Evaporation and air-stripping to assess and reduce ethanolamine s toxicity in oily wastewater

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Abstract

Toxicity from industrial oily wastewater remains a problem even after conventional activated sludge treatment process, because of the persistence of some toxicant compounds. This work verified the removal efficiency of organic and inorganic pollutants and the effects of evaporation and air-stripping techniques on oily wastewater toxicity reduction. In a lab-scale plant, a vacuum evaporation procedure at three different temperatures and an air-stripping stage were tested on oily wastewater. Toxicity reduction/removal was observed at each treatment step via Microtox® bioassay. A case study monitoring real scale evaporation was also done in a full-size wastewater treatment plant (WWTP). To implement part of a general project of toxicity reduction evaluation, additional investigations took into account the monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) role in toxicity definition after the evaporation phase, both as pure substances and mixtures. Only MEA and TEA appeared to contribute towards effluent toxicity.
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Keywords: Oily emulsion; Evaporation; Air-stripping; Microtox® bioassay; Ethanolamine

1. Introduction

There has been a consistent rise in xenobiotic compounds release into the aquatic environment in recent decades due to the rapid increase in wastewater industrial production. Most of these substances are suspected to be toxic and carcinogenic, and generally have low biodegradability. This fact, combined with the high organic pollution load in terms of chemical oxygen demand (COD) and matrix effect [1], makes the purification of such wastewater a difficult task [2–4]. In Italy, as in many other Mediterranean countries, oily wastewater is a major environmental problem in the coastal zone, where the chemical industry produces significant amounts of industrial waste [5].

Control of toxic pollutants is extremely troublesome, time consuming and costly, especially in industrial areas where a large number of complex effluents are collected, combined and treated in wastewater treatment plants (WWTPs) [6]. Kahru et al. [7] proposed a battery of microbiotests for evaluating wastewater pollution from the oil shale industry, showing that chemical analyses can easily miss contaminants with a high toxic impact. Performing a hazard assessment with an appropriate battery of toxicity tests can integrate traditional characterisations for assessing impacts on the target environment. Oily wastewater generated by various industries, frequently occurring in the form of oil-in-water emulsion, creates a major problem around the world [2,8,9]. Oily wastewater is generated by different activities such as refinery, petrochemical and lubricant production units, metal finishing, metal working, textile industry and paper mills [4,10] and can have a complex composition because it may contain mineral, vegetal or synthetic oils, fatty acids, emulsifiers, corrosion inhibitors and bactericides.

This study tested a method to reduce the impact on the aquatic environment of oily wastewater of industrial origin, containing several organic pollutants with varying biodegradability characteristics. Oily wastewater emulsion, after the first step of breaking by a chemical method, was treated by a sequence of evaporation and air-stripping physical processes, in order to verify the removal efficiency of organic and inorganic pollutants as well as the toxicity reduction performance.

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Evaporation and air-stripping were tested in a lab-scale plant facility, while a full-scale WWTP was used as a case study for the evaporation process. Traditional physical and chemical characterizations for raw and treated wastewaters were integrated with Microtox® bioassay results. Furthermore, according to the toxicity reduction evaluation procedure (TRE) [11], a biomonitoring screening survey with *Vibrio fischeri* involved the control of monoethanolamine (MEA, CAS Number: 75-04-7), diethanolamine (DEA, CAS Number: 111-42-2) and triethanolamine (TEA, CAS Number: 102-71-6) roles in toxicity definition, due to their frequent occurrence as emulsifiers and corrosion inhibitors in oily wastewater. They were all monitored as pure substances and as mixtures (MEA and TEA) in order to implement part of a general project of toxicity reduction assessment.

2. Background

2.1. The TRE approach

A TRE investigation is designed to isolate the source of effluent toxicity and determine the effectiveness of various control options (e.g. technological facility) in reducing toxicity. In this work, the TRE procedure was applied to oily wastewater treatment in both a lab-scale plant and a full-scale WWTP. This approach was similar to the USEPA [11] general approach which involves three tiers. The first tier involves the collection of background information on the plant and its past operating history. The second tier evaluates remedial actions to optimise the operation of the facility in order to reduce effluent toxicity. If these improving actions are successful in reducing toxicity to acceptable levels, the TRE procedure is complete, if not, it must proceed to the third tier that may enable toxicity causes to be ascertained by a toxicity identification evaluation procedure (TIE). A TIE procedure focusing mainly on ammonia and ethanolamine compounds role in toxicity definition completed this research.

2.2. Wastewater treatment

The range of some physical and chemical parameters, as measured over a 2-year period in the full-scale WWTP, are reported in Table 1 to provide a general overview of oil-in-water characteristics.

Various processes are used for oily wastewater separation and purification. The first phase consists of a pre-treatment to separate oily emulsion from the wastewater (emulsion breaking). The traditional methods include chemical and physical (mechanical and thermal) technologies. The chemical method is primarily based on the neutralisation of detergents and a change of the pH of the solution followed by further purification for the liquid phase. The physical method is based on the mechanical phenomenon of gravitational breaking (flotation or dissolved air flotation), ultra-filtration membrane separation or micro-filtration, whereas the thermal method mainly focuses on heating or evaporation processes [1,2,4]. The resulting liquid phase, containing residual oil, should be subjected to further

Table 1
Some physical and chemical parameters of oily wastewaters after chemical breaking in the full-scale WWTP near Venice (Italy)

Parameters	Range
pH	7.80–11.00
COD_{tot} (mg O_2/L)	10,200–40,000
COD_{sol} (mg O_2/L)	5300–21,000
TKN (mg N/L)	215–729
$N–NH_4$ (mg/L)	60–300
N_{org} (mg N/L)	120–450
SS (mg SS/L)	2700–20,000
VSS (mg VSS/L)	500–13,500
Chloride (mg/L)	70–450
$N–NO_3^-$ (mg/L)	2–60
$S–SO_4^{2-}$ (mg/L)	50–1500
$P–PO_4^{3-}$ (mg/L)	10–70
Surfactants (mg/L)	100–3000

treatment in order to achieve the current effluent standard for the receiving waters (e.g. stripping, activated sludge biological treatment or carbon adsorption).

3. Materials and methods

The lab-scale plant consisted of a vacuum evaporation (roto-vapour) device, which can operate at different temperatures, and an air-stripping apparatus. The evaporating apparatus was composed of a 1 L Pyrex flask in a thermostatic bath, thermometer, cooler, 100 mL graduated cylinder for condensate collection, an oil rotative vacuum pump and pressure gauge. The air-stripping tests were conducted in a 100 mL beaker with an air bubbling device (50–70 L/h, $T = 50\,°C$ and $P = 1$ atm) in a thermostatic bath, in order to maintain a constant temperature during the experimental runs. The air bubbling device was a ceramic porous distributor submerged in the 100 mL beaker.

The WWTP, located about 20 km from Venice (Italy), was chosen to verify the evaporation experimental results at full scale (the stripping column was under construction). The WWTP is designed to treat biodegradable organic liquid, oily wastewater, metal plating waste (bath solution and rinse water), glass factory discharge, biological and chemical sludges, textile industry and printing wastewaters. The treatment system consists of a primary treatment plant with physical and chemical batch processing units and a secondary biological treatment plant (Fig. 1A). After an inlet pumping station, the effluent from the collector tank is first passed through screens and grit chambers to remove large and coarse particles, and then collected in separate tanks according to treatability characteristics. After laboratory screening procedures, the streams containing only highly biodegradable compounds are directly transferred to a double stage activated sludge sequencing batch reactor (SBR). The streams containing heavy metals or non-biodegradable organic compounds are fed to the physical and chemical treatment plant and successively, transferred to the SBR. After settling, the SBR effluent is filtered in a rapid sand filter and an activated carbon column, before its discharge into publicly owned treatment works (POTW). Before transferring to SBR, in the case of oily wastewater, the effluent, after a breaking treatment with a chemical method and a
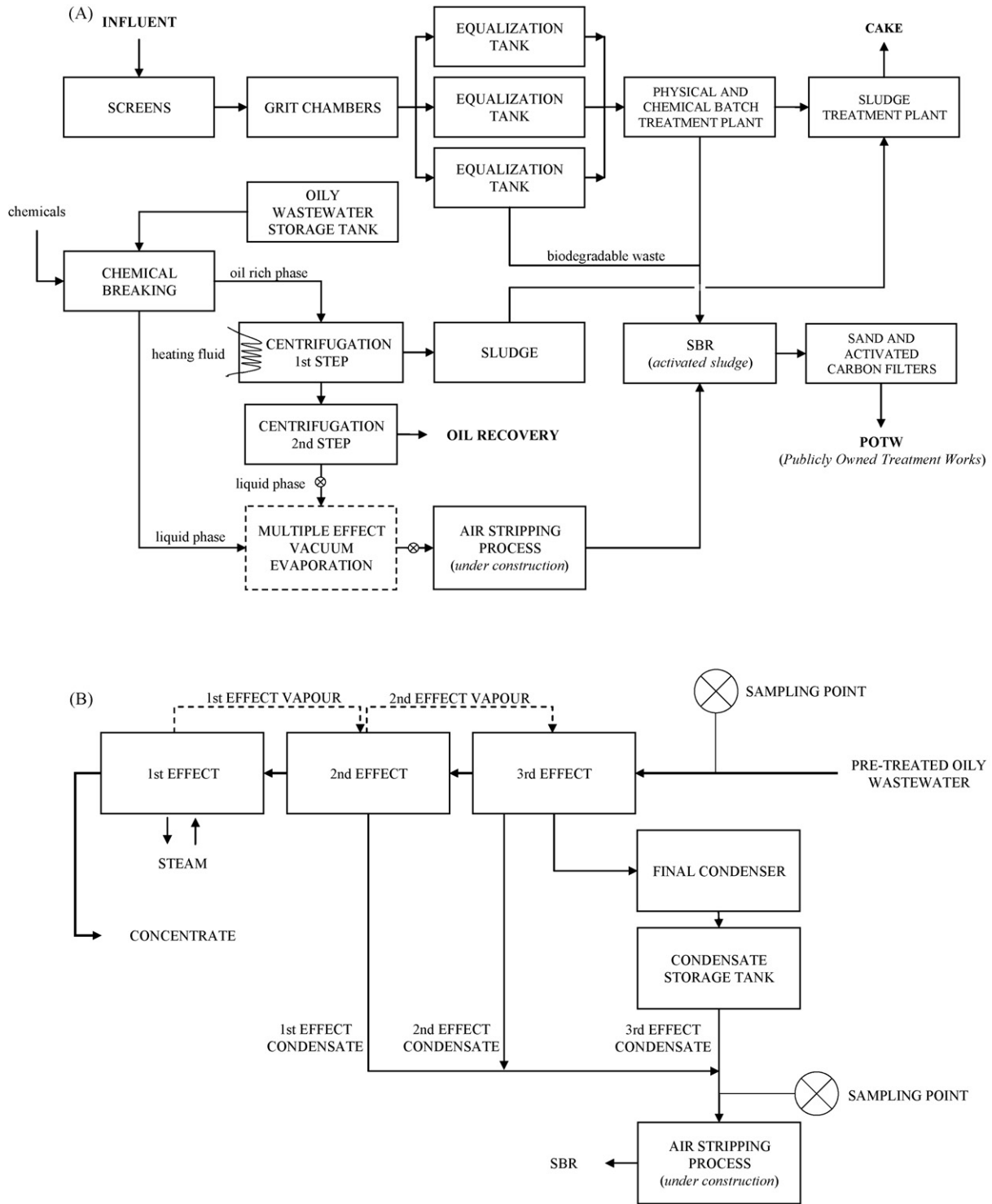
Fig. 1. Diagram of the WWTP (A) and multiple-effect vacuum evaporation and air-stripping apparatus (B). Sampling points (cross marks, ⊗) are shown.

double step centrifugation process, is accumulated in a 30 m³ tank and conveyed to the advanced technology area where it is treated in a multiple-effect vacuum evaporation (Fig. 1B) [12]. After laboratory chemical controls, treated wastewater from the sand and activated carbon filters are transferred to POTW. The plant capacity is 180,000 tonnes/year of industrial wastewater. The multiple-effect evaporation unit capacity is 7.5 tonnes/h of

evaporated waste at 80 °C with a maximum of 3000 kg/h of steam.

3.1. Effluent treatment

3.1.1. Evaporation
In the lab-scale plant, oily emulsion followed a two-step process: a vacuum evaporation process (EP) and stripping
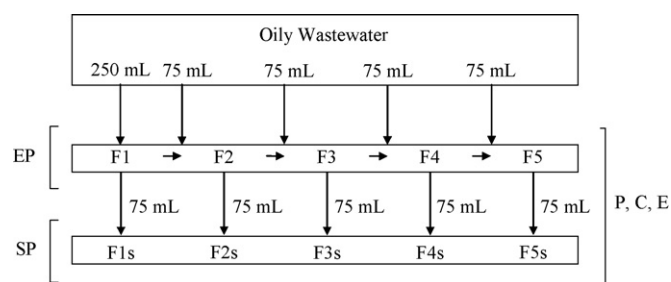
Fig. 2. Lab-scale plant experimental procedure. EP = evaporation process; SP = stripping process; P, C, E = physical, chemical and ecotoxicological analyses; F1–F5 = samples after evaporation; F1s–F5s = samples after evaporation and stripping.

process (SP). After every EP and SP, COD, total ammonia nitrogen (N–NH$_4$), pH and toxicity were determined. The oily wastewaters for the lab-scale plant were sampled from the real WWTP.

The experimental procedure of the lab-scale plant is shown in Fig. 2. The EP consisted of evaporating 75 mL from 250 mL of oily wastewater at three different temperatures and relative pressures (50 °C and 11 kPa, 70 °C and 31 kPa, and 80 °C and 48 kPa), and collecting the condensate samples. At the end of each EP, 75 mL of fresh oily wastewater was added to the remaining solution to reconstitute the initial volume of 250 mL. This operation was repeated four times in order to reach a steady state in the condensate sample parameters and simulate the behaviour of the full-scale plant after continuous feed. A preliminary survey had indicated that the steady state for pH, DO and ammonia values could be reached after the fifth collected condensate fraction. The sample collection resulted in five sub-samples (F1, F2, F3, F4 and F5) for each evaporation temperature. In the lab-scale plant, the condensed wastewater was stripped after every EP.

In the full-scale WWTP, oily wastewater was evaporated in the multiple-effect evaporator from 80 to 50 °C (WWTP1, WWTP2, WWTP3, WWTP4 and WWTP5). The evaporator was a triple effect one with backward feed. Three boilers were arranged in series, each operating at a lower pressure than the preceding one. Operating conditions were: 80 °C and 48 kPa for the first effect, 65 °C and 25 kPa for the second one, and 50 °C and 11 kPa for the last one as mentioned above.

3.1.2. Stripping

Air-stripping is the process involving the mass transfer of volatile contaminants from wastewater to air. Oily emulsion samples, after evaporation and condensation, were basified till pH 11 before air-stripping at 50 °C in the lab-scale plant. Samples were basified in order to transform ionised ammonia into unionised ammonia, facilitating its removal by the stripping procedure. The air-stripping working temperature was similar to the operating condition that will be adopted in the full-scale WWTP plant under construction. Five sub-samples (F1s, F2s, F3s, F4s and F5s) were collected.

3.2. Physical and chemical analyses

COD and COD$_{sol}$ (soluble COD, after filtering at 0.45 μm) were determined according to 5130 procedure [13], BOD according to 5120/A procedure [13], N–NH$_4$ according to 4030/C procedure [13], suspended solids (SS) and volatile suspended solids (VSS) according to 2090 procedure [13] and total Kjeldahl nitrogen (TKN) according to 5030 procedure [13]. pH was measured with pHmeter HI 9025 Microcomputer from HANNA Instrument®. The concentration of unionised ammonia was calculated as a function of temperature and pH. MEA, DEA and TEA were determined by ion chromatograph system (Dionex DX500 with CSRS-I in the external water mode suppressor, column CS-14 ID 4 mm, length 25 cm) as all other anions (chloride, nitrite, nitrate, sulphate and phosphate).

3.3. Ecotoxicological analyses

Samples toxicity was determined according to the reduction of bioluminescence in *Vibrio fischeri* via Microtox® Model 500 Test System. Reagents and supplies were obtained from Microbics Corporation (Carlsbad, California, US). Diluent solution (2% saline) and osmotic adjustment solution (22% saline) were also bought ready to use from Microbics Corporation. The manufacturer's protocol (Basic Test) was followed according to Microbics [14]. This protocol allows measurement of light outputs of Microtox® reagents relative to those of a fresh bacteria control at three exposure times (5, 15 and 30 min, to check the potential role of contact time in toxicity definition) to serial dilutions of samples. The endpoint consists of determining the level of light loss as a consequence of bacteria exposure to the toxic samples. Data were reduced to EC50, as the effective concentration of a test sample that induces a 50% decrease of light output after 5-min contact time for wastewater and after 5-, 15-, and 30-min contact time for pure substances and their mixtures (MEA, DEA and TEA). The values were obtained by linear regression between wastewater concentration (as percentage) and the fraction of light loss to light remaining (Γ) in a logarithmic scale (EC50 is the sample concentration corresponding to $\Gamma = 1$) with 95% confidence limits. The data expressed as EC50 were also transformed into toxicity units, TU50 (TU50 = 100/EC50), to reveal the direct relationship between toxic effects and measurement system used [8]. Bulich's [15] modified classification was adopted to compare toxicity reduction trends during each treatment process (EP and SP) in both the lab- and full-scale WWTP. The Bulich modified score consists of six integer values from 1 to 6, indicating TU50

Table 2
Bulich *modified* score with TU50 ranges [15]

Bulich modified score	TU50 range
1	TU50 < 1.00
2	1.00 ≤ TU50 ≤ 3.13
3	3.13 < TU50 ≤ 10.00
4	10.00 < TU50 ≤ 31.25
5	31.25 < TU50 ≤ 100.00
6	100.00 < TU50

levels rise in increasing order; TU50 ranges are reported in Table 2.

4. Results and discussion

4.1. Physical and chemical parameters evaluation

The evaporation process in the lab-scale plant considered an oily wastewater characterised by COD = 14,760 mg O_2/L, N–NH$_4$ = 1190 mg/L, pH 8.2 and TU50 = 70.00. MEA, DEA and TEA concentrations were not determined in the oily wastewater for the lab-scale plant, because their presence was not at first suspected.

The results for evaporated and condensated samples (F1–F5) are shown in Fig. 3 and summarized as removal efficiencies in Tables 3 and 4. In the condensate samples, pH values remained constant between 9.00 and 9.50. COD trend (Fig. 3A) showed that the vapour phase COD decreased less rapidly after F2, until a steady state was reached after F4, when just the organic volatile compounds of each fraction fed to the lab-scale plant (75 mL) were transferred to the vapour phase. Comparison between the samples obtained at the three temperatures showed that the F1 fractions (from the initial 250 mL of COD oily emulsion) had considerably different COD values. This was perhaps caused by the experimental temperature as its increase corresponded to a higher transfer of organic volatile compounds from liquid to vapour phase. The fractions at $T = 70\,^\circ$C maintained higher COD, ammonia and TU50 values than at $T = 50\,^\circ$C. A COD increase was observed in $T = 80\,^\circ$C samples only for F1. This might suggest that at $T = 80\,^\circ$C most volatile compounds were transferred to the vapour phase during the F1 evaporation step. In samples F3, F4 and F5, the removal efficiency of the evaporation phase could be influenced not only by the evaporation temperature, but also by the evaporation pressure and vapour pressure of volatile compounds.

The best performance for ammonia (Fig. 3B) was always found at $T = 50\,^\circ$C. At $T = 80\,^\circ$C, ammonia was considerably removed from F1 to F2.

There were no big difference in TU50 removal efficiency (Fig. 3C) at F1 for $T = 70\,^\circ$C and $T = 80\,^\circ$C. From F2 to F5, $T = 80\,^\circ$C performed better than $T = 50\,^\circ$C and $T = 70\,^\circ$C. The latter generally showed the worst removal efficiency, similar to that at $T = 50\,^\circ$C for F4. F1 and F5 data are not available for $T = 50\,^\circ$C.

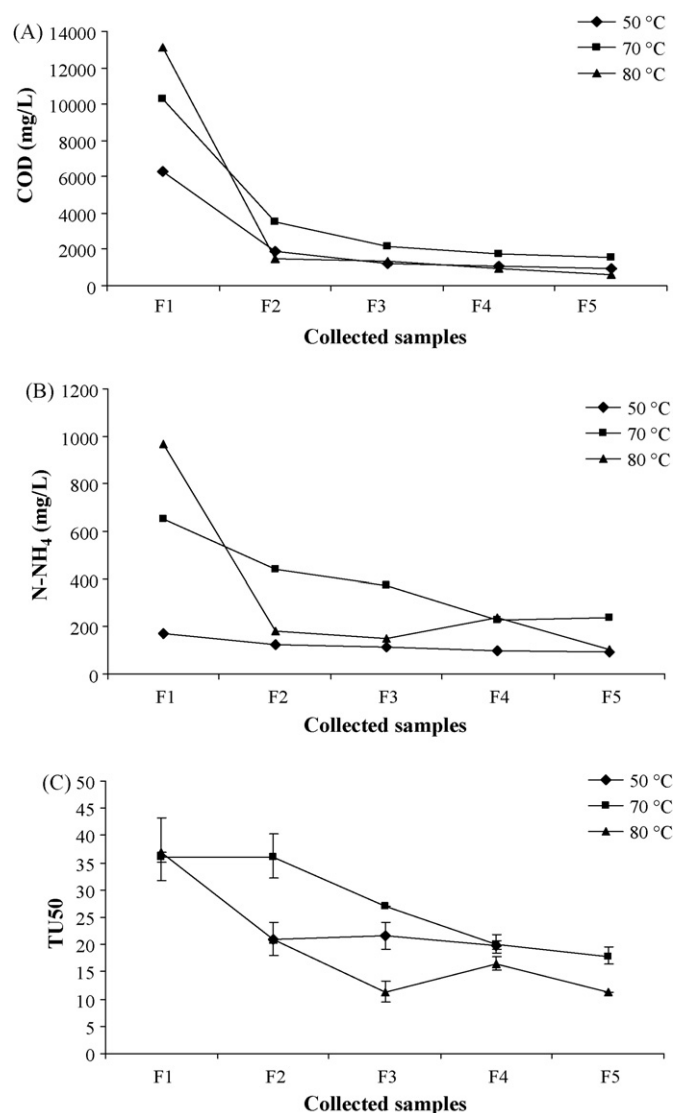Fig. 3. (A) COD (mg O_2/L), (B) N–NH$_4$ (mg/L) and (C) TU50 trends according to different evaporation temperatures ((♦) $T = 50\,^\circ$C, (■) $T = 70\,^\circ$C and (▲) $T = 80\,^\circ$C) for the samples (F1–F5) of oily wastewater after chemical breaking with COD = 14,760 mg O_2/L, N–NH$_4$ = 1190 mg/L, pH 8.2 and TU50 = 70.00.

Increasing efficiency in COD, ammonia and TU50 removal due to operational temperatures and pressures was established as follows, respectively: $70\,^\circ$C $< 50\,^\circ$C $< 80\,^\circ$C (for fractions F4-F5), $70\,^\circ$C $< 80\,^\circ$C $< 50\,^\circ$C (for fractions F4-F5) and

Table 3
COD removal (%) due to the evaporation process (EP), stripping process (SP) and their combination (EP + SP) for an oily wastewater with initial COD = 14,760 mg O_2/L, after chemical breaking

Fractions	50 °C			70 °C			80 °C		
	EP	SP	EP + SP	EP	SP	EP + SP	EP	SP	EP + SP
1	57.2	93.2	97.1	30.3	96.1	96.8	11.3	92.8	93.7
2	87.0	89.6	98.6	76.3	88.5	97.2	90.1	67.8	96.8
3	91.7	84.4	98.7	85.4	82.9	97.4	90.9	63.1	96.7
4	92.8	79.4	98.5	87.9	83.7	98.0	93.8	65.2	97.8
5	93.4	80.6	98.7	89.5	77.2	97.6	95.8	54.8	98.1

Table 4
TU50 reduction (%) due to the evaporation process (EP), stripping process (SP) and their combination (EP + SP) for an oily wastewater with initial TU50 = 70.00 (TU50 = 100/EC50), after chemical breaking

Fractions	50 °C			70 °C			80 °C		
	EP	SP	EP + SP	EP	SP	EP + SP	EP	SP	EP + SP
1	–	–	–	48.4	86.6	93.1	47.1	85.2	92.2
2	70.1	74.5	92.4	48.4	88.2	93.9	70.2	86.5	95.9
3	69.2	86.1	95.7	61.5	86.9	94.9	84.0	74.1	95.8
4	71.6	82.0	94.9	71.4	85.4	95.8	76.4	83.0	96.0
5	–	–	–	73.1	84.2	95.9	84.1	78.0	96.5

(–) Not available.

70 °C < 50 °C < 80 °C (for fractions F3-F4), reaching a maximum COD removal of > 95%, maximum ammonia removal of 92% and maximum TU50 removal of > 84%.

The air-stripping process results are shown in Fig. 4 and summarized as removal efficiencies in Tables 3 and 4, where the
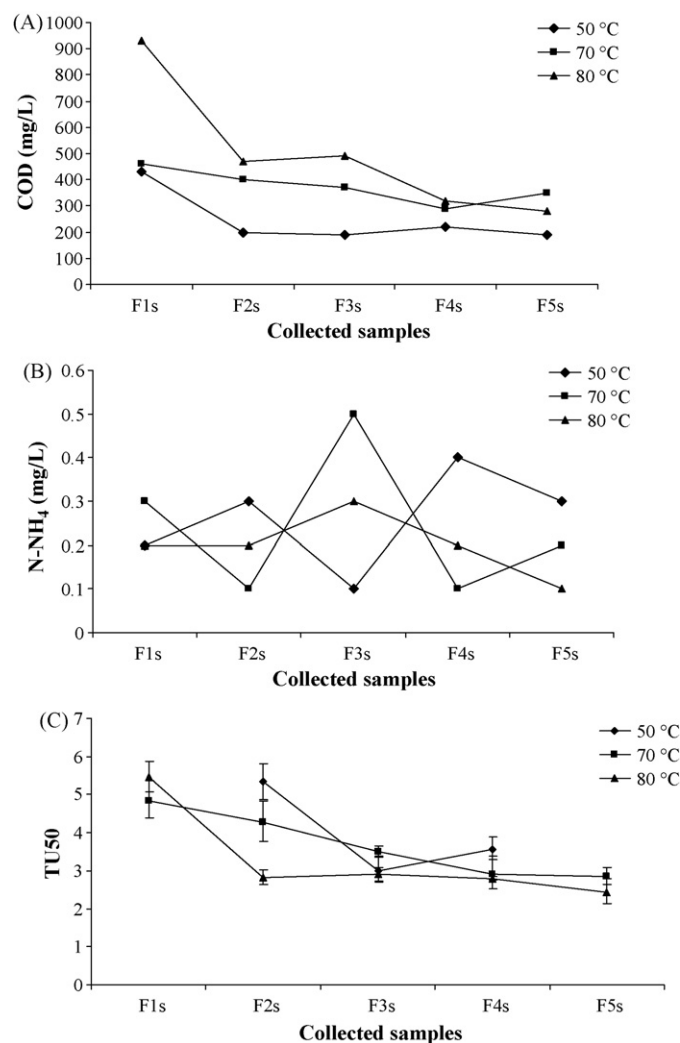

Fig. 4. (A) COD (mg O$_2$/L), (B) N–NH$_4$ (mg/L) and (C) TU50 trends after evaporation and air-stripping at $T = 50$ °C according to samples (F1s–F5s) obtained at different evaporation temperatures (($\blacklozenge$) $T = 50$ °C, ($\blacksquare$) $T = 70$ °C and ($\blacktriangle$) $T = 80$ °C) of oily wastewater after chemical breaking with COD = 14,760 mg O$_2$/L, N–NH$_4$ = 1190 mg/L, pH 8.2 and TU50 = 70.00.

removal efficiency of the coupled evaporation and air-stripping processes is also given.

The air-stripping treatment produced a large reduction in N–NH$_4$ concentration and a noteworthy decrease in COD levels, indicating that oily emulsion condensates were characterised mostly by organic volatile compounds. Further treatments are available for the released gaseous contaminants, such as liquid absorption or thermal oxidation. Residual COD concentrations for F4s-F5s had a range of values between 200 and 350 mg O$_2$/L, so coupled evaporation and stripping processes could have a potentially high COD removal efficiency. Reduction performance in terms of TU50 was always above 90% for all condensate fractions. Coupled evaporation and stripping processes could significantly reduce COD and TU50 by more than 97% (at all temperatures) and 95% (at 70 °C and 80 °C, while for the fourth fraction to a maximum of 95% at 50 °C), respectively.

The results from the full-scale WWTP are reported in Table 5, with further data on biodegradability (BOD$_5$ and BOD$_{20}$), theoretical oxygen demand (ThOD) and ions concentrations. These values refer to a monitoring survey at the plant when the multiple-effect vacuum evaporation was fed in different periods with five oily wastewaters after chemical breaking. Table 5 shows the presence of high concentrations of soluble organic carbon (50–80%), suspended solids, N–NH$_4$ and organic N in the oily wastewater before EP. Multiple-effect vacuum evaporation obtained a high removal efficiency of dissolved salts (>98%) and suspended solids (>99%). The residual concentrations in the condensate samples revealed the presence of liquid drop entrainment phenomena in the WWTP unlike the lab-scale plant. Organic carbon was reduced via the vapour phase to a condensate with a COD range of 1170–1940 mg O$_2$/L (86–94% of COD removal efficiency). There were still considerable concentrations of N-TKN as both ammonia and organic N. This could suggest the presence of non-volatile organic substances as well as volatile ones in the condensates, due to entrainment phenomena. The ratio BOD$_{20}$/COD (0.70–0.83) suggested that this kind of oily wastewater was biodegradable and similar to municipal wastewater (BOD$_{20}$/COD = 0.6–0.9). This is supported by the BOD$_5$/COD ratio (0.37–0.65), which indicated considerable concentrations of rapidly biodegradable compounds [16].

The full-scale WWTP removal/reduction efficiency, reported in Table 6, seemed to confirm the lab-scale plant results, in particular for COD removal (90% average value) and TU50 (54% average value). The removal of ammonia was less efficient, with

Table 5
Oily wastewater characterisation (after chemical breaking) before and after EP in the full-scale WWTP

Parameters	WWTP1		WWTP2		WWTP3		WWTP4		WWTP5	
	Before EP	After EP	Before EP	After EP	Before EP	After EP	Before EP	After EP	Before EP	After EP
pH	10.4	9.37	7.92	9.22	8.47	9.21	9.42	9.60	9.63	9.30
COD_{TOT} (mg O_2/L)	14,830	1690	12,500	1700	10,680	1340	22,000	1940	19,230	1170
COD_{sol} (mg O_2/L)	7910	1520	6730	1630	5920	1210	20,000	1630	15,380	1100
BOD_5 (mg O_2/L)	–	890	–	760	–	590	–	720	–	600
BOD_{20} (mg O_2/L)	–	1320	–	1300	–	940	–	1500	–	890
ThOD (mg O_2/L)	–	1661	–	1336	–	396	–	671	–	383
N–TKN (mg/L)	307	102	288	96	285	53	283	105	221	53
$N\text{-}NH_4$ (mg/L)	114	64	75	65	63	36	126	84	97	41
Organic N (mg/L)	193	38	213	31	222	17	157	21	124	12
SS (mg/L)	2810	<1	6002	<1	1090	<1	18,100	<1	4598	<1
VSS (mg/L)	1938	–	3940	–	660	–	12,505	–	3688	–
Alkalinity (mg/L)	–	467	–	464	–	279	370	497	302	281
Chloride (mg/L)	280	5	305	6	81	3	UR	5	–	6
N–Nitrite (mg/L)	UR	UR	UR	UR	UR	UR	UR	UR	UR	UR
N–Nitrate (mg/L)	1.5	UR	4.4	UR	46	UR	1.9	UR	1.8	UR
SO_4^{2-}–Sulphate (mg/L)	62	2	1431	1	283	5	121	3	67	1
PO_4^{3-}–Phosphate (mg/L)	115	0.1	54	0.1	35	0.2	30	0.1	27	0.1
TU50 (mg/L)	39.06 (37.45–40.65)	29.24 (26.74–32.05)	66.23 (65.36–67.11)	27.55 (25.91–29.24)	–	28.01 (26.95–29.07)	70.42 (68.49–72.46)	22.68 (17.12–30.03)	73.53 (71.94–74.63)	24.63 (23.87–25.38)
MEA (mg/L)	–	82	–	75	–	55	–	41	–	42
DEA (mg/L)	–	ND	–	ND	–	ND	–	ND	–	ND
TEA (mg/L)	–	714	–	547	–	115	–	270	–	127

Microtox® toxicity is reported as TU50 with 95% confidence limits (pH 7); (–) not available; when concentrations were not measurable the detection limits were provided.

Table 6
Removal of COD (%), N–NH4 and TU50 after evaporation in the full-scale WWTP

Samples	% Removal after evaporation		
	COD	N–NH4	TU50
WWTP1	89.4	43.9	25.1
WWTP2	86.4	13.3	58.4
WWTP3	87.5	42.9	–
WWTP4	91.2	33.3	67.8
WWTP5	93.9	57.7	66.5

(–) Not available.

an average value of 38%. It is evident that the condensates contain N-based organic compounds revealed by the concentrations of organic nitrogen in the condensate samples. The presence of entrainment phenomena in the full-scale evaporation plant suggested to hypothesise the presence of MEA, DEA and TEA despite of their relatively low volatile properties [17]. Therefore, after the evaporation phase, the WWTP condensates were also characterised for the presence of MEA, DEA and TEA (Table 5). While no DEA concentration was detected, MEA (41–82 mg/L) and TEA (115–714 mg/L) were found in all wastewater samples. The contribution of MEA and TEA as ThOD in the COD definition appeared to be significant, sometimes more than 90% (ThOD(MEA) = 2.49 mg O_2/ mg MEA; ThDO(TEA) = 2.04 mg O_2/ mg TEA) [18].

In Table 7, TU50s after EP and SP are expressed according to Bulich's [15] modified score for both the lab-scale plant and the full-scale WWTP. In the former, there was a general decreasing trend in wastewater fractions after EP and further SP. TU50 scores showed a general decrease from 5 to 3 or 2, with the lower value being measured at $T = 80\,°C$. In the WWTP, the TU50 of all samples was reduced from 5 to 4 after EP ($T = 50–80\,°C$). A general decreasing toxicity trend was verified in both cases. After the above-mentioned evaporation and stripping procedures, the resulting treated oily wastewater might be discharged into the POTW without compromising the plant performance.

4.2. Toxicity reduction evaluation

For toxicity reduction evaluation, some experimental runs were done in a previous phase on air-stripped oily emulsion condensate samples ($20\,°C$ for 2 h at pH 7) to ascertain the role of ammonia in toxicity definition. Table 8 lists the COD, ammonia concentrations and TU50 values. After SP, the ammonia concentration in samples was reduced by one order of magnitude for both ionised and unionised ammonia, while TU50 (5-min exposure time) did not. There was a low reduction in toxicity effects (average 14%), suggesting that ammonia did not strongly affect sample toxicity. The *Vibrio fischeri* EC50 for ammonia as $N\text{-}NH_4^+$ is 3600 mg/L [19] and as $N\text{-}NH_3$ is 2.00 mg/L [20], or 1.49 mg/L according to Qureshi et al. [19]. Therefore, ammonia contribution to wastewater toxicity could therefore be ignored for both evaporated and air-stripped samples. Further investigations were done via Microtox® in order to determine the EC50 of MEA, DEA and TEA as pure

Table 7
Toxicity data scores from oily wastewater after chemical breaking (W1–W5), from fractions obtained in the lab-scale plant ($T = 50$, 70 and 80 °C) and full-scale WWTP (WWTP1-WWTP5) before and after EP ($T = 50$–80 °C), according to [15] *modified*

Initial wastewater		Pilot plant						WWTP		
		50 °C		70 °C		80 °C		Samples	Before EP	After EP
Samples		EP	SP	EP	SP	EP	SP			
W1	5	–	–	5	3	5	3	WWTP1	5	4
W2	5	4	3	5	3	4	2	WWTP2	5	4
W3	5	4	2	4	3	4	2	WWTP3	–	4
W4	5	4	3	4	2	4	2	WWTP4	5	4
W5	5	–	–	4	2	4	2	WWTP5	5	4

EP = evaporation process (F1–F5); SP = stripping process (F1s–F5s); – = not available.

Table 8
Ionised and unionised ammonia role in TU50 definition for four oily wastewater samples after chemical breaking

	Sample 1		Sample 2		Sample 3		Sample 4	
	BS	AS	BS	AS	BS	AS	BS	AS
$N-NH_4^+$ (mg/L)	214	30	136	16	96	10	79	8
$N-NH_3$ (mg/L)	0.71	0.09	0.45	0.05	0.32	0.03	0.26	0.02
TU50	35.7	29.3	29.8	24.6	27.1	24.1	22.2	20.0
COD (mg O_2/L)	7600	7400	2600	2530	1890	1520	1630	1480

COD values are also reported. BS = before air-stripping and AS = after air-stripping.

Table 9
Microtox® EC50 (mg/L) and relative 95% confidence limits for pure substances (MEA, DEA and TEA) and MEA–TEA mixture (1:6)

Time	Pure substance			Mixture	
	MEA	DEA	TEA	MEA	TEA
5	26.37 (23.24–29.93)	122.13 (116.74–127.76)	547.44 (504.00–594.63)	38.99 (25.18–60.37)	233.95 (151.09–362.16)
15	23.52 (19.51–28.36)	111.17 (106.80–115.72)	504.78 (475.63–535.73)	44.54 (27.17–73.02)	267.25 (163.03–438.10)
30	21.50 (18.60–24.86)	95.51 (90.63–100.66)	425.09 (399.08–452.80)	44.51 (28.40–69.74)	267.06 (170.42–418.45)

Time of exposure is expressed in minutes.

substances and for MEA and TEA as a mixture (1:6 ratio) (Table 9). EC50 data showed an increasing toxicity from TEA to DEA and to MEA (TEA < DEA < MEA), suggesting a possible toxicity dependence on molecules steric bulk. In general, the MEA, DEA and TEA toxicity slightly decreased with increasing contact times (from 5 to 30 min exposure time). The comparison between MEA/TU50 and TEA/TU50 showed that an increase in MEA and TEA concentrations corresponded to an increased toxicity in wastewater samples and a potentially greater problem for the POTW into which the oily wastewater is discharged. MEA showed to be about 20 times more toxic than TEA, while in the mixture, MEA toxicity seemed to be reduced by the presence of TEA and vice versa. The pure substances and MEA and TEA mixture EC50s revealed that they could be responsible for part of the toxicity arising from the studied oily wastewater samples, while the other part might be due to other toxic volatile compounds. Residual toxicities could be tackled by considering further chemical oxidation processes, such as O_3, O_3/H_2O_2 and Fe_2/H_2O_2 or similar [16].

5. Conclusions

This study investigated a procedure for the treatment of oily wastewater posing a serious problem for the aquatic environment. The procedure consisting of a sequence of evaporation and air-stripping processes was tested in a lab-scale plant. The evaporation procedure was also validated in a full-scale WWTP. COD, ammonia and TU50 (via Microtox®) were monitored. After a chemical breaking procedure, oily wastewater was evaporated at three different temperatures ($T = 50$, 70 and 80 °C) and the condensate phases successively stripped at 50 °C. The laboratory results showed a considerable removal efficiency of organic compounds (>97% for COD) and ammonia, plus noteworthy reductions in wastewater toxicity (>95% for TU50). The full-scale WWTP confirmed the performance of multiple-effect vacuum evaporation ($T = 50$–80 °C) in improving oily wastewater quality for both organic and inorganic compounds. Despite the variability of the COD values (12,550–22,000 mg O_2/L), the removal efficiency remained high, as verified in the laboratory. At the same time, TU50 values after evaporation showed

to be comparable with the lab-scale plant results. In addition, the TRE/TIE approach via Microtox® excluded any role of ammonia in the toxicity definition of air-stripped condensates, suggesting that toxicity effects could be partly due to MEA and TEA concentrations. This research also supported the role of bioassay as a practical tool for integrating traditional chemical and physical characterizations in complex wastewater management such as oily wastewater.

Acknowledgment

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