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Occurrence of PAHs and PCBs in petrochemical wastewater

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Abstract The contamination status of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) released from petrochemical wastewater plant located in Constanta, Romania, after chemical and biological treatment were investigated. The samples were collected after tertiary biological treatment from two sampling sites: lagoon and tertiary stage effluent. PAHs have been extracted by stir bar adsorption and transferred in the analytical system by thermal desorption (TDS). The used analytical technique was gas chromatography - mass spectrometry (GC-MS). PCBs were concentrated by liquid-liquid extraction and analysed by GC. The quantification of PAHs and PCBs was accomplished to demonstrate that the lagoon (a natural system) has a very important role to decrease the level of pollution in the discharged effluent in the Black Sea due to the macrophytes and microorganisms activity from this lagoon.

Keywords: petrochemical wastewater, PAHs, PCBs, Black Sea.

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1. Introduction

Wastewater treatment plants, especially those serving industrial areas, consistently receive complex mixtures containing a wide variety of organic pollutants [1].

Petroleum refining uses relatively large quantities of water, especially for cooling systems, desalting crude oil, stripping steam, and water used for flushing during maintenance and shut down. In addition, surface water runoff and sanitary wastewaters are accounted in the wastewater system. The quantity of wastewater generated and their characteristics depend on the process configuration. The composition of the wastewater generated from a refinery is very much dependent on the complexity of the process [2].

The current work deals with the characterization of refinery wastewaters located in Navodari area at about 15 km of Constanta city.

Groups of compounds present in the petrochemical wastewaters include polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). The concentration of these pollutants therefore needs to be controlled in treated wastewater effluents.

PAHs and PCBs are two classes of micropollutants intensively monitored and regulated due to their high toxicity, persistency [3] and large distribution [4, 5]. Some of the PAHs are endocrine disrupting chemicals [6] and because of carcinogenic/mutagenic health effects, these chemicals are among the twelve persistent organic pollutants of the Stockholm Convention of 2001 [7]. These compounds are ubiquitous environmental contaminants that are released in the atmosphere as products of the incomplete combustion of almost any fuel that are manufactured widely during the last half century and used for a variety of industrial applications, such as lubricants, dielectric fluids and plasticizers.

To quantitatively evaluate low concentrations of PAHs and PCBs (ng/L) in water samples it was necessary to incorporate an extraction and clean-up step in the analytical procedure prior to gas chromatographic or liquid chromatographic determinations. Among the extraction methods that are widely applied are liquid-liquid extraction (LLE) [8, 9] and solid phase extraction (SPE) [10, 11].

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The implementation of the simultaneously extraction of both investigated groups of compounds [12], solid-phase microextraction [13] and multiwalled carbon nanotubes solid phase extraction [14] has successfully been applied for the analyses of PAHs and PCBs.

In this study PAHs and PCBs were investigated in petrochemical wastewater samples by GC-MS with thermodesorption combined with stir bar sorptive extraction, respectively by LLE followed by GC- µECD.

All petrochemical wastewaters are finally reaching in the Black Sea. The Black Sea has been widely perceived as being heavily contaminated. The major source of pollution is Danube River, which has been considered responsible for about half of the allochthonous material to the Black Sea [15].

For this reason the present study aimed to predict the PAHs and PCBs pollution levels in petrochemical wastewaters before, during and after tertiary biological treatment.

2. Experimental

2.1. Sample collection

Wastewater samples were collected in January, February and March 2008. The samples were collected and stored in pre-cleaned glass container at -4 ^{o}C before filtration and extraction. The target contaminants were measured in samples of petrochemical wastewater treatment plant effluent from lagoon and tertiary stage effluent (**Fig.1**).

Air temperatures were 1, 10 and 5^{0}C, respectively.

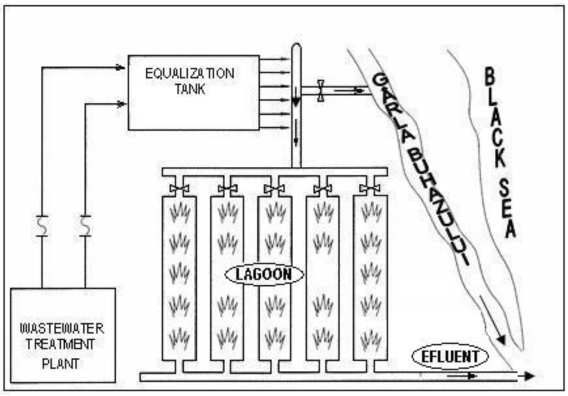

Fig.1. Samples collection points

2.2. Extraction and analyses of PAHs and PCBs in samples

The analytical method used for PAHs was the stir bar sorptive extraction followed by GC-MS with thermodesorption [16]. An aliquot of 25 mL was introduced in a vial of borosilicated glass with sealed cap and then was introduced to the Gerstel twister (10mm coated with 0.5 mm PDMS-polymeric film). The sample prepared in this way was maintained by stirring for 3 hours. At the end of stirring period, the twister was removed, dried well and introduced in the thermodesorption system (TDS).

In order to recover PCBs, a liquid–liquid extraction process was applied to 1 L of water sample with a 60 mL of hexane in three steps. The extract was dried on an anhydrous sodium sulfate column, prior washed with 20 mL of hexane and then the column was washed again with 10 mL of hexane. Both hexane extracts were concentrated to about 15 mL using a rotary evaporator. This extract was concentrated in Kuderna-Danish evaporator up to 5 mL and then cleaned-up using aluminium oxide/silver nitrate chromatography column for the elimination of polar compounds and silica-gel chromatography column to separate PCBs. These columns were washed with 30 mL hexane and then the extract was concentrated using the Kuderna–Danish and blown down with nitrogen up to 0.5 mL.

For PAH analyses an Agilent 6890 N GC equipped with a 5973 Network mass selective detector and a thermodesorption system was used (GC-MS-TDS). An HP–5MS (0.25 mm x 250 µm x 0.25 µm) capillary column was used for separation of these compounds. The GC oven temperature was programmed as follows: 2 min at 40^{o}C and first ramp 10°C/min to 320^{o}C, where is maintained 2 min. Temperature in TDS was scheduled on many ramps: first ramp 0.10 min at 20 ^{0}C, second ramp 0.10 min at 60^{0}C and third ramp 10 min at 300 ^{0}C. The initial temperature of injector (cold injection system) is - 45 ^{0}C where is maintained for 0.40 min. In the moment of injection the temperature has to be 12 ^{0}C for 10 sec and then decreased again to - 45 ^{0}C. Afterwards the temperature increases to 300 ^{0}C, when thermodesorption of compounds takes place. Injection volume was 1.0 µL, and the pulsed splitless time was set at 1.5 min. For each target compound three unique identifier ions were chosen for SIM. Helium was the carrier gas.

Table 1. Quality parameters of the GC-MS-TDS method

No	Compound[a]	m/z	LOD[b] (µg /L)
1	Np	128	0.54
2	Acy	152	0.59
3	Ace	154	0.49
4	F	166	0.066
5	Ph	178	0.06
6	An	178	0.06
7	Fl	202	0.07
8	Py	202	0.06
9	B[α]An	228	0.06
10	Chry	228	0.08
11	B[b]Fl	252	0.06
12	B[k]Fl	252	0.08
13	B[a]Py	252	0.08
14	B[ghi]P	276	0.08
15	B[a,h]An	278	0.08
16	I[1,2,3-cd]Py	276	0.08

[a]Np, naphthalene; Acy, acenaphthylene; Ace, acenaphthene; F, fluorene; Ph, phenanthrene; An, anthracene; Fl, fluoranthene; Py, pyrene; B[a]An, benzo[a]anthracene; Chry, chrysene; B[b]Fl, benzo[b]fluoranthene, B[k]Fl, benzo[k]fluoranthene; B[a]Py, benzo[a]pyrene; B[ghi]P, benzo[ghi]perylene; dB[a,h]An, dibenzo[a,h]anthracene; I[1,2,3-cd]Py, indeno[1,2,3-cd]pyrene.

[b]LOD – limit of detection

Table 1 shows the quality parameters of the method: ratio m/z and the limit of detection (LOD), which was the lowest concentration of PAHs in wastewater samples that was detectable but not necessarily quantified, distinguished from zero (signal/noise).

For PCBs analyses all samples were analyzed with a Agilent 6890 HP gas chromatograph (GC) equipped with an micro-electron capture detector (µECD). The performance characteristics of this method were presented in **Table 2**.

In this paper we consider the use of within-subject coefficient of variation (CV_t) for assessing the reproducibility of measurements. From table 2 was observed a good reproducibility: CV_t values were around 15%, at the limit of acceptability and only in 3 cases the CV_t values were higher than 15% which means that reproducibility is not poor in these cases.

The accuracy of the method was further assessed by recovery studies (standard addition method), each test being performed six times. Satisfactory results were found, with recoveries between 75 and 124% indicating the high accuracy of the proposed method (see **Table 2**).

3. Results and Discussions

Table 3 shows the concentrations of 16 PAHs determined in the wastewater samples collected from lagoon during January, February and March of 2008. From the obtained data it was observed that only naphthalene, acenaphthene and phenanthrene were detected and the values of their concentrations were lower than the limits imposed by the law: naphthalene - 2.4 µg/L, acenaphthene – 0.063 µ/L, phenanthrene -0.03 µg/L (Order 161, 2006).

In March the concentrations values of the detected PAHs were higher than those found in January and February. This fact may be explained by the lower temperatures registered in March and these temperatures can affect the capacity of the reed to retain the organic pollutants.

Table 4 shows that only naphthalene, acenaphthene and phenanthrene were also detected in studied petrochemical wastewater treatment plant effluent after the tertiary treatment stage and the values of their concentrations were slightly lower than those found in wastewater samples. This decrease of the concentrations was higher in March.

Table 2. The performance characteristics of the GC-µECD method

Sample of water	l	n	o %	P ng/L	X ng/L	S_t ng/l	VC_t %	S_R ng/l	VC_R %	R %
PCB 28	13	55	7.3	45.4	41.8	7.3	15	14.0	33.5	92
PCB 52	13	53	0	74.4	86.9	18.3	21	32.7	37.6	116
PCB 101	14	49	0	15.2	19.0	6.6	34	10.9	57.5	124
PCB 138	11	33	9.1	4.3	7.4	1.1	15	3.7	49.5	122
PCB 153	13	52	5.8	136.9	103.6	16.7	15	30.0	28.9	75
PCB 180	15	61	0	217.3	165.2	32.0	20	55.6	33.7	76
PCB 194	11	45	0	72.3	56.0	9.1	15	21.5	38.3	77

l - no. of data sets
n – no. of values
o – percent of wrong results
P – reference concentration
X- found concentration
S_t – standard deviation of repeatability
VC_t – variation coefficient of repeatability
S_R – standard deviation of reproducibility
VC_R – reproducibility coefficient
R – recovery

Table 3. Analytical results for PAHs in lagoon

Compound	**January**	**February**	**March**
	Concentration (µg/L)		
Np	74	79	102.7
Acy	<LOD	<LOD	<LOD
Ace	43	45	98.9
F	<LOD	<LOD	<LOD
Ph	68	71	39.6
An	<LOD	<LOD	<LOD
Fl	<LOD	<LOD	<LOD
Py	<LOD	<LOD	<LOD
B[α]An	<LOD	<LOD	<LOD
Chry	<LOD	<LOD	<LOD
B[b]Fl	<LOD	<LOD	<LOD
B[k]Fl	<LOD	<LOD	<LOD
B[α]Py	<LOD	<LOD	<LOD
I[1,2,3-cd]Py	<LOD	<LOD	<LOD
dB[α,h]An	<LOD	<LOD	<LOD
B[ghi]P	<LOD	<LOD	<LOD
Total	**621.2**		

It can be concluded that the purpose of the lagoon was achieved; even the concentrations of PAHs didn't decreased so much.

Naphthalene is the predominant component present in petrochemical wastewater samples, with the highest concentration 102.7 µg/L detected in March.

Table 4. Analytical results for PAHs in tertiary stage effluent

Compound	**January**	**February**	**March**
	Concentration (µg/L)		
Np	73	76	89.8
Acy	<LOD	<LOD	<LOD
Ace	41	43	53.9
F	<LOD	<LOD	<LOD
Ph	67	69	38.2
An	<LOD	<LOD	<LOD
Fl	<LOD	<LOD	<LOD
Py	<LOD	<LOD	<LOD
B[α]An	<LOD	<LOD	<LOD
Chry	<LOD	<LOD	<LOD
B[b]Fl	<LOD	<LOD	<LOD
B[k]Fl	<LOD	<LOD	<LOD
B[α]Py	<LOD	<LOD	<LOD
I[1,2,3-cd]Py	<LOD	<LOD	<LOD
dB[α,h]An	<LOD	<LOD	<LOD
B[ghi]P	<LOD	<LOD	<LOD
Total	**550.9**		

Table 5. Analytical results of PCBs in petrochemical wastewater treatment plant effluent

Location	**Time of sampling**	**PCB concentration (µg/L)**						
		PCB 28	**PCB 52**	**PCB 101**	**PCB 138**	**PCB 153**	**PCB 180**	**Total**
lagoon	January	1.74	-	2.82	8.24	-	-	12.81
	February	1.68	3.17	4.04	2.86	1.78	2.44	16.00
tertiary stage effluent	January	-	-	-	3.94	-	-	3.94
	February	1.29	-	2.33	-	-	-	3.63

These values (see tables 3 and 4) are lower than those detected in refinery wastewater from Al Ruwais [2].

To predict the PCBs pollution levels in the petrochemical wastewater treatment plant effluent samples, six different polychlorinated biphenyls (PCBs) representing a range of physical– chemical properties (congeners 28, 52, 101, 138, 153 and 180 in order of increasing molecular weight/increasing chlorination/decreasing volatility) were considered for analyses (**Table 5**).

In January, PCB 28, 101 and 138 were detected in wastewater samples and their total concentration was 12.81 µg/L. This value is lower than the imposed limit for PCB in surface waters (0.02 mg/L) [17]. From Table 5 it is observed that in samples collected in January was detected only PCB 138 (3.94 µg/L).

In February all studied PCBs were detected (**Table 5**), but their total concentration (16.00 µg/L) is not higher than those imposed by the law. In petrochemical wastewater effluents in the same month was detected PCB 28 and 101 with total concentration of 3.63µg/L.

It can be observed that the total concentration of PCBs in the effluent samples decrease very much and the number of PCBs decreases also in the tertiary stage. So, it can be concluded that the PCB concentrations decrease in the tertiary lagoon due to the macrophytes and microorganisms activity.

The PCB concentrations detected in the studied petrochemical wastewaters are lower than those encountered in other petrochemical wastewaters (maximum value 67 µg/L) [2].

4. Conclusions

Analysis of PAHs and PCBs released in petrochemical wastewater treatment plant Constanta is of great importance, as it is a discharger to the Black Sea.

The applied methods for separation and determination of PAHs and PCBs from petrochemical wastewater samples are appropriate for the proposed objective.

This study demonstrated that the tertiary lagoon has a very important role to decrease the level of PAHs and PCBs in petrochemical wastewater effluents due to the macrophytes and microorganisms activity.

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