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Evaluation of Organic Compounds Pollution in Wastewater of Petrochemical Industries

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ABSTRACT

The samples were taken to the laboratory for the chemical analysis every day. They were kept inside the bottles until the time of measurement. The research was done in autumn 2009 on the wastewater of the different units of Abadan petrochemical industries in Khozestan. Abadan Petrochemical Industries Produces Ethylene, Propylene, Ethylene dichloride, polyvinyl chloride, Vinyl chloride, Dodecyl Benzene. The reason for this research was that wastewater of these industries, after treatment, pours into Arvand River, and the end destination is Persian Gulf. Sampling from the sewerage outlets in different units of this complex were done on the working days in autumn 2009 in 9 stations during 9weeks. The pollutants of benzene, VC, EDC, DDB, PVC. Phenol, Propylene, Ethylene and PTM were identified in these samples.

Keywords: Organic compounds, GC/MS, HPLC, Wastewater, Petrochemical Industries

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INTRODUCTION

Contrary to the techniques of supplying water, treatment of wastewater has a short history. About one hundred years ago the relationships between disease causing bacteria and microbes was discovered [1].

Human being started thinking about the treatment of the polluted water. Considering the development of cities and the population explosion and the expansion of industries, the importance of environment pollution control gets higher day to day [2]. Wastewater is one of the pollutants of the environment which should be by sanitization methods collected and treated. They should return to the nature afterwards [3]. The disposal of the waste had been a serious problem and its treatment was very important because of public health matters and environment issues. Untreated sewerage contains physical, chemical and microbial pollutant which if they enter the water sources will produce several problems [4]. The sewerage produced from different sources like domestic wastewater, and industrial waste has an unbelievable variety of pollutants [5]. The most important difference between industrial sewerage with domestic sewerage is the possibility of toxic chemical compounds like aromatic hydrocarbons, chlorinate phosphorous organic compounds, Polycyclic Aromatic Hydrocarbons(PAH) which can be found more easily in industrial waste [6]. These compounds often are corrosive and high acidity or alkalinity. If the raw sewerage gets replete, decomposition of the organic compound may cause a lot of bad smelling gases [7]. The suspended materials such as fat, oil and chromatic materials through forming a thin layer over the surface of water, apart from giving a bad looking to the water can use up the oxygen in water and can hinder photosynthesis in the water [8]. Although the use of these materials in different branches will cause economic growth, the studies and experiences have shown that there are many negative effects in this relation [9]. Some of these effects are short and some others are long time. The short time effects are usually severe, but the long time effects, especially toxicity, bioaccumulation and carcinogenic, and mutagenic related. Considering, water for different uses has specific standards, decrease of pollutant to the favorite level needs some costly and specific methods [10].

MATERIALS AND METHODS

The Areas under study

The Abadan petrochemical industry situated in the city of Abadan and its geographical coordinate is 30°, 20′, 21″ North and 48°, 18′, 15″ East. Abadan is a city of Khuzestan province, in Iran. Khuzestan province is one of the 31 provinces of Iran. It's southwest of the country, bordering Iraq's Basra. Province and the Persian Gulf. It's capital is Ahwaz and covers an area of 63.238 $Km^{2.}$ It lies on Abadan island (68 km / 42 miles long, 3-19 Km or 2-12 miles wide). The island is bounded in the west by the Arvand water way and to the east by the bahmanshir out let of the Karun river, 53 Km(33 miles) from the Persian Gulf. The river Karun is navigable all the way to Ahwaz (above which, its flows through rapids).

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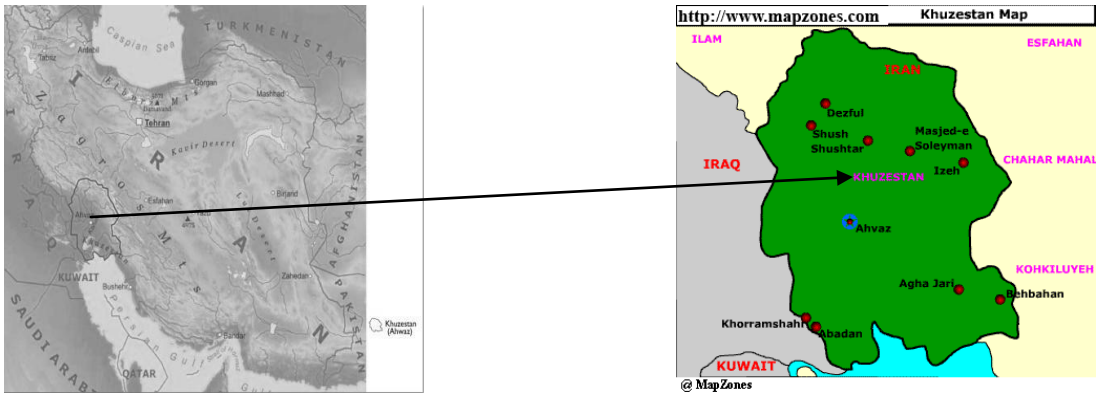

Fig.1 Iran and Khuzestan province map

Sampling Technique

Sampling from different wastewater outlets of the different unites of this complex was done on the working days in autumn 2009 in 9 stations and during 9 weeks (table 1, 2). During each day instant sampling was done every two hours since 8:00am till 8:00pm. In this way 7 samples were taken daily and during and week 49 samples, and during 9 weeks 441 samples were taken. The samples were taken from the sewerage with a stable current, and because the entering sewerage had a higher temperature, compared with the sewerage in the store, it was tried that all the samples were taken under the same condition. The samples were taken to the laboratory for the chemical analysis every day. They were kept inside the bottles until the time of measurement. After preparation with through standard laboratory and instrumental methods, the pollutant parameters in them were analyzed from the view point of quality and quantity. Essential and technical information of this industry was obtain and pollutants were identified for the determination of organic compounds, the samples of wastewater were collected from 9 stations each sample was collected in 1-L glass bottles pre-rinsed with acetone and then with hexane. 1ml of $Hgcl_2$ 1% was added to the samples for preservation. Collected samples were stored in pure polyethylene vials for analysis. The samples were stored at approximately 3-4˚c in refrigerator before analysis and away from light.

Table 1.Name and number of the station

Number	Names
1	Biological Treatment unit
2	Administration wastewater
3	Domestic wastewater
4	Alkaly chlorine unit
5	Ethylen&Propylen unit
6	EDC
7	Vinil chloride
8	Pvc unit
9	Dodecyl benzene

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Table 2.The order of sampling at the determined stations

Day	Number	No	No	No	No	No	No	No	No
Saturday	1	8	6	4	2	9	7	5	3
Sunday	2	9	7	5	3	1	8	6	4
Monday	3	1	8	6	4	2	9	7	5
Tuesday	4	2	9	7	5	3	1	8	6
Wednesday	5	3	1	8	6	4	2	9	7
Thursday	6	4	2	9	7	5	3	1	8
Friday	7	5	3	1	8	6	4	2	9
Number of week	1^{st}	2^{nd}	3^{rd}	4^{th}	5^{th}	6^{th}	7^{th}	8^{th}	9^{th}

Analytical methods

The reference method that was followed is based on EPA reference 508. Wastewater sample of 500 ml was transferred in a separatory funnel of 1L. Five grams of Nacl were added and the funnel was shaken to completely dissolve Nacl [11]. Then 50 ml of CH_2Cl_2 were added and the funnel was shaken vigorously for 3-5 min with periodic venting to release excess pressure. The separatory funnel was then kept undisturbed to separate the two layers i.e. the organic phase was allowed to separate the water phase for a minimum of 10 min [12]. The lower aqueous layer was redrawn into separatory funnel. The process of partitioning was repeated two more times using fresh 50 ml dichloromethane. The organic phase was then collected and transferred in a spherical flask of 250 ml [13]. The extracts were dried by 5g of anhydrous Na_2So_4 were added in the extract in the flask. The flask was stirred and then was left to sit for 20 minutes [14]. The CH_2Cl_2 was filtered into another flask. The remaining sodium sulfate was rinsed gradually with 25 ml of CH_2Cl_2 and the rinses were transferred in the flask. The sample was then evaporated to 1ml using a rotary evaporator [15]. 10 ml of n-hexane (Merck) were added and then the extract was again evaporated to 1 ml. The measurement concentration of organic compounds was conducted by instrumental methods of GC (Gas chromatograph), 3800 Cp, Varian, MS (Mass spectrometer) 2200 saturn, varian, USA. The carrier gas was nitrogen at a flow of 20 ml/min.

The injector was set at 260°c. calibration was based on area given using external standards.[16] Injection of the aliquots were made by micro syringe into the GC. The identification of the suspected organic compounds was carried out in relation to the retention time of pure analytical standard. Quantification was made with a freshly prepared standard curve of the relevant (standard) organic compounds [17]. Another measurements were conducted by HPLC (high performance liquid chromatography) technique. The mobile phase was water/methanol (30/70) and water/acetonitrile (30/70), column: C_{18}, Detector: uv-visible, agilent 1200, us. All standard and sample solutions were prepared with deionized triplet distilled water obtained by aquamax ultra 370, young lin Instrument co, Korea.[18] And another pollutants is measured by these methods : vinyl chloride : GC, shimadzu 14A by injection 120 cc, isothermal condition at 50°c, detector 150. EDC, Benzene : chrompack 9001 cp. Compressed column of carbo borax 600 and temperature conditions from 50°c to 65°c with increasing temperature 0.7°c/min, by injection 170 cc, detector 170 phenol : 4-amino anti pyrine with spectrophotometer device made in HACH model DR/2400 at λ=460 nm [19].

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Table 3.Station number 6

Pollutant	Formulation	Concentration
Benzene	C_6H_6	0.00
DDB	C_6H_5-$C_{12}H_{25}$	0.00
EDC	$C_2H_2Cl_2$	956
PVC	$(-C_2H_3Cl-)_n$	0.02
VC	C_2H_3Cl	0.03
Propylen	C_3H_6	0.03
Phenol	C_6H_5OH	0.06
Ethylene	C_2H_4	0.08
PTM	C_7H_{14}	0.01

RESULTS AND DISCUSSION

In order to study types of organic compounds are studied separately in 9 stations; The data of the measured amounts of the pollutants of the wastewater show that benzene was observed only in the station number 9. The highest amount of ethylene dichloride (EDC) was observed in the station No 6 and the lowest amount in the station No 5 [20]. Meanwhile, there was no EDC in the station NO 2, 3, 7 and 8. Phenol was not observed in the stations No 1, 2, 3 and 8, and its maximum was in the station No 9, minimum was in the statin No 5, and the highest amount of it after No 9 was observed in the stations No 6,7 and 4 accordingly [21]. The stations No 1, 2, 3, 5 and 9 lack pollutant vinyl chloride and the maximum amount was reported in the station No 7, minimum amount was in the station No 4. The highest amount was reported in the station No 6 and 7 accordingly (Fig 2,3);[22] considering the measured amount of the pollutants we can observe that because of the lack of any organic pollutant in the wastewater of station No 2, the station had least amount of pollution and then the station No 1 and 8 and 3 with a pollutant parameter has the next rating [23]. The stations No 4 and 6 with three kind of pollutant have the highest abundance percentage. The station No 9 with No 2 max pollution of benzene and phenol is standing at the next level. The station No 5 and 7 with only two kinds of pollutants in the outlet wastewater can be classified after the above mentioned stations [24]. In a general comparison among the pollutants phenol has the highest abundance percentage and benzene has the least amount in the outlet sewerage. The lightest wastewater in the selected stations was related to No 2 and 3, and the heaviest was related to 4 and 6 [25].

Also the data of the measured amounts of the pollutant of the wastewater show that DDB was observed only in the station numbers 9 and 5. The highest amount in the station 9 and the lowest amount in the station 5. And the maximum amount of PVC in the station 7 and the minimum amount that in the station 6 was observed. Also the highest amount of PTM in the station 5 was observed and the lowest concentration that in the station 6[26]. The maximum amount of Ethylene was observed in the station 5 and the minimum concentration in the station 8. And the end of the highest amount of propylene was observed in the station 5 and the lowest concentration that in the station 4. There was no DDB in the stations 1,2,3,4,6,7 and 8. Also there was no PVC in the stations 1,2,3,4,5 and 9. And there was no PTM in the stations

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2,3,4,7,8 and 9. Also there was no Ethylene in the stations 2,3 and 9. And the end of there was no propylene in the stations 2,3,7,8 and 9 [27].

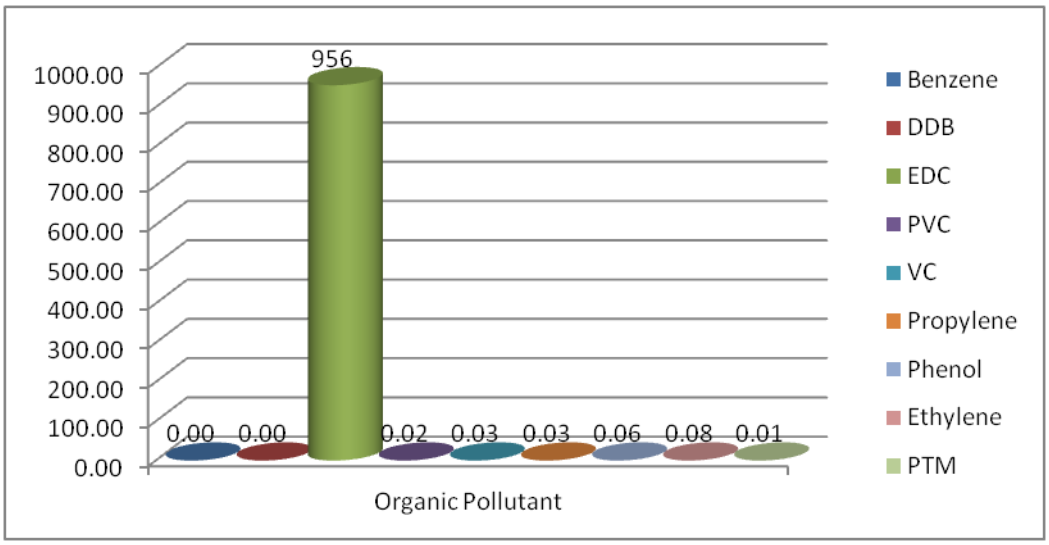

Fig:2 , The diagrams of organic pollutant's in selected station no.6

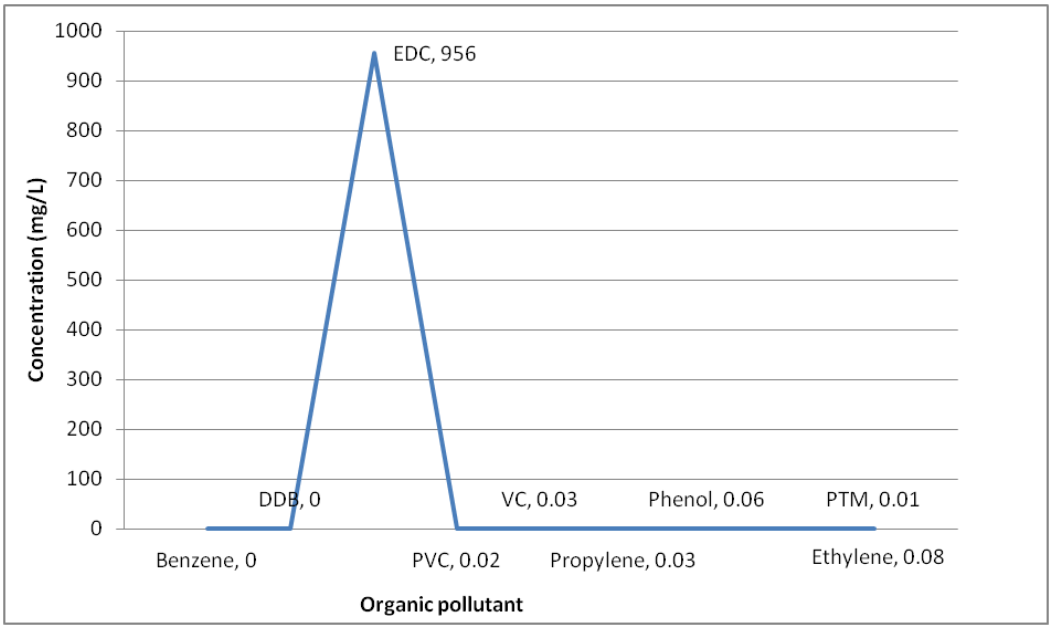

Fig:3 ,The diagrams of organic pollutant's in selected station no.6

Table 4.the international standard amounts of organic pollutants based on EPA (Environmental Protection Agency)

Type of pollutant	Benzene	DDB	EDC	PVC	VC	Propylene	Phenol	Ethylene	PTM
Maximum allowed level(mg/L)	700	-	0.100	0.010	0.050	0.500	1	0.500	-

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CONCLUSION

The amounts of standard of some of the pollutants which was studied in relation to the quality of the wastewater according to the standard of EPA it is according to the before table (table4).considering the measured concentration of the above mentioned pollutants is related to the sewerage of all the units or the selected ones before entry to the treatment plant, so it is suggested that the pollutants at the output should be measured too. Comparing the measured amounts with the above mentioned standards, we see that in many of the measured cases they are higher than the standards. In order to delete the organic pollutant we can use chemical oxidation, aeration, temperature and pressure change, biodegradation and biological treatment methods. The outgoing wastewater from the treatment plant in this industry can be released in the environment after one of these sanitization disposal methods has been applied: diluting the surface water, watering the farms, enrichment of the underground water and returning to the treatment plant.

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