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DETERMINATION OF ORGANIC NITROGEN AND PHENOLIC COMPOUNDS IN SOUR WASTERWATER FROM EBULLATED BED HYDROCRACKING UNIT

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Abstract

This project presents the procedure for determination of forty-five organic compounds in sour wastewater. The procedure is based on liquid-liquid extraction followed by gas chromatography. The analytical method with gas chromatography-mass spectrometry was used for identification of composition of the sour wastewaters with origin from ebullated bed hydrocracking unit. The analysis results are of essential for the optimization of H_2S stripper and NH_3 stripper operation and thus saving the environment. Gas chromatography with flame ionization detector was used to detect the complicated composition of the investigated sour wastewater samples. Among a wide range of detected compounds, in the sour wastewater were found alkyl benzamines, alkyl indoles and alkyl phenols.

The developed procedure allows efficient recovery of the investigated compounds ranging between 85 % and 94 % with a relative standard deviation ≤ 4.6 %. These results show the potential of this technique for organic nitrogen and phenolic compounds monitoring in sour wastewaters coming from hydrocracking of vacuum residue.

Keywords: nitrogen organic compounds; phenolic compounds; sour wastewater; liquid extraction; gas chromatography-mass spectrometry.

1. Introduction

Sour water from the ebullated bed residue H-Oil hydrocracking (EBR H-Oil HC) is an investigation challenge mainly because of its unknown contaminant composition and of not well understood matrices. Sour water in the EBR H-Oil HC is generated as a result of washing the reactor downstream streams with deionized water to prevent solid formation from ammonia salts in the equipment. The composition of contaminants in the EBR H-Oil HC seems to vary in a wide range. The type of the contaminants in the sour water depends on the composition of the residue to hydrocrack and of the unit operation conditions [1-3]. The amount of sour water generated in the LUKOIL Neftohim Burgas (LNB) EBR H-Oil HC unit varies between 45 and 50 t/h. This wastewater is stripped to remove H_2S, and NH_3 and then is routed to the refinery central wastewater purification unit. The identification of the type of contaminants from the LNB EBR H-Oil HC wastewater is of high importance to develop measures to minimize releasing of difficult to remove in the biological purification step compounds. The costs for purification of highly contaminated wastewater are dramatically high which is an additional incentive to minimize sour water contaminants level [4].

The relatively high sulfur and nitrogen containing compounds present in crude sources were constituted serious problems for petroleum producers. The order of difficultly of removing the heteroatoms by hydrotreatment process is following S<O<N, so that oxygen and nitrogen are the most difficult heteroatoms to remove [5-7]. Nitrogen and oxygen containing organic compounds tend to exist in the higher boiling oil fractions and residues [8-9] . Average organic

nitrogen content in conventional oil is around 0.1wt %. Moreover, nitrogen organic compounds often possess carcinogenic and mutagenic activities [10-12]. Oxygen containing organic compounds as phenols are widely applied in the chemical industries. Phenol and its derivatives are among the most common organic pollutants because of their toxicity even at low concentrations and that is very serious problem for the environment. The concentration of phenolic compounds in most produced waters fall in the range of 0.36 mg/L to 23 mg/L[13-15]. According to the Environmental Protection Agency phenol content in wastewater must be less than 1 mg/L[16]. Therefore, wastewater containing nitrogen organic and phenolic compounds present a serious discharge problem due to their poor biodegradability, high toxicity and ecological aspects. Hence, determined the nitrogen organic and phenolic compounds in wastewater and sour water are very important and urgent.

In the literature on this subject only, a small number of research papers were developed to the determination of nitrogen organic and phenolic compounds in the petrochemical wastewater. Several studies covering aliphatic, aromatic amines and phenolic compounds determination in the wastewaters and despite their scientific benefits, it is not well suited to extraction from sour water samples [17-30].

The lack of systematic investigation of the LNB EBR H-Oil HC sour water on the specific contamination stimulate us to study this water and perform of identification of the contaminants. In this respect, the development of simple, rapid and reliable analytical methods are required. Nowadays, extraction and concentration of pollutants from wastewater were made with use of liquid-liquid extraction, dispersive liquid-liquid microextraction, solid-phase extraction, headspace solid-phase microextraction and ion-par extraction were frequently employed [18, 20-21, 23-25, 27-28, 30-32]. Gas chromatography with flame ionization detection, gas chromatography coupled to mass spectrometry and high-performance liquid chromatography were traditionally used as the analytical techniques for determining nitrogen organic and phenolic compounds in wastewater samples [17-32].

The approach of studying the LNB EBR H-Oil HC sour water, described in this work, is not included in procedures for regulation of environmental pollution, including monitoring of the contaminants. The aim of this project is to obtain information about the individual contaminants in the EBR H-Oil HC sour water, before the EBR H-Oil HC sour water to mix with other refinery units wastewaters. That is the reason why this investigation is mainly focused on identification and defining the composition of the contaminants in the LNB EBR H-Oil HC sour water by the use of gas chromatography-mass spectrometry.

2. Experimental

2. 1. Reagents

Analytical grade standards of the aniline, indole, and phenol were obtained from Merck (Bulgaria). Dichloromethane was purchased from Merck and was Uvasol grade solvent. Stock solution 500 mg/L was prepared in deionized water and stored in the refrigerator at 6°C. Working solutions were prepared by appropriate dilution of the stock solution using deionized water.

Potassium carbonate, sodium chloride, sodium sulphate anhydrous (5h at 400°C), sodium hydroxide grade p.a. were obtained from Fluka (Germany).

2.2. Object of study

Sour water samples were collected of three different sampling points identified as sour water from cold high pressure separator D1006, labelled as sample1; sour water from cold medium pressure separator D1008, designated as sample 2 and outlet of the installation Stripping technological condensates, labeled as sample 3 in LNB EBR H-Oil HC.

All wastewater samples were collected in pre-cleaned glass bottles. The filtered wastewater samples were divided in half. On one portion of the sample was reached pH 11.0 by the addition of 1.0 *M* sodium hydroxide for nitrogen organic analytes. The other portion of the sample was reached pH 11.0 by adding potassium carbonate for phenolic compounds determined. Samples were stored in the dark at 4°C until analysis.

2.3. Sample preparation procedure

Liquid-liquid extraction was used for the extraction of nitrogen organic and phenolic compounds in sour water samples.

A. Nitrogen organic compounds: 500 mL of sour water sample was placed in a 1 L separating funnel, was added 10 g sodium chloride and extracted two times under automatic mechanical agitation for 5 min. 35 mL of dichloromethane was used for each extraction step. The phases were allowed to separate and the organic layer was filtered through a filter impregnated with dichloromethane and 1 g of sodium sulphate anhydrous. The total extracted volume was 65 mL of dichloromethane.

B. Phenolic compounds: 500 mL of sour water sample was placed in a 1 L separating funnel, was added 10 g sodium chloride and extracted two times under automatic mechanical agitation for 5 min. 35 mL of dichloromethane was used for each extraction step. The phases were allowed to separate and the organic layer was filtered through a filter impregnated with dichloromethane and 1 g of anhydrous sodium sulphate. The total extracted volume was 65 mL of dichloromethane.

Both extracted volumes of dichloromethane were combined and they were concentrated by rotary evaporation to approximately 1 mL. Then the extract was concentrated to 0.2 mL under a stream of nitrogen. Then 1.0 μL of the extract was injected into the apparatus.

2.4. Apparatus and analytical conditions

Capillary gas chromatography-mass spectrometry was carried out using an Agilent Technologies 7890A model gas chromatograph connected to a 5975C Inert XL EI/CI Agilent Technologies mass selective detector (Agilent Technologies, Inc., USA). The system control and data acquisition were controlled by HP G1033A D.05.01 MSD ChemStation Revision E.02.00.493. For identification of contaminants the mass selective detector was operated in the electron impact ionization mode (70 eV) with continuous scan acquisition from 15 to 350 *m/z* at a cycling rate of 1.5 scan/s. The parameters were set up with the electron multiplier at 1660 V, source temperature of 230°C, quadrupole temperature 150°C and transfer line temperature at 250°C.The compounds were identified by means of the NIST MS Search version 2.0 mass spectral library using similarity indices of > 85 %, or by comparison with published mass spectral data for similar compounds.

A capillary column HP PONA 50 length m × 0.2 mm id ×0.5 μm film thickness was used. High purity helium was used as carrier gas at a flow rate of 0.8 mL/min. The injection port was held at 250°C and the injection volume of sample 1 μL of sample. The instrument parameters were as follow: initial oven column temperature of 80 °C, then increased at increments of 6°C/min to 250°C and was kept at final temperature 40 min.

The content of pollutants was investigated by gas chromatography with flame ionization detector. The apparatus was comprised of a Hewlett Packard 5890 Series II GC and flame ionization detector using (Agilent Technologies, Inc., USA). The column (length: 50 m, diameter: 0.20 mm) was a PONA (100 % crosslinked methyl siloxane column: 0.5 μm coating thickness from Agilent J&W). The injector and the detector temperatures were 200°C and 250°C respectively. The oven temperature program was 0 min isothermal at 80ºC and then a 6ºC/min ramp to 250ºC, held for 60 min. Hydrogen (1.4 mL/min) was used as carrier gas. Column inlet pressure and a split ration were 150 kPa and 1:90 respectively. The volume that was injected and analyzed was 1.0 μL. Data acquisition parameters, instrument operation and chromatographic data were collected and recorded by means of Clarity 2.6.

3. Results and Discussion

Increase in solution ionic strength has been found to improve extraction efficiency. Sodium chloride is generally use in this regard. It was found that 10 g salt produced the highest extraction efficiency. This amount was consequently utilized in our study.

In order to examine the effect of reaction time on the extraction procedures, different times of 2, 5, 10, 20 min were tested at room temperature. Other fixed experimental conditions include 35 mL dichloromethane and 10 g sodium chloride. At 5 min, the best response (peak area) was obtained for aniline and phenol compounds while the worst response was for indole. However, the response for all the compounds were improvement compared to other extraction times.

To examine the appropriate of solvent on extraction procedure, two different solvents were tested toluene and dichloromethane. Other fixed experimental conditions include 35 mL dichloromethane and 10 g sodium chloride for the extraction duration of 5 min. It was found that using dichloromethane gives an advantage indicated by the appreciable increase in peak areas of compound analytes.

Base on the above results, the determined procedures were applied in measuring recovery, precision using relative standard deviation and linearity on developed method. The efficiencie of the extraction methods were studied by analysing samples prepared by adding known amounts of nitrogen organic compounds and phenol to the water matrix. The recoveries obtained for the phenol and nitrogen compounds were acceptable (Table 1). Recovers were in the range of 82 % for phenol to 94 % for aniline with a mean total recovery value of 89.7±4.5 %. The result indicated that the extraction procedures give a high recovery with good precision within a shorter time scale. One reason for the good recovery may be that there is no loss of nitrogen containing compounds and phenol because of their low volatility during extraction.

The linearity and linear range of the gas chromatographic method were established using calibration curves obtained via the duplicate analysis of compounds at four concentration levels 0.05, 10, 50 and 100 mg/L. These results were presented in Table 1. The result indicates good linearity by the correlation coefficient R^2 between 0.9965 and 0.9998. Under these conditions, the detection limit (LD) was 0.05 mg/L for phenolic and 0.2 mg/L for nitrogen containing compounds, respectively. LDs were calculated by multiplying the standard deviations of the obtained linear regressions by 3.3 and dividing by the slope of the respective linear regression equation [33]. These results show that developed method can be used for monitoring purposes.

Table 1. Parameters of method validation

Compound	Range mg/L	Intercept *a*	Slope *b*	Correlation coefficient R^2	Relative standard deviation, % (n=5, c=10)	Recovery, %
Phenol	0.05-100	2.18 E^{-04}	26.97	0.9965	1.5	85
Aniline	0.2-100	1.51 E^{-04}	4.73	0.9995	3.4	94
Indole	0.2-100	1.21 E^{-04}	7.57	0.9998	4.6	92

c – concentration level, mg/L

The composition of the sour water samples depends on some factors, such as the type of refining plants connected to the wastewater treatment plant and the management of waste-water treatment processes. The identification of compounds in sour water was based on mass spectral NIST library data, comparison of gas chromatographic retention times with reference standard, calculation of retention index values and comparison with literature same values (Table 2). Exemplary the total ion GC-MS chromatogram was depicted in Figure 1 which presents the distribution of various types of nitrogen and phenolic compounds in sour water in EBR H-Oil HC unit. Figures 2-3 present the GC-MS extracted ion profiles of benzenamines at m/z 93 and m/z 106, of quinoline at m/z 129, and of indoles at m/z 117, m/z 130, m/z 144, m/z 159. The benzenamine and C_1-C_2 alkyl-benzenamines were detected from 9.7 to 15.20 min, and quinolone was detected at 16.2 min, respectively. The indole was detected at 17.1 min and C_1-C_3 alkyl-indoles were detected from 18.6 to 24.0 min. Table 3 was contained a list of nitrogen organic compounds extracted from sour water samples investigated. Twenty-nine nitrogen containing compounds were identified in this study but only 16 of them were determined in all of the samples during the course of this study while the other 13 were below detectable limits. It was apparent that nitrogen organic compounds were dominated by benzenamine, 2-methyl-benzenamine and 3-methyl-benzenamine.

Table 2. Compounds identified in sour wastewater samples

Compounds	RI $_{Cal}$	RI [34-39]	Formula	Characteristic mass fragment ions, m/z
Nitrogen organic compounds				
Benzenamine (aniline)	962	955	C_6H_7N	93, 66, 39
2-Methyl-benzenamine	1065	1054	C_7H_9N	106, 107, 77, 79, 51
3-Methyl-benzenamine	1072	1064	C_7H_9N	106, 107, 79, 77, 39
2,5-Dimethyl-benzenamine	1154	1143	$C_8H_{11}N$	121, 120, 106, 77, 122
3,4-Dimethyl-benzenamine	1182	1196	$C_8H_{11}N$	121, 120, 106, 77, 91
Indoline	1192	1140	C_8H_9N	118, 119, 91, 117, 58
Indole	1247	1248	C_8H_7N	117, 90, 89, 63
6-Methyl-indole	1282	1273	C_9H_9N	131, 130, 77, 132, 103
7-Methyl-indole	1368	1353	C_9H_9N	130, 131, 77, 103, 132
4-Methyl-indole	1388	1390	C_9H_9N	130, 131, 77, 103, 132
2-Methyl-indole	1446	1423	C_9H_9N	130, 131, 77, 103, 51
2,5-Dimethyl-indole	1497	1499	$C_{10}H_{11}N$	144, 145, 130, 143, 115
2,3-Dimethyl-indole	1453	1472	$C_{10}H_{11}N$	144, 145, 130, 143, 77
2,3,5-Trimethyl-indole	1576	1597	$C_{11}H_{13}N$	158, 159, 144, 115, 160
Benzopyridine (quinoline)	1235	1245	C_9H_7N	129, 102, 128, 130, 51
Phenolic compounds				
Phenol	941	954	C_6H_6O	94, 66, 39
2-Methyl-phenol	1002	1024	C_7H_8O	108, 107, 79, 77, 90
3-Methyl-phenol	1014	1057	C_7H_8O	108, 107, 79, 90
2-Ethyl-phenol	1114	1115	$C_8H_{10}O$	107, 122, 77
3-Ethyl-phenol	1121	1130	$C_8H_{10}O$	107, 122, 77
4-Ethyl-phenol	1134	1142	$C_8H_{10}O$	107, 122, 77
2,4- Dimethyl-phenol	1127	1123	$C_8H_{10}O$	107, 122, 121, 77, 91
2,5- Dimethyl-phenol	1126	1125	$C_8H_{10}O$	107, 122, 121, 77, 91
2,3- Dimethyl-phenol	1130	1132	$C_8H_{10}O$	107, 122, 77, 121, 91
2,6- Dimethyl-phenol	1132		$C_8H_{10}O$	
3,4- Dimethyl-phenol	1133		$C_8H_{10}O$	107, 122, 121, 77, 91
3-Isopropylphenol	1209	1207	$C_9H_{12}O$	121, 136, 77, 103, 91
3-n-Propylphenol	1213	1236	$C_9H_{12}O$	107, 108, 136, 77, 121
2,4,6-Trimethyl-phenol	1241	1229	$C_9H_{12}O$	121, 136, 91, 135, 77
2-Ethyl-6-methyl-phenol	1227	1240	$C_9H_{12}O$	121, 136, 77, 91, 39
3,4,5-Trimethyl-phenol	1305	1320	$C_9H_{12}O$	121, 136, 135, 91, 39

RI-retention index

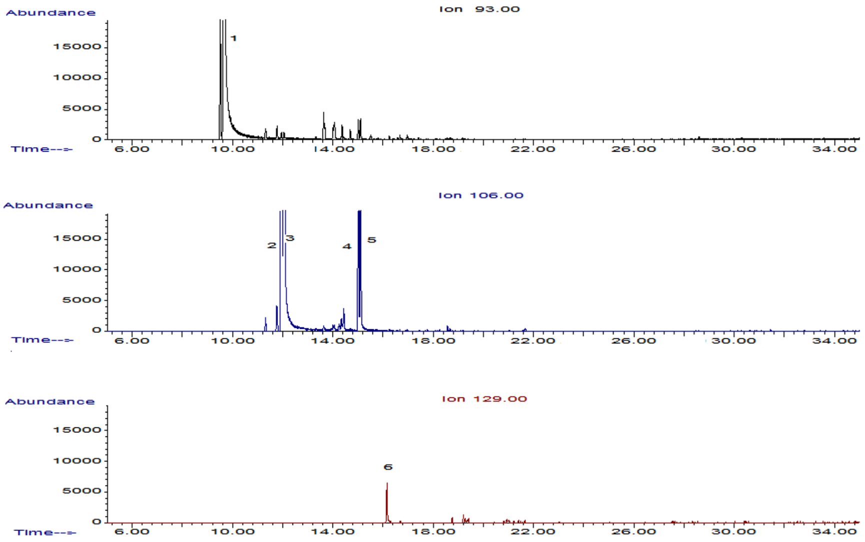

Figure 1. GC-MS extracted ion profiles of benzenamine and alkyl-benzenamines (1-benzenamine; 2-2-methyl-benzenamine; 3-3-methyl-benzenamine; 4-2,5-dimethyl-benzenamine; 5-3,4-dimethyl-benzenamine)

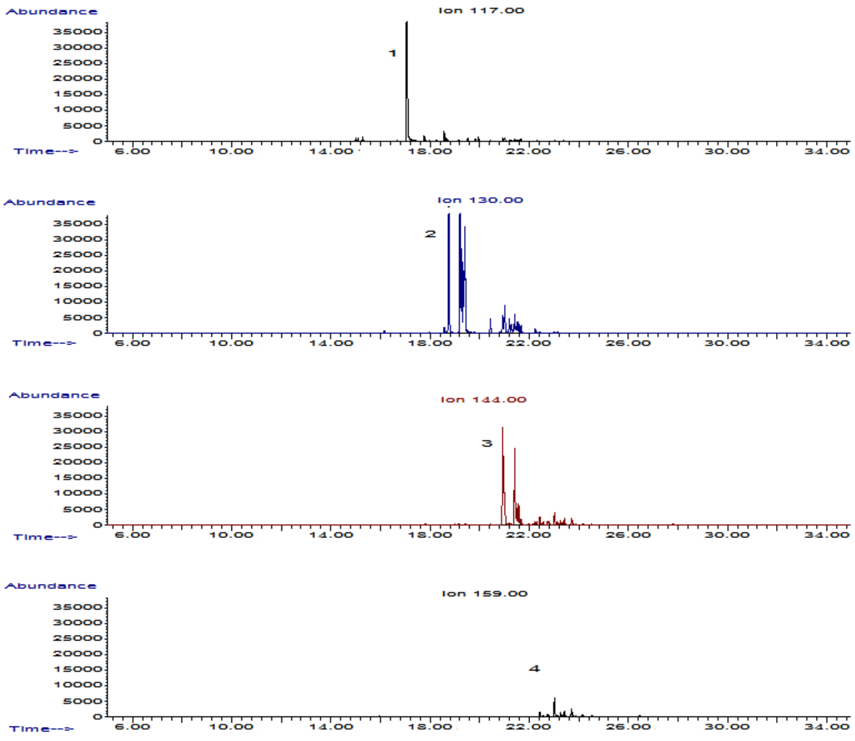

Figure 2. GC-MS extracted ion profiles of indole and C_1-C_3 alkyl-indoles (1-indole; 2-C_1-indoles; 3- C_2-indoles; 4-C_3-indoles)

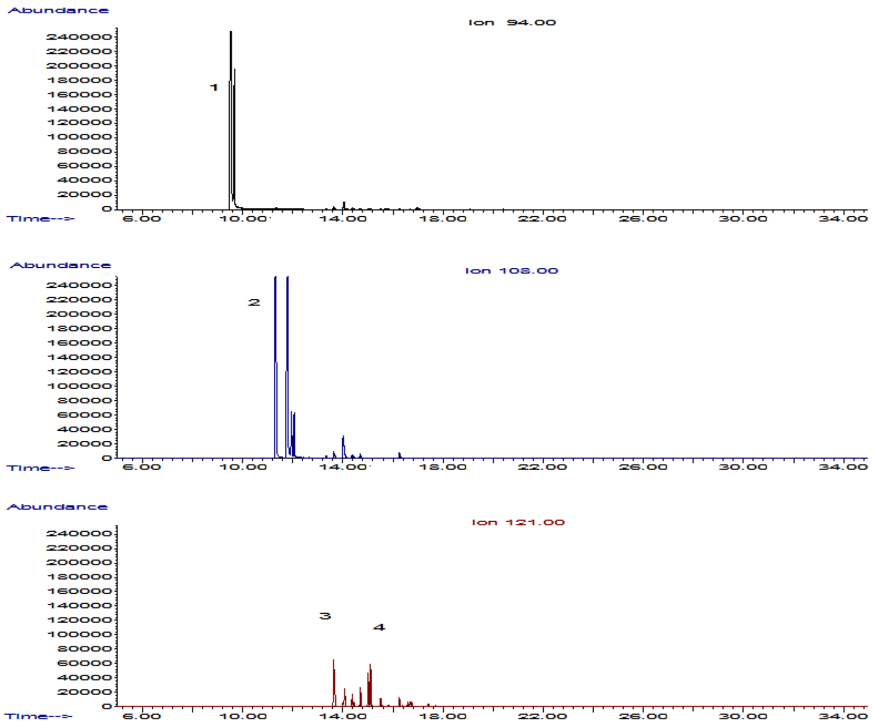

Figure 3. GC-MS extracted ion profiles of phenol and C_1-C_3 alkyl-phenols (1-phenol; 2-C_1-phenols; 3-C_2-phenols; 4- C_3-phenols)

The phenolic compounds in sour waste samples mainly consist of phenol and C_1-C_3 alkyl substituted phenolic compounds. They were identified based on m/z 94, m/z 108 and m/z 121 fragment chromatograms (Figure 3). It can be seen from Table 3 more homologues of phenol with alkyl substituting groups located at the position 2 and 3, such as 2-methyl-phenol, 3-methyl-phenol, 2-ethyl-phenol and 3-ethyl-phenol.

Table 3. Content of nitrogen organic and phenolic compounds of sour wastewater samples

Compounds	Concentration, mg/L		
	Sample 1	Sample 2	Sample 3
	Nitrogen organic compounds		
Benzenamine (aniline)	67	25	58
2-Methyl-benzenamine	41	17	20
3-Methyl-benzenamine	23	11	18
2,5-Dimethyl-benzenamine	2.4	1.7	0.3
3,4-Dimethyl-benzenamine	2.8	1.9	1.7
C_2-benzenamine	5.5	3.6	< 0.2
C_2-benzenamine	10	5.3	1.9
C_2-benzenamine	9.6	5.4	< 0.2
C_2-benzenamine	11	4.2	< 0.2
C_3-benzenamine	2.8	1.6	< 0.2
C_3-benzenamine	1.9	1.3	< 0.2
C_3-benzenamine	1.8	1.2	< 0.2
C_3-benzenamine	15	3.0	< 0.2
Indoline	5.4	< 0.2	< 0.2
Indole	2.7	1.7	2.8
6-Methyl-indole	2.3	0.5	1.9
7-Methyl-indole	3.2	0.6	0.4
4-Methyl-indole	3.3	0.9	0.9
2-Methyl-indole	3.3	1.7	0.5
2,5-Dimethyl-indole	1.6	0.2	0.9
2,3-Dimethyl-indole	4.1	0.5	0.9
C_2-indole	3.0	2.1	0.3
C_2-indole	2.3	0.2	0.7
C_2-indole	2.0	1.0	0.4
2,3,5-Trimethyl-indole	5.3	< 0.2	0.3
C_3-indole	6.2	< 0.2	0.2
C_3-indole	6.0	< 0.2	0.4
C_3-indole	7.2	< 0.2	0.3
Benzopyridine (quinoline)	4.0	< 0.2	0.3
	Phenolic compounds		
Phenol	30	23	32
2-Methyl-phenol	26	13	22
3-Methyl-phenol	26	15	28
2-Ethyl-phenol	1.6	3.4	0.8
3-Ethyl-phenol	1.2	1.1	5.9
4-Ethyl-phenol	2.8	1.6	2.5
2,4- Dimethyl-phenol	2.9	3.1	4.1
2,5- Dimethyl-phenol	2.9	0.8	1.9
2,3- Dimethyl-phenol	1.1	< 0.05	1.9
3,4- Dimethyl-phenol	3.1	1.9	3.5
3-Isopropylphenol	< 0.05	< 0.05	0.4
3-n-Propylphenol	< 0.05	< 0.05	1.1
2,4,6-Trimethyl-phenol	< 0.05	< 0.05	0.6
2-Ethyl-6-methyl-phenol	< 0.05	< 0.05	0.2
3,4,5-Trimethyl-phenol	< 0.05	< 0.05	0.2
C_3-phenol	< 0.05	< 0.05	0.3
Total nitrogen organic compounds content	257.7	91.6	111.1
Total phenolic compounds content	97.6	62.9	105.4

It can be seen from Table 3 that the nitrogen compounds in samples investigated mainly include the homologs of benzenamines and indoles. The concentrations of benzaenamine homologues, which consist of C_1-C_3 alkyl benzenamines, in sour water samples varied between 1.2 and 41 mg/L and below detection limit to 0.2 mg/L, respectively. Sour water sample 1 was recorded higher total benzenamines levels (193.8 mg/L) than water sample 2 (82.2 mg/L) and water sample 3 (99.9 mg/L). Similarly, the levels of indole homologues (C_1-C_3 alkyl indoles) determined in water samples were ranged between 0.3 and 7.2 mg/L and below detection limit to 0.2 mg/L, respectively. The total indoles levels in water sample 1 (61.9 mg/L) was also higher than same in the sample 2 (9.4 mg/L) and sample 3 (11.2 mg/L), respectively.

The levels of phenolic compounds in sour water samples ranges from below detection limit to 32 mg/L, respectively. The total content of phenolic compounds from sample 3 recorded higher total concentration level (105.4 mg/L) than sample 1 (97.6 mg/L) and sample 2 (62.9 mg/L), respectively (Table 3). Both type compounds were regarded as contributors of nitrogen organic and phenolic compounds loadings into wastewater treatment plant. Therefore, these sour wastewater in this study can be regarded as point sources with nitrogen organic and phenolic compounds contamination to the environment.

4. Conclusions

This work describes an analytical method developed and successfully applied for determination of the nitrogen organic and phenolic compounds in the sour waste waters of LNB ebullated bed residue H-Oil hydrocracking unit. All experiments were conducted to characterize the composition of the sour waters, at that forty-five organic compounds were identified and determined in the sour water samples. We were optimized the method for a list of com-pounds belonging to different chemical families, including nitrogen organic compounds and phenols. The developed method was validated using spiked sample and real sour wastewater samples. It was found good recovery (ranging from 85 % and 94%) and method precision ≤ 4.6 %.

The investigations, characterizing the composition of the sour wastewaters from ebullated bed residue H-Oil hydrocracking unit, were not published thus far. The analysis of composition of the sour wastewater allows estimating environmental hazards associated with possible contamination of water. Examination of the nitrogen organic and phenolic compounds content provides information on the pollutants of environmental. The results of investigation were demonstrated the presence of a large number of nitrogen organic and phenolic compounds.

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