



Challenges in Pretreatment/Treatment of Oil in Water Emulsions for Oil Waste Management in the Context of Sustainable Development

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Abstract: *The purpose of the article is to present practical, technical and ecological challenges in the pretreatment/treatment technologies of spent oil waste that are oil-in-water emulsion systems containing high volumes of water difficult to be temporary stored. A set of experimental tests on representative oil-in-water spent emulsions have been realized based on a set of treatment screening criteria so that any oil-waste producer/holder can use them to find best pretreatment solutions preventing on-site oil waste generation and preserving in the same time depletion of non-renewable natural resources by recovery of valuable components in the context of sustainable development.*

Keywords: *emulsions, oil-in water emulsions, waste oils*

1. Introduction

In the present paper we are focusing on oil/waste containing spent emulsions of oil-in-water type named also “soluble oils” made of mineral oil, additives (emulsifiers, corrosion inhibitors, anti-foaming agents) and water coming from a large class of products used in metal surface processing as lubrication and cooling agents [1]. Basel Convention defines as used oil, liquid or semi-solid products being made totally or partially of 1) mineral oils or synthetic hydrocarbons, 2) oil residues from the oil storage tanks and 3) mixtures of water-oil including the emulsionated ones that are coming from a large range of applications from different industries [2]. Their mismanagement, i.e. their inappropriate discharge in the sewage systems and other places can induce serious negative impacts to environment and human health. The efforts made for their correct evaluation and characterization [3-8] leading to their recovery - reuse, recycling or incineration - can bring important economic, ecologic and social benefits [9]. Waste oils recovery [10] is recognized as especially appropriate for the implementation of circular economy concept [11], intensely promoted in latest years within EU countries and adopted worldwide as a sustainable development strategic approach. This aiming for the creation of close economic models able to minimize the environmental negative impacts generated along the life cycle of the product/service and if it is possible even to bring them to “zero”, transforming waste from one industry in raw materials for another [12 - 13]. Although circular economy is not an easy to implement concept [14 - 15] systematic efforts have been made in Europe for its implementation. In this context, in order to help achieving good management practices, EU Directive 2008/98/CE [16] requires for all hazardous waste including waste oils to be collected separately where this is technically feasible and not hamper their subsequent pretreatment/treatment. The challenges in finding best waste oil pretreatment/treatment technologies for recovery purposes are linked to the large amounts of water and a high variety of additives they contain. The water makes “soluble oils” more susceptible to rust problems, bacterial growth, evaporation losses that is precisely why a variety of different additives are added to control such problems and to increase their useful life [9]. In this respect, a set of technical screening criteria for finding on-site best oil waste pretreatment/treatment technologies should represent a useful management tool for each oil waste producer/holder

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because an increasing use of those additives is reflected in modified characteristics of oil-in-water emulsions. These modified characteristics lead to the “need for selecting a combination of different separation technologies that fulfill stringent legislation norms for reuse of water and also other valuable components” [17] as we will show in this paper.

2. Materials and methods

To fulfill our proposed objective, we performed a set of demonstrative experimental tests with two sample types (S1 and S2) representing spent cutting oil fluids that generally are classified under the code 12 01 09* - machining emulsions and solutions free of halogens. The two primary functionalities of spent cutting oil fluids are lubrication and cooling. They are generally made of: mineral oils (naphthenic or paraffinic), emulsifiers (one or more emulsifiers generally mono- and poly-alkyl amines), anticorrosive agents (glycol or fatty acids). The description and content of the wastes are given in Table 1.

Table 1. Description and content of the waste

Sample Type	Description	Content
S1	- liquid with milky aspect and a pH: 9.5÷10.0; - left without shaking at the room temperature after one week tends to separate an oil phase with a volume up to 1 % of the initial sample volume without sedimented solids.	-mineral oil (petroleum distillates–hydro treated heavy paraffinic components); -additives (mono-ethanol-amines; -R-tert-alkyl amines; -tert-alkanolamines; -ethoxylated amines; -morpholine derivatives; -sodium sulphonates; -ethoxylated polymer; -3 iodoprop-2 yn-1-yl butyl carbamate -polyglycol; -5-chloro-2-methyl-4-isothiazolin-3-one
S2	- liquid with brown dark color, boiling point of 100° C and pH 7÷8; - left without shaking at the room temperature after one week has no tendency to separate an oil phase or solid sediments	-hydro treated naphthenic distillates (petroleum); -hydroxyl ethyl oleamides; -sulphonic acid sodium salts; -amino-ethanol; -2-(2-butoxyethoxy) ethanol;

For a successful on-spot general pretreatment of oily waste for phases separation, it is advisable that any waste oil producer/holder consider some important aspects/criteria before a pretreatment plan should to be set: I) visual aspect (color transparency); II) tendency to separate in gravitational field when left without heating and without shaking and the presence of sediments; III) pH waste; IV) composition from specifications of concentrated “soluble oil” used to prepare the oil in water emulsions that become actually components of the oil waste. To demonstrate how to use these criteria we realized experimental tests presented in Table 2, for the two above-mentioned sample types S1 and S2.

Table 2. Experimental tests conditions

Sample	Experimental tests
S1	<i>Test A</i> temperature modification (50÷60°C) coupled with settling for 2, 4, and 24 h
	<i>Test B</i> pH modification (pH:9.0 ÷10.5 towards final pH: 3÷4) coupled with settling for 2, 4, and 24 h
	<i>Test C</i> temperature and pH modifications coupled with settling for 2, 4, 24 h
	<i>Test D</i> temperature and pH modifications with progressive centrifugation for 10 min followed by settling for 2, 4, 24 h
S2	<i>Test E</i> adding low and high molecular weight substances

The relevant investigated indicators for the water and oil phases and the analytical used methods for their determination are given in Table 3.

**Table 3.** Investigated indicators and analytical methods-equipment

Indicators	Analytical methods-equipment
Water phase	
pH	SR EN ISO 10523:2012 – pH-meter MULTI 9430-WTW
Turbidity	SR EN ISO 7072:2001 – SPECORD 2015 - Analytic Jena
Petroleum Products (PP)	SR7877/1-95; IR SR 7877-2:1995 - FT-IR Spectrum BX Perkin Elmer
Chemical Oxygen Demand (COD)	SR ISO 6060:1996 - Volumetric Method
Dissolved Organic Carbon (DOC)	SR EN 1484 :2006 - Analyzer DOC Analytic Jena Multi N/C 3100
Oil phase	
Water content	SR 13484:2012
Superior Calorific Power (Q _s)	ASTM D240:17 - Parr 6200 Calorimeter Off Systems
Inferior Calorific Power (Q _i)	ASTM D 240:17; PIS 35 by computation
Carbon (C)	ASTM D 5291:16 - Elemental Analyzer FLASH EA 112 Pro Analysis
Hydrogen (H)	ASTM D 5291:16 - Elemental Analyzer FLASH EA 112 Pro Analysis
Azote (N)	ASTM D 5291:16 - Elemental Analyzer FLASH EA 112 Pro Analysis

3. Results and discussions

According to the presented criteria, we have tried to use the simplest ways to test how to increase phase separation for the sample S1 and S2. The results are presented and discussed next.

Test A - sample S1 - temperature modification (heating) and 2, 4, 24 h settling - Heating is known to produce a reduction of viscosity of the oil phase, increasing the mobility and promoting coalescence of particles, and phase separation can be improved if coupled with 2, 4, 24 h settling. However, progressive heating up to 50÷60°C showed irrelevant changes in destroying stability of the tested sample 1 system even if it was coupled with 2, 4, 24 h settling process.

Test B - sample S1 - pH modification and 2, 4, 24 h settling - Progressive change of initial pH from pH_i: 9.0 ÷10.5 towards final pH_f: 3÷4 have been performed in order to note changes in the range of intermediate pH 5÷8. In extreme pH range less than 4 the emulsions regain stability. Although creaming process occurred, the lower layer is still emulsinated enough (still milky). The optimum pH ranges to destroy stability should not go under pH 4 and not over 5 with small variations depending on specific composition of the corresponding used sample.

Test C - sample S1 - progressive heating coupled with pH changes and settling for 2, 4, and 24 hours. Going with pH about 4 we have tried to see if we can obtain a better value for the COD indicator (Chemical Oxygen Demand) – removal of organic substances from the system and to note the importance of hydration/dehydration process of different ions in the system with different radii using only concentrated acids (H₂SO₄, H₃PO₄, HCl). Only the water and oil phases separated after 24 h have been analyzed. Results are presented in Table 4. The efficiency has been computed as 100 x (C_i-C_f /C_i) where C_i is the initial started concentration and C_f is the final concentration.

For the recovered water phase obtained as a result of test C the abatement efficiencies for the relevant investigated indicators were: in the range of 99.2÷99.9% for turbidity and petroleum products and about 90 % for COD and DOC.

For the recovered oil phase obtained as a result of test C, the values of the investigated relevant indicators were pretty close to the characteristics of a diesel type fuel which makes this technological approach suitable for further optimization.

Table 4. Results for the recovered water and oil phase - Test C

Water Phase Sample Name: W1 (from sample type S1)	Recovered water phase indicators from Test C					
	pH _i	pH _f	Turbidity NTU	COD mg/L	DOC mg/L	PP mg/L
W1 ₀ (initial sample S1)	9÷10	9÷10	242100	311040	86700	73253
W1 _{H2SO4 t, s} (heated sample type S1 – treated)	9÷10	3÷4	224	34992	8320	28



with H ₂ SO ₄ conc. followed by settling)						
Efficiency (%)	-	-	<u>99.91</u>	<u>88.75</u>	<u>90.40</u>	<u>99.96</u>
W₁H₃PO₄ t, s (heated sample type S1 – treated with H ₃ PO ₄ conc. followed by settling)	9÷10	3÷4	213	50058	8970	339
Efficiency (%)			<u>99.91</u>	<u>83.91</u>	<u>89.65</u>	<u>99.53</u>
W₁HCL t, s (heated sample type S1 – treated with HCl conc. followed by settling)	9÷10	3÷4	1784	30132	7685	250
Efficiency (%)			<u>99.26</u>	<u>90.31</u>	<u>91.14</u>	<u>99.65</u>
Oil Phase Sample Name O1 (from sample type S1)	Recovered oil phase indicators from Test C					
	Q_s	Q_i	Total	C_{total}	H_{total}	N_{total}
O1_{t, s} (combined oil phases separated by settling from the three above-mentioned - treatments - heated sample type S1 - treated with conc. acids followed by settling)	Humidity					
	Kcal/Kg	Kcal/Kg	%	%	%	%
	<u>8312</u>	<u>7656</u>	<u>21.26</u>	<u>70.83</u>	<u>12.95</u>	<u>0.56</u>

Test D - sample type S1 - progressive heating coupled with pH changes and progressive centrifugation for 10 min at 6000 rpm followed by settling for 2, 4, and 24 h in order to note changes. Using a centrifugation process we have tried to show that with the usual capabilities of an industrial centrifuge used in the oil field for example the results that are presented in Table 5 are pretty similar for water phase indicators to those obtained following a simple settling process presented in Table 4 but not for oil phase which have a much higher water content.

Table 5. Results for the recovered water and oil phase - Test D

Water Phase Sample Name: W2 (from sample type S1)	Recovered water phase indicators from Test D					
	pH_i	pH_f	Turbidity	COD	DOC	PP
			<i>NTU</i>	<i>mg/L</i>	<i>mg/l</i>	<i>mg/L</i>
W2₀ (initial sample S1)	9÷10	9÷10	242100	311040	86700	73253
W2H₂SO₄ t,c (heated sample type S1 – treated with H ₂ SO ₄ conc. followed by centrifugation.)	9÷10	3÷4	121	38800	8250	28
Efficiency (%)	-	-	<u>99.95</u>	<u>87.52</u>	<u>90.48</u>	<u>99.96</u>
W2H₃PO₄ t,c (heated sample type S1 – treated with H ₃ PO ₄ conc. followed by centrifugation)	9÷10	3÷4	196	39852	9020	34
Efficiency (%)			<u>99.91</u>	<u>87.19</u>	<u>89.60</u>	<u>99.95</u>
W2HCL t,c (heated sample type S1 – treated with HCl conc. followed by centrifugation)	9÷10	3÷4	1203	34020	7962	600
Efficiency (%)			<u>99.50</u>	<u>89.06</u>	<u>90.82</u>	<u>99.18</u>

Oil Phase Sample Name: O2 (from sample type S1)	Q_s	Q_i	Total	C_{total}	H_{total}	N_{total}
	Humidity					
O2 t.c (combined oil phases separated by settling from the three above-mentioned treatments - heated sample type S1 - treated with conc. acids followed by centrifugation)	Kcal/Kg	Kcal/Kg	%	%	%	%
	<u>3318</u>	<u>2975</u>	<u>49.62</u>	<u>36.44</u>	<u>8.75</u>	<u>0.55</u>

With the presented pretreatment approaches we concluded that a balance should be made between obtained efficiencies of separation and costs of heating, reagents and certain type of equipment in order to find optimum costs of pretreatment. In this respect we can make some useful practical remarks from the technical point of view. In the case of those emulsions types, efficiency of phases separation will increase each time we will increase a residence time of settling, decrease the pH (see good results from tests A, B, C, and D with optimum pH being in the range of 4÷5) and increase temperature (heating), the latest option being obviously more expensive. Any other option without heating that gives results in the same range should be considered in balance with generated costs. For example, the obtained efficiencies after pH adjustment, heating, and 24 h settling time and after pH adjustment, heating, and 10 min centrifugation are in the same range (see results from Table 4 and Table 5) for water phase but not for oil phase. In this example the investigation of using a more expensive equipment (an industrial centrifuge) should be justified only when large volumes of emulsions should be treated in order to speed up the process. For small volumes to be treated a usual settling equipment will be always preferred to a more expensive centrifugation equipment. For the sample type S2 we have tried to demonstrate how criteria IV - composition – can orient about finding optimum pretreatment/treatment solutions and we realized test E (Table 2). In this test, for phases separation we used small and high molecular weight compounds to produce aggregation through mainly cationic species in the range of almost neutral pH decreasing in the same time the time oh operation. Initial sample type S2 (Figure 1 a)) contains about 11.79% of water with a carbon content of 80.01 % having a superior calorific power Q_s of 8739 kcal/kg. The initial sample type S2 has been treated with small molecular weight coagulants - $FeCl_3$ sol 5 % 150÷200 ppm and $CaCl_2$ sol 5 % 25÷50 ppm and a macromolecular cationic type of polyelectrolyte - sol. 0.2% 25÷50 ppm, used mainly as flocculant [18 - 19] reaching a final pH of 5.5-6.0. The presented test E is a pretreatment/preliminary test. Our intention was just to have a rough orientation about the treatment that should be followed and optimized, therefore the presented obtained results should be regarded only as a rough guidance for future technological optimization. For this preliminary test E, we used a medium charged cationic type polymer because this type of polymer has well known particles aggregation capabilities in the chosen treatment pH range and for the sample type S2 with composition presented in Table 1. The formed floccons characteristics are facilitating both rapid sedimentation and phases separation leading to a clear supernatant and afterwards to a clear filtrate. Good and rapid cake filterability was also obtained for the separated solid phase. In Figure 1 a), b), c), d) are presented the visual modifications of the sample S2 in the proposed pretreatment method marking the emulsion destabilization.

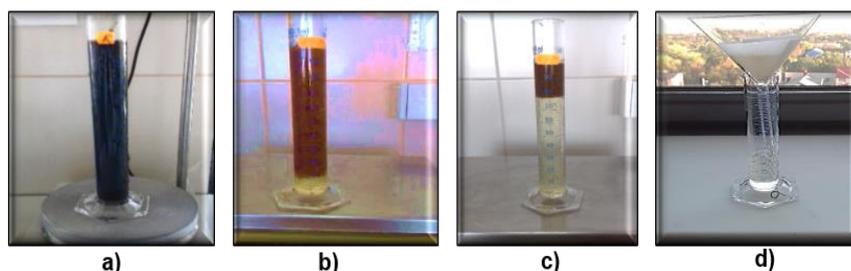


Figure 1. The sample S2 aspect in the phase separation process
a) initial sample; b) coagulated sample; c) sample after 1hour settling;



d) sample filtrated after has been coagulated and left 1 hour for settling

The system changed the color from brown dark to reddish brown and phase separation was immediately (Figure 1 b)). The creaming process after one hour is presented in Figure 1 c). A superior reddish brown layer representing about 20 % in volumes of the initial treated sample was separated. The sample was filtered through a filter paper retaining 2÷3 microns. The filtration process was rapid 100 mL in 10 min and the turbidity for the filtrate reached 6 NTU and a COD of approximately 2200 mg/L (Figure 1 d)). As reference a potable water should have a turbidity < 5 NTU and the quality of water that can be discharged into a surface water should have a COD of 500 mg/L according to Romanian laws [20]. Those techniques supported by good analytical monitoring practices and increased waste management efforts can help protect the environment from pollution [21-24].

4. Conclusions

The purpose of our paper was to offer a set of technical screening criteria I-IV that should be considered when setting on-site pretreatment methods. They are a useful instrument to guide any producer/holder that have oil wastes classified under the code 12.01.09* to manage them on site by applying the principle of treating wastes as close as possible to the generation place avoiding this way the transport of large quantities of liquid hazardous wastes and their associated costs. The benefits of such pretreatment on-site technologies are: on site preventing generation and storage of large volumes of wastes, preserving the depletion of non-renewable natural resources by recovery of valuable oil and water components in the spirit of sustainable development with minimum costs, implementation of circular economy principle stating that wastes from one activity/industry can become raw material substitute for another activity/industry, targeting the “zero” waste approach.

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