater utilized in the present study is called metalworking fluids (MWF), and it was obtained from the metalworking industry. MWF samples were collected from the industry for a 3-month period, and the average parameter values are presented in Table 1 [17]. The complete wastewater analysis was performed in accordance with standard techniques [27].

The granular sludge from the anaerobic digester section was obtained from Adana Seyhan Wastewater Treatment Plant. The total solids (TS), pH, mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS), volatile solids (VS), and COD values of the granular sludge were 21.5 g/L, 7.45, 22 g/L, 12.5 g/L, 13.5 g/L, and 17 g/L, respectively.

Molasses was utilized as a co-substrate in the present study. Molasses was obtained from a commercial sugar plant situated in Nigde, Turkey and kept in the refrigerator at the temperature of 4°C for the purpose of bringing substrate decomposition to minimum prior to the study. Molasses takes place among the substrates of organic nature available on the market. Molasses represents an inexpensive by-product of sugar refining, and it has a high concentration of sugars, including fructose, sucrose, and glucose, along with nutrient minerals. The molasses utilized as a co-substrate had the COD concentration of 1000 g COD/L.

#### 2.1.2. Experimental procedure

Before adding wastewater into the UASB reactor, the acid cracking process was applied. For the removal of oil from wastewater, the acid cracking procedure was first applied by the manual setting of pH at 2 using sulphuric acid. The reaction time for this operation was 1 h. Then, the collection of oil from wastewater was performed by the manual setting of pH at 8 using NaOH. FeCl<sub>3</sub>·6H<sub>2</sub>O (supplied from Merck, Germany) reagents were utilized at 2.3 g/L in chemical treatment studies using a Jar test apparatus (Velp Scientifica model, Italy). Sedimentation for one hour was applied after the coagulation time of 30

Table 1  
Wastewater characteristics

Wastewater characteristics	Values
pH	8.8–9.05
COD	63000–90000 mgCOD/L, usually 70000 mgCOD/L
SS	2700–3400 mg/L
Oil / grease	700 mg/L
BOD <sub>5</sub>	6000–7000 mg/L
Conductivity	> 3.36 ms
Turbidity	150–900NTU

min (40 rpm) following flash mixing for a period of one minute (200 rpm).

### 2.1.3. Anaerobic reactor

A steel UASB reactor which had a working volume of 7 L and was 0.1 m in internal diameter was used in this study (as shown in Fig. 1) and operated in the mesophilic range ( $37 \pm 1^\circ\text{C}$ ). The temperature in the reactor is disposed outside the reactor heating jacket for the purpose of maintaining temperature at  $37 \pm 1^\circ\text{C}$ . The temperature of the water inside the tank is automatically adjusted by the resistor. The gasometer is used to collect and measure the biogas produced during anaerobic degradation. The peristaltic pump is used during the feeding of the reactor to maintain a constant feed flow. During the entire performance, the hydraulic retention time (HRT) was maintained at 2 d. Temperature, pH, COD, alkalinity and biogas were monitored on a daily basis. Volatile fatty acid (VFA) was monitored on a weekly basis.

### 2.2. Analytical procedures

The determination of COD concentrations was performed by means of the closed reflux colorimetric technique after standard methods (Standard Methods 5220 C). Alkalinity was analyzed by a titrimetric method using standard methods (Standard Methods 2320 B). The measurement of the pH of wastewater specimens was performed using a

WTW Inolab pH 7110 SET 2 Model pH Meter. Gas measurement was performed from the upper outlet of the UASB reactor. Measurements were taken by a wet-type gas meter. The wet-type gas meter operates based on the positive displacement principle. The gas flow of the sample rotates the measuring cylinder containing water. Depending on the rotating cylinder, the counting mechanism measures and records the incoming gas flow as it is filled and discharged in measuring compartments.

The samples taken for VFA were taken from the reactor outlet once a week. The samples taken were stored at  $-18^\circ\text{C}$  until performing measurements in GC by adjusting pH to 2 with 10% (v/v) phosphoric acid after passing through the  $0.45 \mu\text{m}$  membrane. VFA measurements were made in a Shimadzu brand GC-MS QP2010 Plus model device. Measurements were performed as VFA acetic acid (AA), isobutyric acid (izoBA), propionic acid (PA), isovaleric acid (izoVA), butyric acid (BA), valeric acid (VA), isocaproic acid (izoKA), caproic acid (KA) and heptanoic acid (HA).

### 2.3. Kinetic studies

Process modeling in anaerobic treatment systems is a beneficial instrument for predicting and identifying system performance. The kinetics of anaerobic processes is concentrated at different stages of food decomposition [28,29].

The Monod-type kinetic models have been commonly employed for completing the kinetic routes of anaerobic

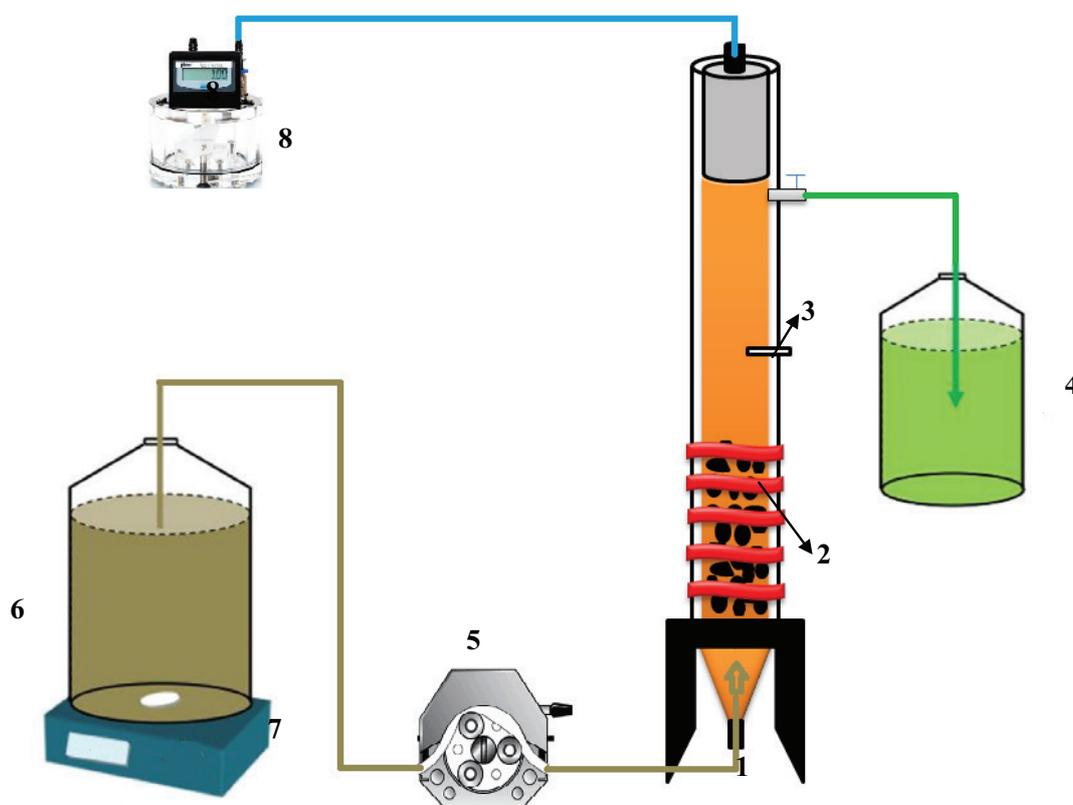


Fig. 1. Schematic presentation of the UASB experimental setup: (1) UASB reactor; (2) heat jacket; (3) thermostat; (4) outlet tank; (5) peristaltic pump; (6) inlet tank; (7) magnetic stirrer; (8) wet-type gas meter.

processes. Although the successful samples of the Monod-type kinetic models for anaerobic processes have been known, it is stated that this procedure is very difficult for specific cases. The kinetic models used in anaerobic and aerobic studies are given below [30]:

- Monod kinetic model
- Improved Stover-Kincannon model
- Contois kinetic model
- Chen-Hashimoto kinetic model
- Grau model
- Zero, first and second-order nutrient recovery model

### 2.3.1. Monod model

In early studies, Monod found out in 1949 that the rapid growth of bacteria, the growth rate of nutrients and whole bacteria at a high concentration are associated with a limited amount of an element. The value of the specific growth rate depends on factors that an organism needs to grow, nitrogen, the concentration of limiting nutrients such as dissolved oxygen and carbon source [30]. The Monod kinetic model has a wide usage area to identify co-substrate removal and simple biodegradation rate. A deterministic model in a batch reactor usually defines the nutrient removal rate in Monod kinetics as in Eq. (1) [31].

$$-\frac{ds}{dt} = U = \frac{k_{\max} \cdot X \cdot S}{K_s + S} \quad (1)$$

When  $X$  is assumed to be constant in Eq. (2),  $(k_{\max} \cdot X)$  is expressed as  $U_{\max}$  as a result of integration with  $S = S_0$  acceptance at  $t_0 = 0$ ;

$$\frac{1}{U} = \frac{K_s}{U_{\max}} \frac{1}{S} + \frac{1}{U_{\max}} \quad (2)$$

where  $U$  is the nutrient consumption rate (mg/Lh),  $U_{\max}$  is the maximum nutrient recovery rate (mg/Lh),  $S$  is the nutrient concentration (mg/L), and  $K_s$  is the semi-saturation concentration (mg/L).

It is possible to acquire the  $U_{\max}$  and  $K_s$  values as a result of plotting  $(1/U)$  versus  $(1/S)$  in Eq. (2). The calculation of the  $U_{\max}$  value may be performed from the intercept of a straight line, and it is possible to acquire  $K_s$  from the line slope.

### 2.3.2. Stover-Kincannon model

The Stover-Kincannon model takes place among mathematical models that are most commonly employed to determine kinetic constants for immobilized systems. The substrate utilization rate is given as a function of the organic loading rate in the modified Stover-Kincannon model for the UASB reactor. It is possible to determine the organic substrate removal in the UASB process on the basis of the substrate removal rate as a function of substrate concentration [32]. The modified Stover/Kincannon model is presented below [33]:

$$\frac{ds}{dt} = \frac{Q}{V} (S_0 - S) \quad (3)$$

$$\frac{ds}{dt} = \frac{U_{\max} \left( \frac{QS}{V} \right)}{K_B + \left( \frac{QS}{V} \right)} \quad (4)$$

where  $ds/dt$  represents the rate of substrate removal (g/L·d),  $U_{\max}$  represents the maximum utilization rate constant (g/L·d),  $K_B$  represents the saturation value constant (g/L·d),  $Q$  represents the flow rate (L/d), and  $V$  represents the reactor's effective volume (L),  $S_0$  represents the influent substrate concentration (g L<sup>-1</sup>), and  $S$  represents the effluent substrate concentration (g L<sup>-1</sup>). The final form of the modified Stover-Kincannon model can be obtained as a result of combining the reverses of Eqs. (4) and (5) [34]:

$$\left( \frac{ds}{dt} \right)^{-1} = \frac{V}{(S_0 - S)} = \frac{K_B}{U_{\max}} \frac{V}{QS_0} + \frac{1}{U_{\max}} \quad (5)$$

In the case of plotting  $V/Q(S_0 - S)$  against  $1/OLR$ ,  $K_B/U_{\max}$  represents the slope and  $1/U_{\max}$  represents the straight line's intercept point. The mathematical expressions of the specific substrate utilization rates for the established kinetic models are given in Table 2. The kinetic parameters of the models applied for different wastewater and reactor types in the literature are presented in Table 3.

## 3. Results and discussion

Fig. 2a shows that 2 gCOD/L·d was applied for 16 d. The COD removal efficiency for 2 g COD/L·d OLR value varies between 56 and 86%. By increasing OLR to 2.5 g COD/L·d, the COD removal efficiency was gradually increased with respect to 2 g COD/L·d. Depending on organic loading variations, it was decreased to 64%. By increasing OLR to 3.5 g COD/L·d, the variations of the COD removal efficiency were observed to be between 73% and 80%. The COD removal efficiency was almost constantly 75% for 3.5 g COD/L·d OLR value.

Although automotive industry wastewaters contain high organic matter, molasses was used as a co-substrate since it is difficult biodegradable wastewater. Because molasses has a very high organic matter content, the system has high COD removal. Sugar molasses and automotive industry wastewater were not used together in the literature. Studies conducted with different industrial wastewa-

Table 2  
Mathematical expressions of the specific substrate utilization rates for known kinetic models

Kinetic model	Constants	Results
Monod model	$U_{\max}$ (mg/L.h)	8.03
	$K_s$ (mg/L)	6.73
	$R^2$	0.0058
Stover-Kincannon model	$U_{\max}$	7.7
	$K_B$	13.836
	$R^2$	0.88

Table 3  
Comparison of kinetic parameters

Reactor type	Wastewater source	Applied model	Kinetic parameters	Reference
UASB	Molasses + industrial wastewater mixture	Stover-Kincannon model Monod model	$U_{max} = 7.7 \text{ g/L}\cdot\text{d}$ , $K_B = 13.836 \text{ g/L}$ $K_S = 6.73 \text{ mg/L}$ , $U_{max} = 8.03 \text{ (mg/L}\cdot\text{h)}$	The present study
UASB	2,4 dichlorophenol	Stover-Kincannon model Monod model	$U_{max} = 10 \text{ g/L}\cdot\text{d}$ , $K_B = 9.8 \text{ g/L}$ $K_S = 2.02 \text{ g/L}$ , $U_{max} = 0.000062 \text{ (g/L}\cdot\text{d)}$	[27]
Upflow anaerobic filter	Agricultural feed wastewaters	Stover-Kincannon model	$U_{max} = 109.9 \text{ g/L}\cdot\text{d}$ , $K_B = 109.7 \text{ g/L}$	[30]
UASB	Synthetic wastewater	Stover-Kincannon model	$U_{max} = 15 \text{ g/L}\cdot\text{d}$ , $K_B = 17.5 \text{ g/L}$	[31]
UASB	Salty synthetic wastewater	Stover-Kincannon model	$U_{max} = 7.05 \text{ g/L}\cdot\text{d}$ , $K_B = 5.3 \text{ g/L}$	[32]
UASB	Synthetic textile wastewater	Stover-Kincannon model	$U_{max} = 8.211 \text{ g/L}\cdot\text{d}$ , $K_B = 7.501 \text{ g/L}$	[28]

ters and molasses are encountered in the literature [2–4] [11–14]. In other studies using molasses, the recovery of COD is similar to the present study.

Fig. 2b shows an increase in biogas production from 1.46 L/d to 3.41 L/d with increasing from 2 g COD/L·d to 3.5 g COD/L·d. Biogas production increased in parallel with an increase in the COD removal efficiency with increasing OLR to 3.5 gCOD/L·d. The maximum biogas production efficiency throughout the operating period of the reactor was obtained as 0.46 L biogas/g COD removal for the highest OLR values.

When the total gas measurements were examined, deviations were observed in OLR transitions. This is thought to be caused by the fact that although the ratio of automotive industry wastewater is low (molasses/wastewater = 3) in the reactor, the increased concentration of automotive industry wastewater along with increasing loads can decrease the total amount of gas since they will increase the inhibition effect. In the study conducted by Silva et al. (2009) among similar studies, the evaporator condensate coming out of a wood pulp factory was treated in a full-scale anaerobic reactor. Molasses was added to the system continuously as an external carbon source. The COD removal at 2.6 g COD/L·d OLR increased from 52% to 77%. Methane production increased from 460 mL/d to 1650 mL/d. In the study of Rico et al. [35] conducted on the treatment of whey at 1.3 HRT in a USB reactor, they achieved a high biogas production rate (16.6 m<sup>3</sup>/m<sup>3</sup>·d) at the highest OLR (28.7 g COD/L·d). Aksoy [36] obtained 143 L/d biogas production at 15 g COD/L·d 143 L/d organic loading in an upflow sludge blanket reactor of the synthetic wastewater prepared using diluted molasses.

The first loading was performed at 2 g COD/L·d OLR, and loading continued for 37 d. During the first 29 d, gas collection and measurement failed due to the inability to ensure the hydraulics of the system. According to the data obtained during 37 d, the mean, minimum, and

maximum values in terms of the removal efficiency are 51.63%, 24%, and 86.36%, respectively. The average biogas production is 0.8 L/d. The reactor was operated for 45 d at 2.5 g COD/L·d OLR. The other organic loading was initiated after stabilizing the removal efficiency and biogas production. The mean, maximum and minimum values for the removal efficiency at 2.5 g COD/L·d are 68.47%, 83.05%, and 55.01%, respectively. The average is 2.24 L/d with regard to biogas production. Studies were conducted for 30 d in the reactor at 3.5 g COD/L·d. The COD removal efficiency is maximum 80% and minimum 70.71%. The average biogas production is 5.44 L/d. In anaerobic systems, the proper pH range of the system is 6–8, especially for the survival of methane bacteria, because the activity of methane bacteria decreases below 6.3 and above 7.8. pH is an important factor that prevents acid bacteria from becoming predominant and limits methane bacteria in an anaerobic system. The acidogenic population exhibits less sensitivity at low and high pHs. Thus, methanogens become predominant and cause acidification in the reactor [37].

In order to stabilize anaerobic reactors, it is important that pH and alkalinity values can be tracked in the observation and determination of optimal medium conditions. When the COD removal efficiencies and biogas production results are taken together with alkalinity and pH values in Fig. 2c, it seems to protect the stability of organic load in the anaerobic reactor. For 2 and 2.5 g COD/L·d OLR values, pH varies between 7 and 8.38. On the other hand, total alkalinity varies between 1450 and 3450 mgCaCO<sub>3</sub>/L. Alkalinity at 2 g COD/L·d OLR is of lower alkalinity values (1900–2800 mgCaCO<sub>3</sub>/L).

Wastewater acetic acid, which is the source of organic matter in anaerobic treatment systems, decomposes into volatile fatty acids, including butyric and propionic acid. The concentration of acetic acid is generally higher in the reactor, and this concentration is followed by propionic acid and butyric acid [38]. In the study carried out, Fig. 3a

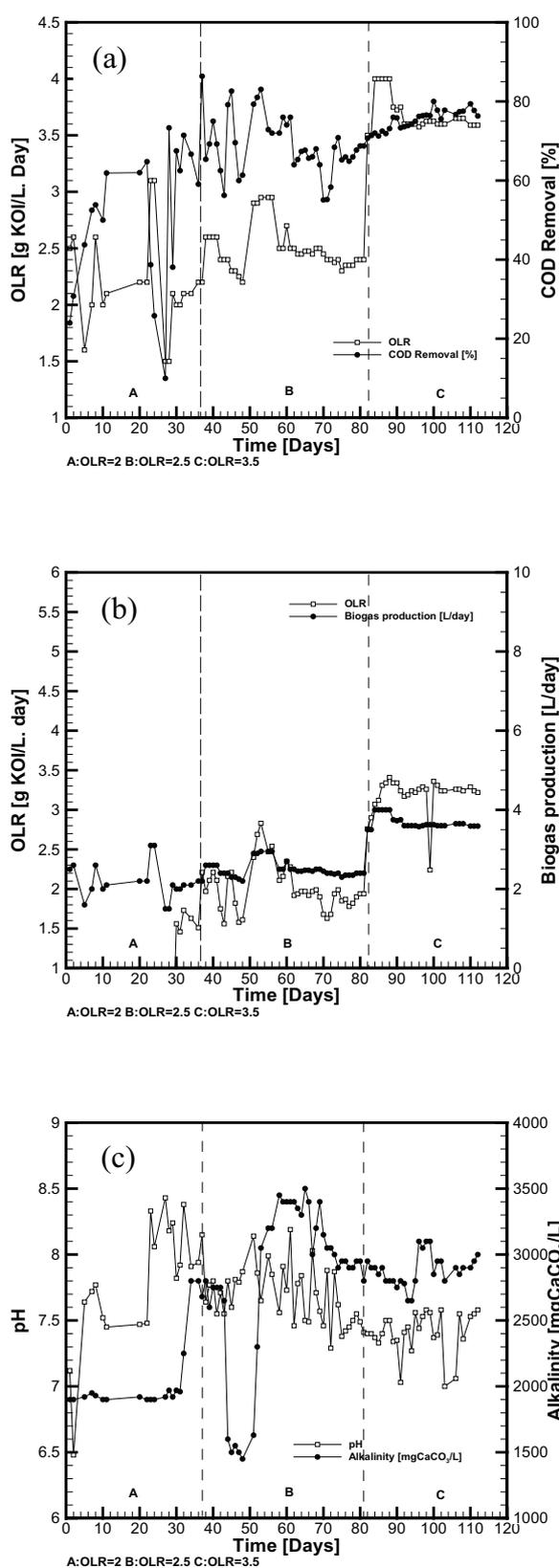


Fig. 2. UASB reactor COD removal efficiency (a); UASB reactor biogas production (b); UASB reactor pH and alkalinity relation (c)

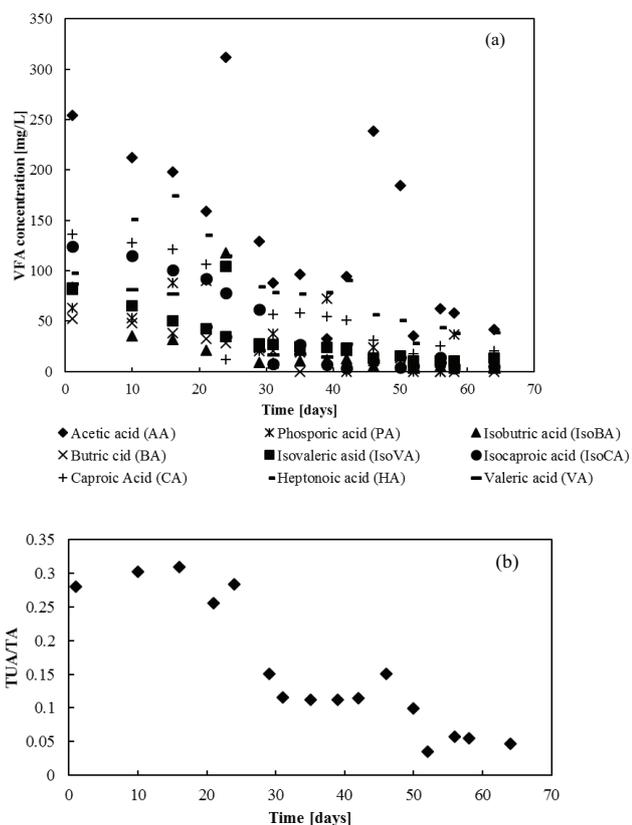


Fig. 3. VFA concentration for different OLRs (a); The total volatile acid concentration to the total alkalinity ratio of the anaerobic reactor (b).

presents the VFA concentrations of 2.5 and 3.5 g COD/L-d organic loading. As can be observed from Fig. 3a, acetic acid concentrations and other VFA concentrations are higher at 2.5 g COD/L. The acetate concentration began to decrease because of the fact that methanogens converted acetic acid into methane. The acetic acid concentration and the propionic, isobutyric, butyric, valeric, caproic, isocaproic, heptanoic and isovaleric acid depositions, which are the other decomposition by-products of VFA, were observed at 2.5 g COD/L-d OLR. When OLR is 3.5 g COD/L, the acetic acid concentration and the other VFA deposition, which is the other VFA decomposition by-product, decrease.

It was stated by Öztürk [39] that the total volatile fatty acid/total alkaline ratio, which is an important parameter for the optimum environmental conditions of anaerobic microorganisms, should be below 0.1 for anaerobic bacteria. The ratios of 0.3–0.4 for reactors are determined as critical values in the literature [40,41]. Upon examining Fig. 3b, the total acid/total alkalinity ratio of the anaerobic reactor was calculated to be 0.29–0.08, respectively, at 2.5–3.5 g COD/L-d OLR values. The total acid/total alkalinity value was above 0.2 at 2.5 g COD/L-d OLR, but the stability of the reactor was unaffected by it.

### 3.1. SEM-FTIR analyses

After completing the experiments carried out in the UASB reactor, the anaerobic sludge sample taken from the

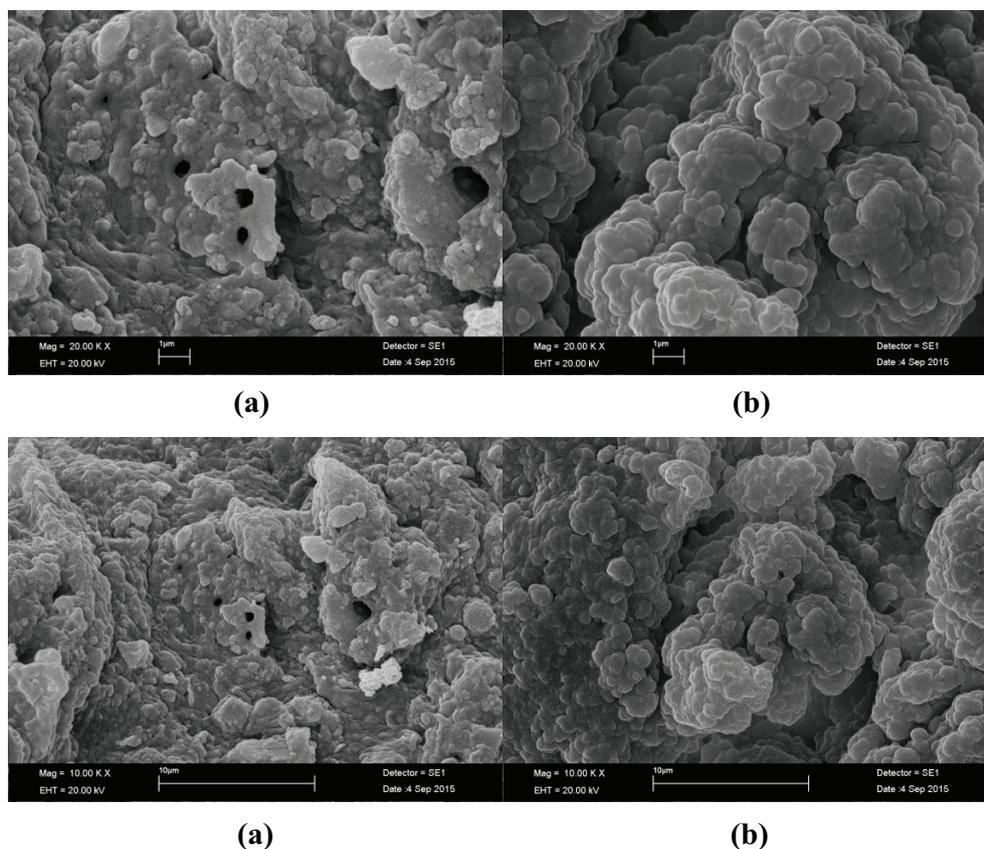


Fig. 4. (a) SEM images of the sludge before the anaerobic treatment (b) SEM images of the sludge after the anaerobic treatment.

reactor’s bottom and the anaerobic sludge sample taken before the start of the experiments were dried in a water bath at the temperature of 60°C for the period of 24 h. After bringing the sediments obtained for this purpose to smaller dimensions, they were analyzed using a scanning electron microscope (SEM) and Fourier transform infrared spectrometer (FTIR), and their morphology and composition were investigated.

Upon examining the SEM images of anaerobic sludge, it is observed in Fig. 4a that raw anaerobic sludge has a heterogeneous structure. Upon examining the image of granular sludge with a loose and hollow appearance taken from the UASB reactor after the experiments in Fig. 4b, it is observed that pollutants are stored on the surface, the surfaces of granules are filled with cocoid and *Methanosarcina* bacteria as biogas production has taken place.

Fourier transform infrared (FTIR) spectroscopy is a technique that enables obtaining structural, compositional and functional information resulting from the vibrations of the functional groups of the sample macromolecules to be investigated. Upon examining the FTIR spectrum of the anaerobic sludge before treatment in Fig. 6, 3262  $\text{cm}^{-1}$  band corresponds to a C-H phenol stretching. 2919  $\text{cm}^{-1}$  band and 2849  $\text{cm}^{-1}$  band correspond to a C-H alkane group stretching, 2320  $\text{cm}^{-1}$  band corresponds to C=C stretching, 1625  $\text{cm}^{-1}$  band corresponds to C=C stretching, 1412  $\text{cm}^{-1}$  band corresponds to C-O stretching vibrations, 1010  $\text{cm}^{-1}$  band corresponds to

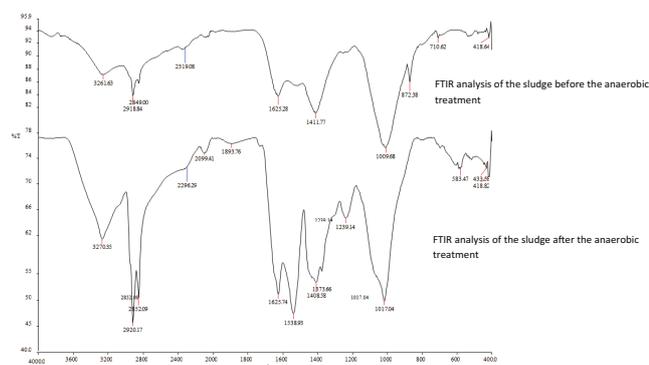


Fig. 5. FTIR analysis of the anaerobic sludge.

C-O stretching vibration, 873  $\text{cm}^{-1}$  band corresponds to Si-H stretching vibrations. 1000–650  $\text{cm}^{-1}$  band is called the =C-H out-of-plane bending zone. The =C-H out-of-plane bending vibrations are collected under two groups as alkenes and benzenes.

Upon examining the FTIR spectrum of the anaerobic sludge after treatment in Fig. 6, it is observed that 3270  $\text{cm}^{-1}$  band corresponds to C-H stretching vibrations, 2920 and 2852  $\text{cm}^{-1}$  bands correspond to C-H alkane group stretching

vibrations, 2296  $\text{cm}^{-1}$  band corresponds to C=C stretching vibrations, 2100  $\text{cm}^{-1}$  band corresponds to Si-H stretching vibration, 1625 and 1540  $\text{cm}^{-1}$  band correspond to C=C stretching vibration, 1400  $\text{cm}^{-1}$  band corresponds to C-O stretching vibrations, 1240  $\text{cm}^{-1}$  band corresponds to C-N stretching vibrations, 1017  $\text{cm}^{-1}$  band corresponds to C-O stretching vibration. 1000–650  $\text{cm}^{-1}$  band is called the =C-H out-of-plane bending zone. The =C-H out-of-plane bending vibrations are collected under two groups as alkenes and benzenes. When the FTIR analyses of the sludge before and after anaerobic treatment are examined, the peaks are bigger since the density of the anaerobic sludge after treatment is higher.

#### 4. Conclusion

In the present study, the anaerobic treatability of automotive industry wastewater by using molasses, which is a sugar industry waste, as a co-substrate was investigated. The anaerobic treatment of automotive industry wastewater was studied at mesophilic temperature (37°C) in the UASB reactor. The performance of the system (pH, alkalinity, COD, and VFA) was evaluated by feeding to the UASB reactor at different OLRs. The mean, minimum and maximum values in terms of the removal efficiency at 2 g COD/L·d OLR are 51.63%, 24%, and 86.36%, respectively. The average biogas production is 0.51 L/d. The mean, maximum and minimum values for the removal efficiency at 2.5 g COD/L·d are 68.47%, 83.05%, and 55.01%, respectively. The average biogas production is 2.01 L/d. The maximum removal efficiency is 80%, the minimum is 70.71%, the mean is 75.24% at 3.5 g COD/L·d. The average biogas production is 3.23 L/d. Upon examining the mean removal efficiencies, it was observed that removal efficiency and biogas production increased as OLR increased. The pH and alkalinity values were under normal operating conditions. In the VFA concentrations, OLR reduces accumulation as it increases. The application of the data obtained from the UASB reactor to the modified Stover-Kincannon and Monod kinetic models was performed, and the  $U_{\max}$ ,  $K_B$ ,  $K_S$ , and  $U_{\max}$  constants were determined. The organic material removal is suitable for the Stover-Kincannon kinetic model at most, as can be observed from the verification constant ( $R^2$ ).

Anaerobic sludge samples were taken before the start of the experiments and after completing the experiments performed in the UASB reactor. The SEM and FTIR analyses were performed after drying the obtained sludges and bringing them to small dimensions.

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