

Stripping as a pretreatment process of industrial oily wastewater

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Abstract

In the present work, the potential of purifying an oily wastewater from a lubricant production unit, consisting mainly of alcohols, phenols and heavy linear saturated hydrocarbons, using the stripping process was examined. The effect of stripping gas flow ($75\text{--}300\text{ L}_{\text{N}_2}\text{ L}_{\text{WW}}^{-1}\text{ h}^{-1}$) and system temperature ($295\text{--}355\text{ K}$) on the chemical oxygen demand (COD) of the effluent was investigated. A decrease in COD content of 25–30% was achieved after 4 h for stripping gas flow rates over $150\text{ L}_{\text{N}_2}\text{ L}_{\text{WW}}^{-1}\text{ h}^{-1}$, whereas the rate of organic compounds removal was enhanced by increasing temperature up to 333 K. At higher temperatures an effluent condensation was observed. Gas chromatography–mass spectrometry analysis of both liquid and gas phase showed that linear saturated hydrocarbons of high molecular weight were stripped out from the wastewater. The results are in agreement with the equilibrium ratio of these compounds as predicted from by theoretical calculations.

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1. Introduction

The industrial growth and the production of commercial chemical products are accompanied by the discharge of various organic compounds in the aquatic environment. Industrial wastewaters usually contain a number of organic pollutants of various biodegradability characteristics. This fact combined with the generally high pollution load, in terms of chemical oxygen demand, makes the purification of such wastewaters a rather difficult task.

Oily wastewaters are produced in refineries, petrochemical and lubricant production units and they are usually in the form of emulsions. Various processes are employed for their purification, ranging from conventional methods such as flocculation followed by air flotation to advanced ones such as ultra- or microfiltration combined with biological

treatment [1–9]. Advanced oxidation processes have been also tested [10–12] as well as land treatment for such wastes [13].

The fact that the activity coefficient of oily constituents in wastewater is very high, even if their vapor pressure is low, implies the possibility of effective removal of such compounds from wastewater by stripping methods. The design of a steam stripper for removal of organic pollutants from water has been studied and a simple guideline has been proposed for effective stripping [14–20].

In the present study, stripping was used for removing organic pollutants from the effluent of a lubricant production unit, as a pretreatment step before the biological oxidation of the effluent. The effect of stripping gas flow rate and system temperature on the removal of pollutants load, expressed as chemical oxygen demand, was investigated. Furthermore, the profile of the compounds present in the wastewater was examined before and after the stripping treatment and the experimental results were compared to vapor–liquid equilibrium predictions.

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Table 1
The composition of the wastewater

Peak	Retention time (min)	Compound	% of total
1	3.11	Isobutanol	22.4
2	4.32	Acetic acid	3.8
3	6.74	Ethylene glycol	20.7
4	7.40	2-Methyl-1-butanol	4.5
5	8.18	4-Methyl-2-pentanol	15.9
6	8.40	1-Pentanol	4.5
7	14.48	Benzeneamine	2.0
8	14.56	Phenol	6.9
9	16.28	<i>o</i> -Cresol	1.8
10	16.68	<i>p</i> -Cresol	1.6
11	18.17	2,5-Dimethyl-phenol	0.7
12	18.50	3,5-Dimethyl-phenol	0.8
13	18.96	3,4-Dimethyl-phenol	0.6
14	19.24	1,2,3-Trimethoxy-propane	2.0
15	20.99	Tridecane	0.8
16	22.43	Tetradecane	1.5
17	23.88	Pentadecane	1.8
18	25.03	Hexadecane	1.7
19	25.97	Heptadecane	1.7
20	26.77	Octadecane	1.5
21	27.49	Nonadecane	1.4
22	28.23	Eicosane	1.4

2. Experimental details

2.1. Materials and experimental procedure

The effluent from a lubricant production unit of a petroleum company (LPC Hellas) with a COD of $7900 \pm 500 \text{ mg L}^{-1}$ and pH of 7.6 was used as the wastewater. The composition of the wastewater is presented in Table 1. The volume of the wastewater used in experiments was 0.2 L.

All reagents used in COD analysis were of analytical grade. Nitrogen of 99.9% purity, purchased from L' Air Liquide, was used as the stripping agent at flow rates $75\text{--}300 \text{ L}_{\text{N}_2} \text{ L}_{\text{WW}}^{-1} \text{ h}^{-1}$ (WW: wastewater) and was introduced to the bottom of a jacketed tube containing the wastewater. The temperature was varied between 295 and 355 K through circulating water. Samples from both gas and liquid phase were withdrawn at specific time periods and analyzed for their content.

2.2. Analysis

Chemical oxygen demand (COD) measurements were carried out using the dichromate reflux method [21].

The profile of the compounds contained in the wastewater as well as the constituents of the gas phase stripped out were determined with a Hewlett Packard gas chromatograph HP 6890 equipped with a mass spectrometry detector HP 5973 (GC-MS). The column used was an HP1-MS (HP 19091S-733) with 30 m length and internal diameter of $250 \times 10^{-6} \text{ m}$. It was operated at 323 K for 5 min, then its temperature was raised to 473 K with a rate of 10 K min^{-1} and finally to 553 K

with 20 K min^{-1} . Helium was used as carrier gas with total flow of 9.7 mL min^{-1} in pulsed split (1:10) mode. The temperature of the injector and the detector was 523 and 423 K, respectively.

3. Results and discussion

3.1. Effect of gas flow rate on pollutant removal

The effect of nitrogen flow rate, at ambient temperature and pressure, on pollutant removal, expressed in terms of COD, is presented in Fig. 1. It is obvious that above $150 \text{ L}_{\text{N}_2} \text{ L}_{\text{WW}}^{-1} \text{ h}^{-1}$, COD removal was almost independent from nitrogen flow rate and reached 29% after 4 h. The rate of COD removal decreased with time because it was dependent on the pollutant concentration in the liquid phase, which also decreased gradually. From a practical point of view, the contact time can be limited to about 120 min and the flow rate of nitrogen can be adjusted to $150 \text{ L}_{\text{N}_2} \text{ L}_{\text{WW}}^{-1} \text{ h}^{-1}$, corresponding to a decrease in COD content of about 22%.

3.2. Effect of temperature on pollutant removal

The effect of temperature on COD removal (gas flow rate = $150 \text{ L}_{\text{N}_2} \text{ L}_{\text{WW}}^{-1} \text{ h}^{-1}$) is presented in Fig. 2. It is clear that an increase in temperature in the range 295–337 K enhanced significantly the rate of organic compounds removal. That was expected since the relative mass-transfer coefficient also increases with temperature. However, after a certain point, pollutant removal decreased with time at temperatures above 330 K. That fact was more pronounced at higher temperatures, occurring earlier in the time scale. A possible explanation is that at elevated temperatures, the evaporation rate of the solvent (water) reached at higher values than the rate of organic compounds stripping, resulting thus in condensation of the wastewater instead of its purification. Consequently, temperature is a crucial factor in the stripping process. Taking all

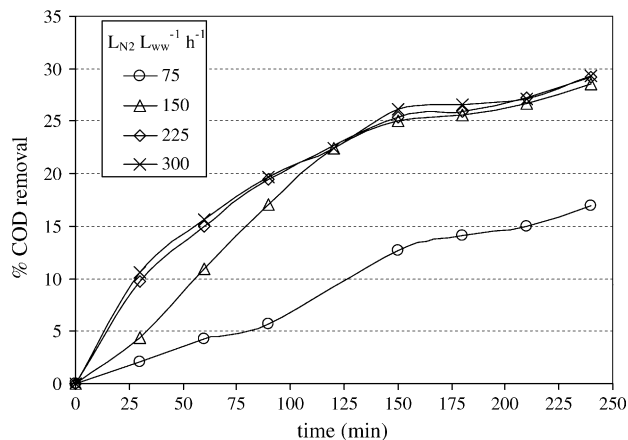


Fig. 1. Effect of nitrogen flow rate on COD removal at 20 °C, under atmospheric pressure.

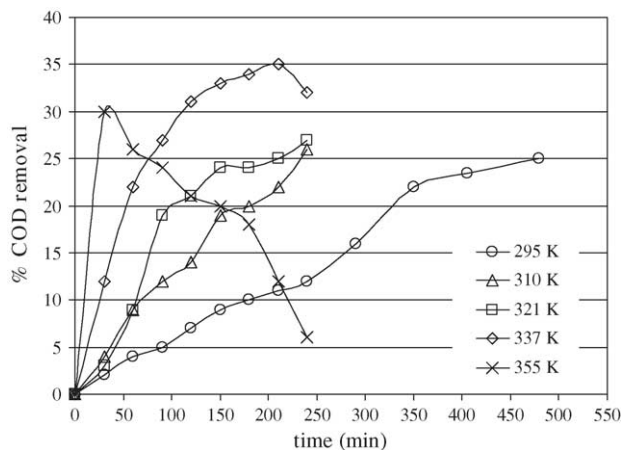


Fig. 2. Effect of temperature on COD removal for gas flow rate of $150 \text{ L}_{\text{N}_2} \text{ L}_{\text{WW}}^{-1} \text{ h}^{-1}$.

experiments into account, it seems that the optimum conditions in the stripping process of the wastewater studied are: gas flow rate = $150 \text{ L}_{\text{N}_2} \text{ L}_{\text{WW}}^{-1} \text{ h}^{-1}$, temperature = 337 K and contact time = 200 min , resulting in 35% COD removal.

3.3. Nature of compounds being stripped out of the wastewater

In Fig. 3, the spectra of organic compounds that were contained in the wastewater before and after stripping are presented as obtained with GC–MS analysis. In Fig. 4, the spectra of compounds present in the gas phase stripped out from wastewater are shown, in relation to the wastewater analysis before stripping. As it can be seen, all compounds corresponding to retention times above 20 min were removed from the wastewater and detected in the gas phase. These compounds were the linear saturated hydrocarbons of high molecular weight (more than 13 carbon atoms in the carbon

chain) initially present in wastewater, as presented in Table 1 (peaks 15–22).

These experimental findings can be explained by means of equilibrium ratio K for the different compounds initially present in wastewater.

Equilibrium ratio (K_i) is defined as the ratio of y_i to x_i , i.e. $K_i = y_i/x_i$, where y_i and x_i are the mole fractions of the component i in the mixture vapor and liquid phases, respectively. At low pressures, vapor phase can be accurately assumed that behaves ideally, and K_i can be expressed as:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P^{\text{sat}}}{P} \quad (1)$$

where γ_i is the activity coefficient of component i and P^{sat} its vapor pressure at the mixture temperature. For very dilute solutions, γ_i is approximately constant and equal to its infinite dilution value (γ_i^∞). Substitution in Eq. (1) gives, thus, the infinite dilution equilibrium ratio:

$$K_i^\infty = \frac{\gamma_i^\infty P^{\text{sat}}}{P} = \frac{H_i}{P} \quad (2)$$

where H_i is the Henry's law constant of component i .

A simple guideline has been proposed [14] for the evaluation of stripping effectiveness and is the following:

$$\begin{aligned} \log K_i^\infty < 1 & \text{ ineffective} \\ 1 < \log K_i^\infty < 2 & \text{ strippable} \\ 2 \leq \log K_i^\infty & \text{ effective} \end{aligned} \quad (3)$$

The wastewater used in the present study can be viewed as a dilute aqueous solution, since a value of 8000 mg COD/L corresponds to about 10^{-2} M , for a typical composition of wastewater, as reported in Table 1.

Equilibrium ratios at atmospheric pressure were estimated through Eq. (2) using either experimental or predicted Henry's law constant (H) values. Experimental H values were

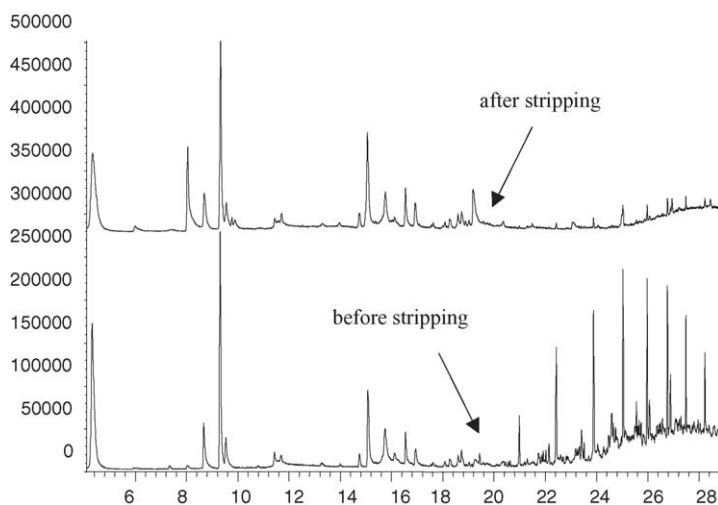


Fig. 3. Organic compounds present in oily wastewater before and after stripping through GC–MS analysis.

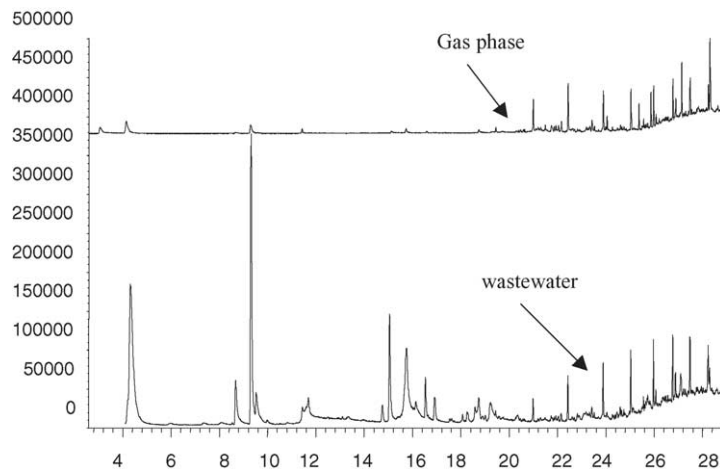


Fig. 4. Organic compounds present in the gas phase stripped out from oily wastewater through GC–MS analysis.

obtained from [22], while when they were not experimentally available they were predicted from the Bond Contribution (BC) model, which was originally developed by Hine and Mookerjee [23] and updated by Meylan and Howard [24]. The BC model calculates the Henry's law constant, as the summation of the contributions of the individual bonds that comprise the compound. Values of bond contributions are given in the original publication of Meylan and Howard [24].

Experimental H values or predicted ones from the BC model are, however, available only at 298 K. H values at 353 K were predicted with a simple empirical method from the knowledge of its value at some temperature T_0 . This method is based on the observation that the major, by far, effect on the variation of H with T comes from change in vapor pressure rather than from γ^∞ .

From Eq. (2) we obtain:

$$H(T) = H(T_0) \frac{\gamma^\infty(T) P^s(T)}{\gamma^\infty(T_0) P^s(T_0)} \quad (4)$$

where T_0 is selected to be 298 K.

As mentioned above, it can be assumed that $\gamma^\infty(T)$ is equal to $\gamma^\infty(T_0)$ at the relatively narrow temperature interval considered here, i.e. from 298 to 353 K. Moreover, vapor pressures can be expressed by the following equation [25], involving the normal boiling point (T_b):

$$\ln P^s = 19 \left(1 - \frac{T_b}{T} \right) + 8.5 \ln \left(\frac{T_b}{T} \right) \quad (5)$$

where P^s is given in atm and T_b in K.

Eq. (3) can be, thus, rewritten as:

$$H(T) \cong H(T_0) \exp \left[19 \left(\frac{T_b}{T_0} - \frac{T_b}{T} \right) + 8.5 \ln \left(\frac{T_0}{T} \right) \right] \quad (6)$$

No experimental data were available at high temperatures and pressures for the compounds of our interest. Furthermore, Eq. (2) is not applicable since ideal vapor phase behavior cannot be assumed. In this case equilibrium ratios were predicted

from the equation:

$$K_i = \frac{y_i}{x_i} = \frac{\varphi_i^L}{\varphi_i^V} \quad (7)$$

where φ_i^L and φ_i^V are the fugacity coefficient of component i in the mixture. Fugacity coefficients were predicted from the so-called LCVM model [26], which couples a modified Peng–Robinson equation of state [27] with the UNIFAC group contribution activity coefficient model [28].

In Table 2 experimental and predicted values of $\log K_i^\infty$ are reported for the organic compounds present in wastewater.

Table 2

Values of infinite dilution equilibrium ratio K^∞ for the wastewater constituents

Compound	$\log K^\infty$ at 298 K	$\log K^\infty$ at 353 K
Isobutanol	-0.30	0.68
Acetic acid	-2.25	-1.19
Ethylene glycol	-2.48	-1.07
2-Methyl-1-butanol	-0.11	1.00
4-Methyl-2-pentanol	0.39	1.51
1-Pentanol	-0.14	1.01
Benzeneamine	-0.95	0.40
Phenol	-1.73	-0.40
<i>o</i> -Cresol	-1.18	0.20
<i>p</i> -Cresol	-1.25	0.17
2,5-Dimethyl-phenol	-1.21	0.26
3,5-Dimethyl-phenol	-2.47	-0.96
3,4-Dimethyl-phenol	-1.64	-0.11
1,2,3-Trimethoxy-propane ^a	-1.94	-0.75
Tridecane	5.20	6.77
Tetradecane	5.71	7.35
Pentadecane	5.85	7.56
Hexadecane ^a	6.21	8.00
Heptadecane ^a	6.33	8.18
Octadecane ^a	6.45	8.37
Nonadecane ^a	6.58	8.55
Eicosane ^a	6.70	8.73

^a Predicted values.

It can be seen that the heavy linear saturated hydrocarbons present in wastewater possess $\log K^\infty$ values greater than 5, being classified according to guideline (3) as effectively removable by stripping, while the rest of the compounds (phenols etc.) are classified as practically non-removable. This is in close accordance with the composition of wastewater before and after stripping, as reported in Fig. 3 and the composition of the gas phase as shown in Fig. 4.

4. Conclusions

In the present work, the effect of gas flow rate and system temperature on the stripping of the wastewater from a lubricant production plant was investigated. Moreover, the profile of the compounds present in the wastewater before and after the stripping process was examined with GC–MS analysis. The main results obtained are the following:

- (1) For gas flow rates above $150 \text{ L}_{\text{N}_2} \text{ L}_{\text{WW}}^{-1} \text{ h}^{-1}$, COD removal was almost unaffected by nitrogen flow variation and reached 29% after 4 h. The rate of COD removal decreased with time.
- (2) In the range 295–337 K, an increase in system temperature enhanced significantly the rate of organic compounds removal. However, after a certain point, pollutant removal decreased with time at temperatures above 330 K due to higher values of the evaporation rate of the solvent in comparison with the rate of organic compounds stripping.
- (3) The linear saturated hydrocarbons of high molecular weight (13–20 carbon atoms in the carbon chain) contained in the wastewater were removed by the stripping process, as determined with GC–MS analysis. It was shown that K^∞ values can be used as a simple tool for determining which organic compounds may be removed from an effluent through stripping.

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