

Determination of Toxic Organic Compounds in Waste Waters

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ABSTRACT

It is known that, phenol and its derivatives are major pollutants that contaminate the water pools. These compounds are discharged into the water basins so, affect their flora and fauna. After the catalytic cracking process of the Oil Refinery Plant in Azerbaijan, waste water is refined and discharged into the sea, however, after the treatment, the phenol and its derivatives remain the same in the waste water, which influence on the water ecosystem. In this article, 3 water samples from different units of catalytic cracking plant at Azerbaijan Oil Refinery were taken and the composition was analyzed. The main purpose of the work was to determine the presence and quantity of toxic substances in waste water after the treatment. In order to achieve accurate results, the composition of the water samples was analyzed by gas chromatographic mass detector. Also organic and inorganic C as well as the total number of N atoms was determined in the water samples taken for analysis and the results are graphically illustrated.

Keywords: *toxic organic compounds, phenol, wastewater, inorganic and organic C atoms and so on.*

INTRODUCTION

In sewage waters of industrial enterprises, the content of phenols can exceed 5-10 g/l in very diverse combinations, while the maximum allowable concentration of phenols in drinking water and fishery reservoirs is 1 µg/l. Phenol concentrations are especially high inside the effluent of coke-chemical plants - up to 20 g/l, while a modern coke-chemical plant discharges up to 4–10 tons of phenol per day into reservoirs. Exceeding the natural background of phenol can serve as an indicator of the water reservoirs pollution. In phenol-contaminated natural waters, their content can reach tens and even hundreds of micrograms in 1 liter [1, 2].

However, according to the experts, the presence of phenols in the air leads to circulatory system diseases. Phenol derivatives are very toxic: nitrophenolic compounds - nitroce (carboniferous phenols), dinitrophenol, etc. These compounds are used as insecticides, fungicides and herbicides [3,4]. Influencing on the oxidative processes in tissues, they cause dissociation of oxidative forcing, which, in turn, enhances the processes of cellular oxidation, increases the oxygen demand of tissues and disrupts heat production

and thermo regulation. In reservoirs, the maximum allowable concentration for phenol is 0.001 mg/l. Thus, the content of phenols in the shallow water areas of the Caspian Sea - one of the most polluted ponds - reached 8 µg/l. The average content of phenols in the water of the Northern Caspian reaches 6 µg/l, and the average value for the waters of this region is 3 µg/l. Phenols are chemically unstable, and undergo active decay in an aqueous medium. The process of self-purification of water from phenols proceeds along the path of biochemical oxidation under the influence of enzymes produced by microorganisms [5–7]. Simple phenols are prone to biochemical oxidation. The destruction of phenols takes place fairly quickly at a concentration of more than 1 mg/l and phenol loss is 50–75% in a three days, however, at a concentration of several tens of micrograms in 1 liter this process slows down and the loss for the same duration is 10–15%. The fastest of all is the destruction of phenol proper, more slower cresols, even slower xylenol. Polyatomic phenols are destroyed mainly through chemical oxidation. The presence of oil pollution slows the decay of phenols, as biodegradation of petroleum hydrocarbons forms its own phenols,

Determination of Toxic Organic Compounds in Waste Waters

increasing the overall picture of contamination [8]. The concentration of phenols in surface waters is subject to seasonal changes. During the summer period, the content of phenols decreases (with increasing temperature, the rate of decay increases)[9–10]. The process of self-purification of reservoirs from phenol proceeds relatively slowly and its traces can be carried away by the flow of the river over long distances, therefore, before discharge, the phenol-containing reservoirs are exposed to sufficient purification [11]. As we already know, in order to get rid of phenolic compounds in wastewater, it is possible to apply the modification of the Klibanov method with the use of peroxidase and talc. Peroxidase degrades phenolic compounds to polyphenols which is insoluble in water[12–14]. When this method is modified, namely when talc is added to the reaction mixture, the insoluble reaction products on the talc are absorbed and precipitated out of the solution. Due to this method, it is possible to completely remove the phenol from the solution, as well as to remove the reaction products. Initially, polyvinylpyrrolidone was used to remove phenolic compounds. In connection with the relative cheapness talc is being used [15–17].

EXPERIMENTAL PART

We used mass spectroscopy for the analytical determination of contaminated water taken from an oil refinery. Our goal was to determine mainly the phenol in the samples. Dichloroethane for (GC-MS) was used for water extraction. After that, phenol was determined on

ANALYSIS OF RESULTS

Below, mass chromatography of these samples were carried out:(Fig. 1,2,3)

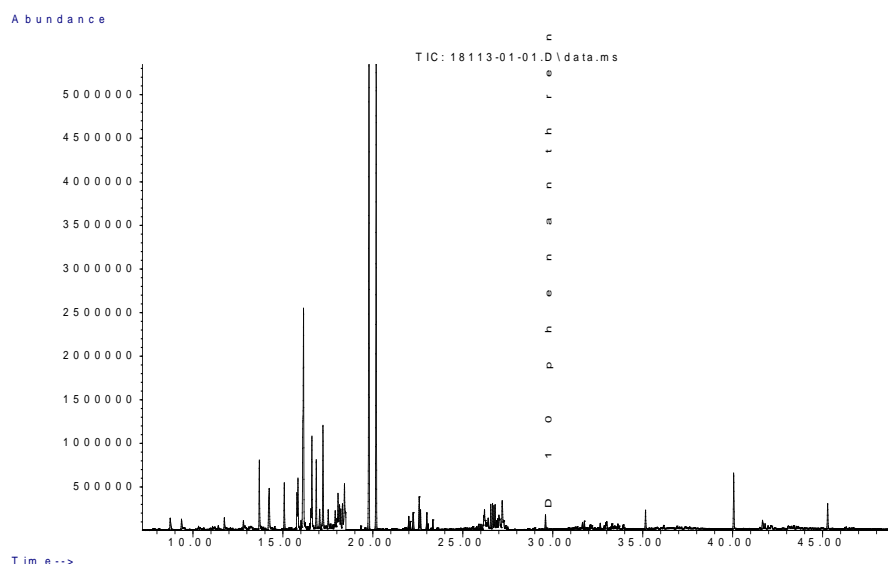


Fig1. Mass chromatography of wastewater -1.

samples 1,2,3. For more accurate analysis, mass chromatography was carried out. The amount of phenol was determined by mass chromatography, and outweighed the MPC (Table 1). Water samples were extracted into a separatory funnel. Before the extraction, the hydrogen index of the samples was reduced to pH <4. Methylene chloride was used as solvent. To prevent contamination of the extracts, samples were analyzed using a dichloromethane solvent (Rathburn, Scotland) with chromatographic purity[18–20]. As internal standard, two deuterated polycyclic aromatic compounds, naphthalene-d8 and phenanthrene-d10 (Cambridge Isotope Laboratories, Inc., Andover, USA) were added to all samples. Extraction was carried out three times. The obtained extracts were combined in round-bottomed flasks and concentrated firstly on a rotary evaporator at a water bath temperature of $35 \pm 5^\circ\text{C}$ to a volume of 5 ml, then under a thin stream of nitrogen. Concentrated extracts were transferred to samplers in a volume of 1 ml. A chemical analysis of water samples was carried out on a GC-MSD gas chromatograph 6890N with a highly efficient mass-selective detector-Agilent 5975 from Agilent Technologies (USA). During the analysis of the samples, solvents were used with a chromatographic level of purity.

Injector temperature	270°C
The volume of the sample	1µl (manual or automatic injection)
Gas carrier	Helium
Temperature of reservoirs	230°C.

Determination of Toxic Organic Compounds in Waste Waters

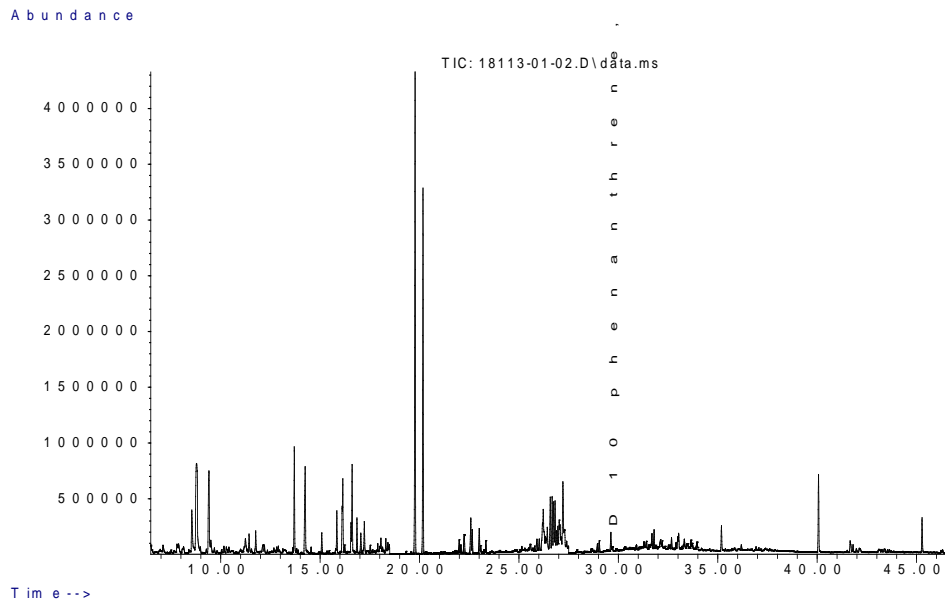


Fig2. Mass chromatography of wastewater- 2.

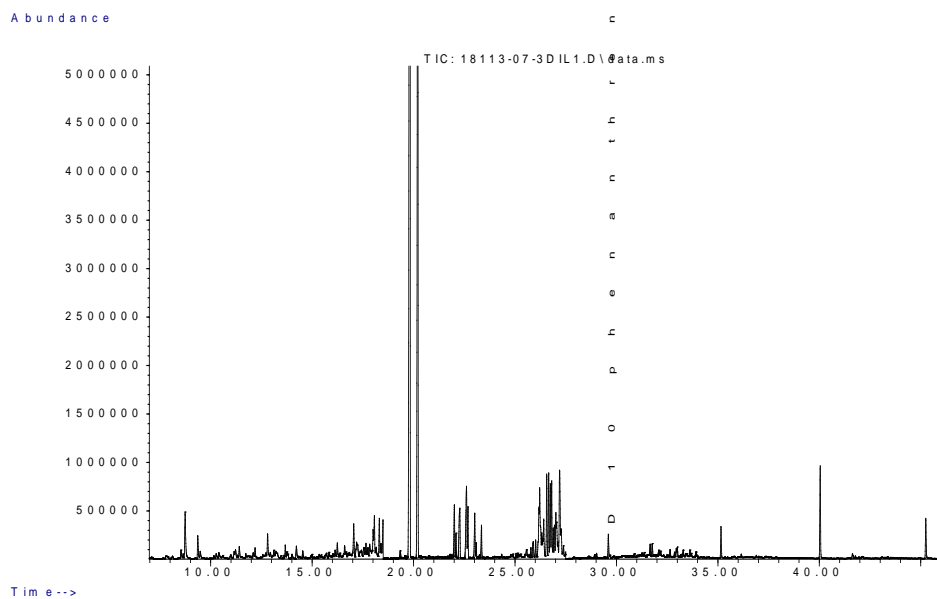


Fig3. Mass chromatography of wastewater -3.

Also the total number of inorganic and organic C atoms and N atoms in the water samples- 1,2,3 is found (table 2).The curves in the graph below are shown:(Fig. 4,5,6).

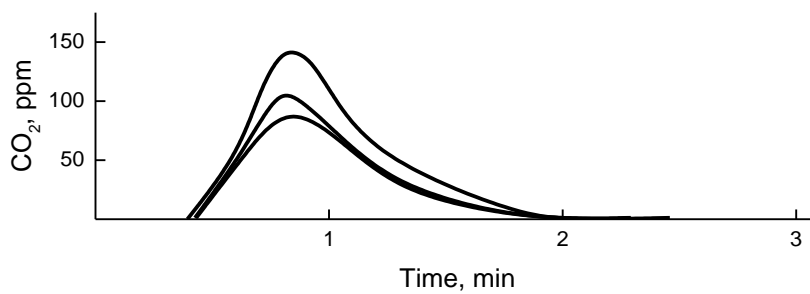


Fig4. Dependence of concentration of inorganic C atoms from time.

Determination of Toxic Organic Compounds in Waste Waters

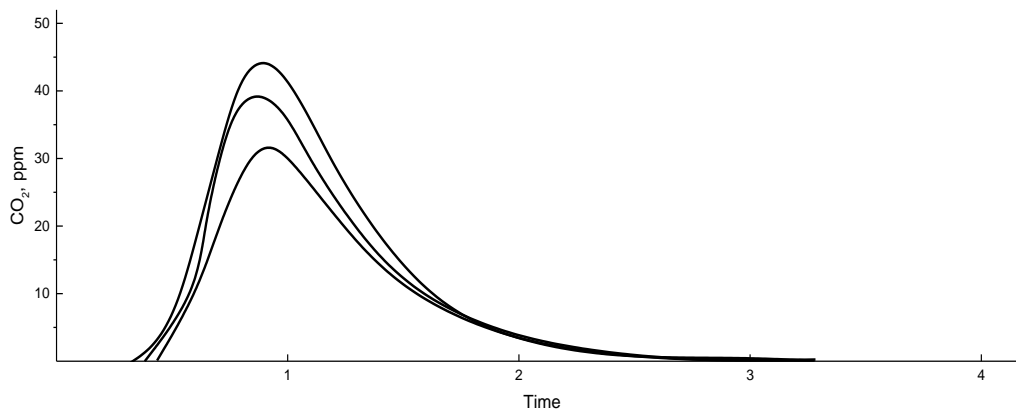


Fig5. Dependence of concentration of organic C atoms from time.

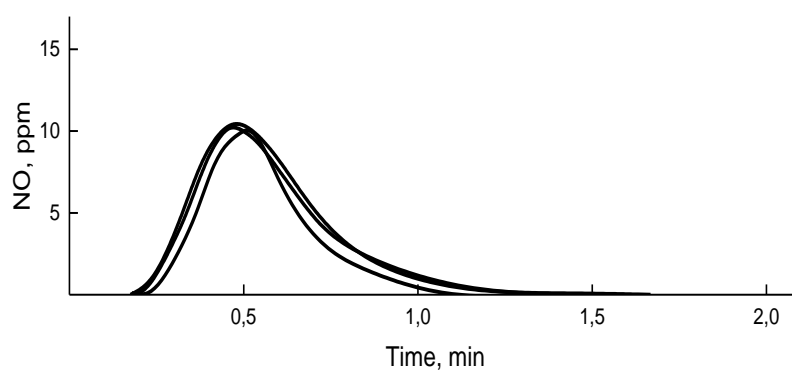


Fig6. Dependence of concentration of N atoms from time.

Table1. The amount of phenol in the samples taken from the refinery

Determinable substances	1	2	3
Phenol, mkq/l	5.33	5.66	1.45
o-cresol, mkq/l	0.76	0.26	0.16
2-nitrophenol, mkq/l	0.59	0.48	0.08
2,4-dimethylphenol, mkq/l	31.99	8.71	0.20
m,p-cresol, mkq/l	20.59	3.81	0.85
2,6-dichlorphenol, mkq/l	1.14	0.67	1.80
4-chloro-3-methylphenol, mkq/l	0.63	0.43	0.69
2,4,5-TCP, mkq/l	0.48	0.28	0.18
2,4,6-TCP, mkq/l	0.14	0.04	0.25
2,3,4,6-tetrachlorophenol, mkq/l	0.27	0.18	0.002
2-methyl-4,6-dinitrophenol, mkq/l	<0.04	<0.04	<0.04
pentachlorphenol, mkq/l	0.27	0.25	0.06
2-sec-Butyl-4,6-dinitrophenol (Dinoseb), mkq/l	<0.08	<0.08	<0.08
TotalPhenols	62.19	20.77	5.722

Table2. Total number of inorganic (IC) and organic (TOC) C and N (TN) atoms in the water samples

	c	I _{eff}
TOC	15.10 mg/l	
IC	27.61 mg/l	3961
TC	42.70 mg/l	6989
TN	53.81 mg/l	629.1

At concentrations of 75 mg/l phenol inhibits the biological purification process in the pond; at a concentration of 0.01–0.1 mg/l, an unpleasant taste appears in the meat of fish; the unpleasant taste and smell of water disappear only when the phenol is diluted to a 0.1mg/l concentration. In surface waters, phenols can be in a dissolved state in the form of phenols, phenolate ions and free phenols. Phenols in water can enter condensation and polymerization reactions, forming complex humus-like and other fairly stable compounds) [21].

As can be seen from Table 1, the quantity of taken phenols increases: 1.45–5.33–5.66 75 mg/l. The amount of phenol increases at the samples 1 and 2, since these contaminated waters were taken from the initial stage of the cracking process at the refinery. The amount of phenol at the total yield was 1.45 mg/l; as we see in the third trial, the amount of toxic substance decreases due to dilution. Such contaminated water must be cleaned, and after the flow of water can be poured into water resources. The maximum permissible concentration (MPC) of phenol should not exceed 0.1 mg/l in water resources, and in other case, it is already a serious reason for the flora and fauna of water resources [22].

CONCLUSION

In conclusion, we can say that phenol and phenolic derivatives were calculated in the analyzed samples, and in the future we will examine effective and new ways of purifying phenol from polluted waters that are released into water resources. In the future, methods of cleaning using nanoparticles will be considered.

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Determination of Toxic Organic Compounds in Waste Waters

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