Wastewater treatment from a motor-oil reforming company using a sequencing batch reactor (SBR)

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Abstract The main aim of this work was to study the ability of an aerobically operated sequencing batch reactor (SBR) to effectively treat the wastewaters produced by a motor-oil reforming company. In fact, the most important goal was to substantially reduce the organic load of these wastewaters before their disposal to an open trench, since the currently installed wastewater treatment plant, that includes an API separator followed by physico-chemical pre-treatment and an oxidation ditch, has proved today to be completely inefficient. The wastewater to be treated was mainly composed of five different streams from various points of the motor-oil reforming plant (e.g. gas washing tanks, cooling pumps, used motor oils holding tanks, etc). The major problem faced in this work was the high organic load (about 12,000 mg COD/L) and the free and dissolved oil contained in the wastewater (around 6–7%). Moreover, two of the streams, contributing to the mixed wastewater up to 30%, were unable to sustain dissolved oxygen and unfortunately their mixing with the other three streams resulted in the same detrimental effect. Therefore, experiments were conducted using either three or all of the contributing streams. The mixed wastewater was fed to the reactor either untreated or pre-treated with ceramic membranes in order to exclude all the free and dissolved oil. The application of pre-treated wastewater with membranes to the SBR system resulted in 75.2% and 81.9% total and dissolved COD reduction, respectively.

Keywords Ceramic membranes; motor oil wastewaters; sequencing batch reactor; wastewater treatment

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Introduction

According to the international regulations, waste motor oils are considered as hazardous substances. Hence, their transport, use and disposal are regulated. The amounts of waste oils generated every year have been estimated for selected countries for the late 1980s or early 1990s and range around 500,000 T/y, on average, for the developed European countries and Canada, to around 5 million T/y for USA (Wolfe, 1992; Renaux, 1993). The worldwide annual consumption of lubricants today exceeds 40 million tons.

A large part of these waste motor oils contain mainly paraffinic, naphthenic and aromatic hydrocarbons, additives, degradation products and metals. Specifically, elements such as calcium, magnesium, barium, zinc, phosphorus and sulfur are constituents of additives in motor oil, e.g. anti-corrosives, anti-oxidants or detergents, and their concentrations vary according to the type of oil. In addition, metals such as iron, copper, calcium and lead appearing in the waste oils, originate from parts of the engine by wear, so their concentration rises with time (Zieba-Palus and Kościelniak, 2000). The lead content of the used motor oils is mainly caused by the use of tetraalkyl lead in the fuel (Cotton *et al*., 1977).

The discharge of used motor oils in the environment poses public health problems because of the mutagenic/carcinogenic compounds in them. Among these hazardous chemicals, polycyclic aromatic hydrocarbons (PAHs) are of particular interest since the carcinogenic properties of some of them are well established (Pasquini and Monarca, 1983). Recently, Clonfero *et al*. (1996) have determined the mutagenicity of the extracts and their contents of polyaromatic fraction (PAF) and PAHs in 13 samples of used motor oil and 33 recycled fractions. They concluded that used motor oils are mutagenic, both directly and indirectly, and the highest values were found in used oils from motor vehicles using leaded petrol. Unfortunately, hundreds of thousands of gallons of used motor oil containing PAHs are burned or improperly disposed of each year to both soil and water. This has prompted an intense search for an effective treatment for waste motor oil for recycling in fresh oil production. Therefore, processes such as the sulfuric acid/Fuller's, the Mohawk/Evergreen, the Entra re-refining and others have been developed for recovering up to 80% of the waste motor oil as reclaimed oil. Other novel processes have also been patented using propane, butane or similar solvents, mixed with the used oil to form a solution which, after the gravitational separation of asphaltic pollutants, is percolated through a columned filter and the oil is finally recovered by heating the solution (Mellen, 1997).

In all oil reclamation or reforming plant wastewaters are produced at various points of the process facilities (waste oil holding tanks, tower condensations, flame traps, purification of gases, oil spills, etc) and they are naturally contaminated with all the polluting compounds contained in the used motor oils as well as with the oil itself. The improper dumping of these wastewaters to soil or to natural water reserves can result in the same detrimental effects as the used motor oil itself. As a consequence of their chemical composition, worldwide dispersion and effects on the environment, these wastewaters are considered a serious environmental problem and their treatment prior to their disposal is considered mandatory.

For the effective decontamination of these wastewaters, either physico-chemical selective processes, such as solvent extraction followed by heterogenous photocatalytic decomposition or incineration of PAHs (Ireland *et al.*, 1995), ultrasonic removal of heavy metals (Fontana *et al.*, 1996) etc., or biological processes accomplished by either bacteria (El-Sayed *et al.*, 1996; Walker *et al.*, 1975a) or even algae (Walker *et al.*, 1975b), have been involved. Due to the xenobiotic and recalcitrant content of the wastewaters, an appropriate combination of these methods is mostly preferred in order to reduce the polluting constituents to permissible levels for safe disposal.

The ability of a sequencing batch reactor (SBR) system, alone or in combination with pre-treatment using ceramic membranes, to effectively treat the wastewaters generated by a motor oil reforming company was addressed in this work. The company produces over 25,000 MT of lubricants per year by reforming about 36,000 MT of used motor oils applying a novel hydrogenation method.

A typical SBR operation cycle includes five distinct phases for waste processing: namely fill, react, settle, decant and idle. All of these are taking place time-sequenced in a single basin. Application of this configuration can result in substantial space savings as there is no need for separate reaction and settling tanks. In addition, due to its operational flexibility, it is quite simple to achieve any improvement in wastewater treatment by changing phase duration rather than by adding or removing tanks in continuous flow systems (Norcross, 1992).

The wastewater that was used in this work was mainly composed of five different streams coming from various points of the motor-oil reforming plant (e.g. gas washing tanks, cooling pumps, used motor oils holding tanks, etc). The ability of the SBR system to provide effective removal of the wastewater organic loading was investigated using different operating strategies.

Materials and methods

Raw wastewater

The wastewater to be treated was composed of five main wastewater streams produced from respective points of the motor-oil reforming plant, i.e. tower condensations, gas washing tanks, water/diesel separation tanks, emulsions and flame traps. Immediately after the delivery of raw wastewater to the lab it was placed and maintained in a refrigerator, at 4°C, throughout the experimentation period. A detailed characterization was carried out for each of these streams including total COD, TSS, pH, various nitrogen forms (total and organic nitrogen, ammonium, nitrate, nitrite), total and dissolved phosphorus and dissolved oxygen concentration at saturation. The characteristics of each stream are given in Table 1. A representative wastewater was formed by mixing the separate streams, according to their volumetric proportion, depending on the studied conditions. As shown in Table 1, two of the streams contributing to the mixed wastewater up to 30%, were unable to sustain dissolved oxygen and unfortunately their mixing with the other three streams resulted in the same detrimental effect. Therefore, experiments were conducted using either three (mix#1) or all (mix#2) of the contributing streams. Since oil, in free and dissolved form, was mainly present in the stream V-304, a gravitational separation of free oil from the aqueous phase was implemented prior to its mixing with the rest of the streams (in mix#2). As anticipated, this resulted to a radical decrease of the V-304 total COD concentration to 27,712 mg/L. The total concentration of free oil in the mixed wastewater, without applying gravitational separation in V-304, was found to be 6.34 ± 0.017% (v/v). The mixed wastewaters (mix#1 and mix#2) were fed to the reactor either untreated or pre-treated with ceramic membranes in order to exclude all of the free and dissolved oil from all streams. The ceramic membranes were from Tami Industries (France) and their technical characteristics are shown in Table 2. The main characteristics of each stream after membrane treatment are given in Table 3.

SBR reactor

A lab scale reactor with an operating volume of 1 L was used in the present work. The reactor was seeded in some experiments with sludge from the aerobic basin of the wastewater treatment plant of the University of Patras and in others with an acclimated bacterial culture with specific degradative abilities (degradation of phenolic compounds, hydrocarbons and related compounds contained in petrochemical wastewaters), obtained commercially from Sybron Chemicals Inc. (USA). The minimum reactor volume at the end of the decant phase

Table 1 Wastewater stream characteristics

Stream ID	COD (mg O_2/L)	NH_4^+ (mg N/L)	NO_2^- (mg N/L)	NO_3^- (mg N/L)	Org. N (mg N/L)	Total N (mg N/L)
V-101	19,601	163.6	0.04	9.31	28.0	201
V-102	18,919	239.0	0.00	18.28	29.7	287
V-704	4,120	27.9	0.21	1.68	1.9	32
V-304	808,217	382.7	0.00	1.66	71.2	456
V-503	14,573	36.9	0.01	1.05	5.4	43
Mix#1	12,098	144.7	0.54	N/D	N/D	191
Mix#2	11,710	158.2	1.00	N/D	N/D	185

Stream ID	Total P (mg P/L)	Dissolved reactive P (mg P/L)	Disolved oxygen (at saturation) (mg O_2/L)	TSS (g/L)	pH	Volumetric proportions
V-101	0.44	0.21	5.7	0.95	4.43	
V-102	0.98	0.41	7.3	0.13	4.39	
V-704	0.32	0.09	7.3	0.42	7.29	
V-304	0.05	0.04	0.0	0.42	8.82	
V-503	0.09	0.04	0.0	0.00	9.13	
Mix#1	0.51	0.20	6.4	0.14	4.49	5:1:1[1]
Mix#2	0.39	N/D	0.0	0.21	9.28	5:1:1:1:2[2]

[1] (V-101:V-102:V-704), [2] (V-101:V-102:V-704:V-304:V-503)

Table 2 Technical characteristics of membranes

Trade name	Dimensions (mm) ($d_{out} \times d_{in} \times$ length)	Number of channels	Cut off (kD)	Membrane material
Trefle	10 × 3.6 × 254	3	(i) 300kD (ii) 150kD	ZrO_2–TiO_2

Table 3 Wastewater stream characteristics after membrane treatment

Stream ID	COD (mg O_2/L)	TSS (g/L)	NH_4^+ (mg N/L)	Dissolved reactive P (mg P/L)	pH
V-101	17,411	0.06	336.9	0.27	4.00
V-102	18,290	0.06	135.7	0.67	4.13
V-704	3,390	0.02	24.2	0.02	7.98
V-304	27,712	0.41	0	0.01	8.42
V-503	3,869	0.03	63.4	0.05	8.46
Mix#1	10,745	0.25	50.4	0.12	4.61
Mix#2	11,302	0.20	194.1	N/D	9.28

was one-third of the effective SBR volume. The temperature was adjusted at 25 ± 0.2°C with a temperature P-controller (Shimaden) using an electrical resistance, a thermocouple and a U-shaped tube connected to a tap water supply. The system was also equipped with facilities for wastewater inflow (variable speed pump), effluent discharge (variable speed pump), aeration (air pump) and mixing (magnetic stirrer). Digital timers controlled the operation of the system.

During the fill phase, 0.67 L of wastewater were fed to the reactor, increasing the liquid volume from 0.33 L (minimum level) to1 L (maximum level). The fill phase took place under anoxic conditions, providing only mixing of the reactor content. During the react phase, air was supplied to the system ensuring a dissolved oxygen concentration above 3 mg/L throughout the aeration period (except for the case of mix#2). Aeration and agitation of the reactor ceased during the settle phase and sludge was allowed to settle under quiescent conditions. During the decant phase, the clarified supernatant was withdrawn by pumping through a solenoid valve from a fixed port at the minimum liquid level. During one SBR cycle, samples were collected from the reactor at the beginning of the cycle, the end of fill, and the end of the aerobic phase, as well as from the effluent on the end of the decant phase. The duration of the SBR operation cycle was determined each time, based on preliminary batch degradation tests that were carried out for every type of treated wastewater (mix#1 or mix#2) and biomass used in the reactor.

Analytical methods

The wastewater samples were analyzed for COD according to the closed reflux method (*Standard Methods*, 1995). The pH was measured by an electrode (HI 8424 Hanna), while total and volatile suspended solids were determined according to Standard Methods (1995). The concentrations of nitrite- and nitrate-nitrogen were measured by ion chromatography (DX 300, Dionex Corp.). Ammonia-nitrogen was assessed using the Kjendahl method while total nitrogen was measured via the persulfate method (*Standard Methods*, 1995). Total and ortho-phosphate concentrations were measured using the ascorbic acid method, with and without persulfate digestion (*Standard Methods*, 1995). Assessment of the SBR reactor performance took place at regular intervals. The mixed liquor samples drawn from the SBR, during its operation, were analyzed for COD, pH, volatile suspended solids (VSS) and total suspended solids (TSS) concentrations according to *Standard*

Methods (1995). The sampling intervals during a typical SBR cycle were more frequent in order to obtain a detailed profile of the reactor performance during that cycle. Measurements of dissolved oxygen concentrations were performed using a DO-meter (RL450, Russell).

Results

The SBR system was initially fed with a mixture of three wastewater streams, i.e. mix#1 (adjusted pH to 7.0), which was able to sustain dissolved oxygen in high concentrations (6.4 mg/L at saturation). The reactor was inoculated with activated sludge and was operated aerobically in a 24 hour cycle. The operating cycle included a filling phase (30 minutes), an aerobic reaction phase (22 hours), settling (1 hour), decant (15 minutes) and an idle phase (15 minutes). No sludge wasting was implemented since the biomass productivity was very low. This type of operation resulted in a 29.3% and 37.8% reduction of the total and dissolved COD, respectively. A typical cycle of the reactor operation is shown in Figure 1. The dissolved oxygen concentration in the reactor, during the aerobic reaction, was constantly above 3.9 mg/L, which was considered adequate for microbial growth under these conditions. However, the SBR system operating with activated sludge proved unable to cope with the mix#2 wastewater (mixture of all wastewater streams), since the dissolved oxygen concentration in the reactor was constantly zero despite the continuous supply of air to the mixed liquor.

The system was then operated with the same mixture of the three wastewater streams (adjusted pH to 7.0), but this time the reactor was inoculated with an acclimated bacterial culture. This was able to degrade phenolic compounds, hydrocarbons and related compounds contained in petrochemical wastewaters, that was obtained commercially from Sybron Chemicals Inc. (USA). In this case, the reactor was operated in a 4 day cycle based on preliminary biodegradation tests that were conducted. The operating cycle now included a filling phase (30 minutes), an aerobic reaction phase (94 hours), settling (1 hour) and decant/idle (30 minutes). The results obtained for this type of operation, after the system reached a periodical steady state were 73.3% and 80.7% reduction of the total and dissolved COD, respectively. A typical behavior of the system during one operation cycle is shown in Figure 2. The last point in Figure 2 denotes effluent concentrations.

In the sequel, the reactor was fed with a mixture of all five wastewater streams (mix#2) without any pre-treatment. Although the dissolved oxygen during the first 24 hours of each aerobic phase was zero, the bacterial population was not seriously affected and finally the culture medium restored high dissolved oxygen values. The system was operated in a 10 day cycle based on preliminary biodegradation results. The operating cycle included a filling phase (30 minutes), an aerobic reaction phase (238 hours), settling (1 hour) and

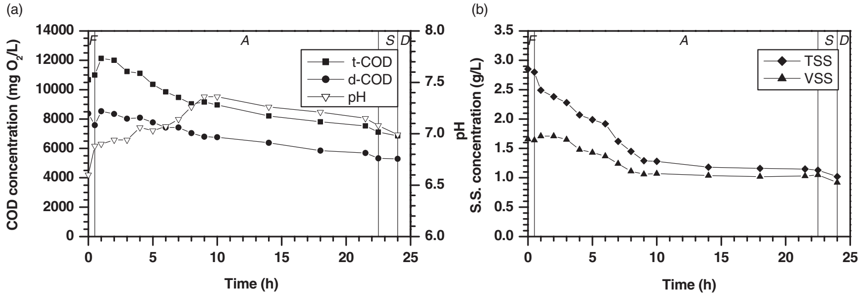

Figure 1 Concentration profiles of: (a) total and dissolved COD, pH and (b) total and volatile suspended solids during a typical operation cycle (24 hour cycle). SBR was fed with mix#1 wastewater. (F: fill phase; A: aerobic react phase, S: settle phase; D: draw/idle phase)

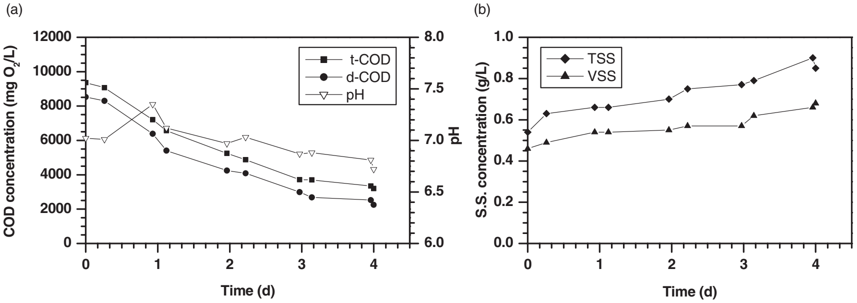

Figure 2 Concentration profiles of: (a) total and dissolved COD, pH and (a) total and volatile suspended solids during a typical operation cycle (4 day cycle). SBR was fed with mix#1 wastewater

decant/idle (30 minutes). The obtained results were a 72.8% and 75.1% reduction of the total and dissolved COD, respectively. Figure 3 presents the typical behavior of the system during one operation cycle.

Aiming to increase the COD removal efficiency of the system, a new series of experiments were carried out, where the application of pre-treated mixtures of wastewaters with ceramic membranes to the system, was evaluated. The performance of the reactor, operating on a 4 day cycle with the same phase durations as in the case of feed with raw mix#1 (Figure 2), was investigated by feeding the SBR with the pre-treated with membranes mix#1 wastewater. The obtained results for this type of operation, after the system reached a periodic steady state, were 71.8% and 81.8% reduction of the total and dissolved COD, respectively. This is almost the same as before. A typical behavior of the system during one operation cycle is shown in Figure 4.

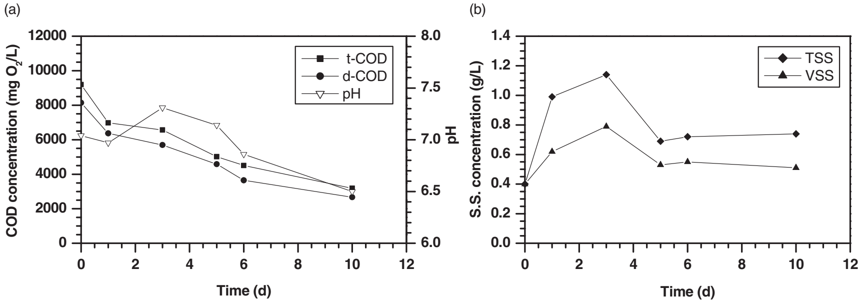

Figure 3 Concentration profiles of: (a) total and dissolved COD, pH and (b) total and volatile suspended solids during a typical operation cycle (10 day cycle). SBR was fed with mix#2 wastewater

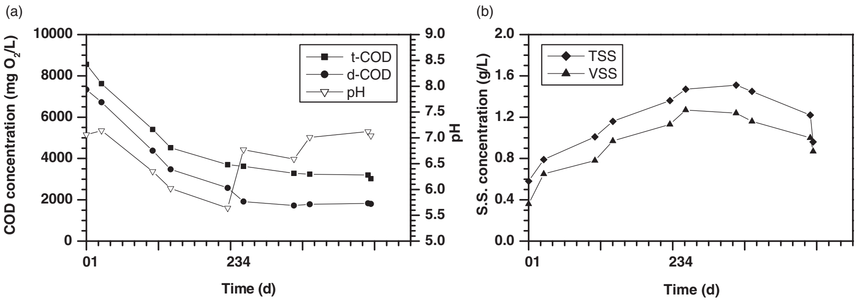

Figure 4 Concentration profiles of: (a) total and dissolved COD, pH and (b) total and volatile suspended solids during a typical operation cycle (4 day cycle). SBR was fed with mix#1 wastewater pre-treated with membranes

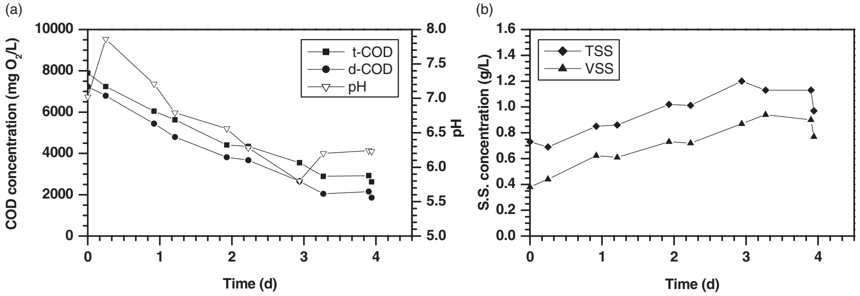

Figure 5 Concentration profiles of: (a) total and dissolved COD, pH and (b) total and volatile suspended solids during a typical operation cycle (4 day cycle). SBR was fed with mix#2 wastewater pre-treated with membranes

The mix#2 wastewater, pre-treated with membranes, was fed to the system in the sequel, and the reactor was operated until a stable periodic performance was reached. In this case, a 4 day cycle was used instead of the 10 day cycle that was used when the raw mix#2 wastewater was fed to the system. A typical cycle is shown in Figure 5. The last point in Figure 5 again indicate effluent concentrations. The application of this operation strategy to the system resulted in a 75.2% and 81.9% reduction of the total and dissolved COD, respectively. The performance of the system, in terms of effluent quality, was slightly increased but the treated wastewater throughput was 2.5 times higher than before (raw mix#2 feed). The BOD_5 concentration of the treated effluents was estimated as 56 mgO_2/L.

It is worthwhile noting that, as in the case of the raw mix#2 feed, the dissolved oxygen concentration in the reactor at the start of each operation cycle was zero. During the cycle, however, the dissolved oxygen concentration gradually increased and by the end of the first day it was over 6.5 $ppmO_2$, where it finally stabilized, thus sustaining microbial growth in the system. This is probably attributed to the presence of certain organic compounds which inhibited the oxygen's solubility to the specific type of wastewater and which, during the reaction phase were probably metabolized microbially, at least to some extent, thus raising their inhibiting effect on the oxygen's solubility.

Conclusions

The performance of the SBR system using the acclimated bacterial culture was increased from 29.3% and 37.8% reduction of the total and dissolved COD, achieved by using typical activated sludge, to 73.3% and 80.7%, respectively, for the case of treatment of the mix#1 wastewater (three wastewater streams). Moreover, the acclimated bacterial culture was able to treat the raw mix#2 wastewater (all wastewater streams) by effectively facilitating the solubility of oxygen in the mixed liquor, thus sustaining microbial grow th in the system. The SBR system was therefore able to perform a 72.8% and 75.1% reduction of the total and dissolved COD, respectively and a 75.2% and 81.9% reduction of the total and dissolved COD, when treating the pre-treated with membranes mix#2, whereas the SBR operating with activated sludge proved unable to cope with this type of wastewater.

The application of ceramic membranes, as a stage of pre-treatment of the mixed wastewaters, can lead to an improvement of the reduction performance of total COD by 2.4% and for dissolved COD by 6.8%. More importantly, it can result in a significant reduction of the required operating cycle of the SBR system from 10 days to 4 days for the achievement of the same performance.

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