

PHYSICO-CHEMICAL STUDY OF EFFLUENTS  
WHICH DISCHARGE FROM THE OIL  
REFINING AT SUEZ PROVINCE

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ABSTRACT

Different samples were collected from the inflow and the outflow of the Suez oil refinery company during summer, autumn 2003 and winter 2004. The organic pollutants in the collected wastewater samples were identified using Ultra violet (UV) technique. The UV spectra of the collected samples show the presence of Mercaptans (absorption band at 197nm), acyclic disulfide (absorption band at 202 nm, benzene (absorption band at 202 nm), acyclic compounds (absorption band at 219 nm) and unsaturated organic acid (absorption band at 205 nm). Furthermore, the suspended solids, turbidity, sulphate and sulphide were measured in water samples of the Suez oil refinery company, which were in harmony with the UV spectral data obtained. However, the high values of suspended solids, sulphide and turbidity recorded in the wastewater of the Suez oil refinery are most probably attributed to discharge of huge amounts of suspended wastes from the dewaxing and coke distillation units directly into the outflow drain.

I. INTRODUCTION

Crude oil fractionated into liquefied petroleum gas, naphtha, kerosene, diesel oil, residual fuel oil. Certain refineries also produce lubricating oils and bitumen's. Furthermore, boilers, process heaters and other equipment are responsible for the emission of particulates and volatile organic compounds such as benzene, toluene and xylene [World

**Bank (1996)**]. It has been estimated that a quantity of 2.35million tons oil per year enter the marine environment of Suez Bay from petroleum refineries, oil spills, transport loss, explosions and marine accidents [**Awad (2002)**]. Petroleum is a complex mixture of aliphatic, alicyclic and aromatic hydrocarbons, it contains also a smaller proportions of non hydrocarbon compounds such as naphthenic acids, phenols, thiols, heterocyclic nitrogen and sulfur compounds [**Atlas & Barther (1987)**]. In recent years, the interest for removal of organic pollutants polycyclic aromatic hydrocarbons (PAHs) has considerably increased. Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings. They are mutagenic and carcinogenic contaminants that are widely present in the environment [**Mastral et al., (2003)**]. Consequently, communities surrounding petroleum and chemical plants can be placed at increased risk of cancer and other adverse health outcomes [**Nadal et al., (2004)**]. Oil pollution in sea water is determined by gravimetric, IR, HPLC, GC, GC/MS and Ultraviolet fluorospectrophotometer methods [**Uenlue & Gueven (2001)**].

The objective of this work is to investigate the presence of the oil organic compounds, which found in the effluents of the Suez Oil processing company at Suez region using the Ultraviolet spectrophotometer tool. As well as, some of the physical and chemical parameters which would be measured for water samples such as suspended solids, turbidity, dissolved oxygen, chemical oxygen demand, sulphates and sulphides.

## II. MATERIALS AND METIIODS

### 1. Sampling

Water samples were collected from the inlet and outlet of Suez oil processing company in clean dark glass bottles during summer, autumn and winter.

### 2. Turbidity

The method was based upon a comparison between the intensity of light scattered of the sample under defined conditions and the intensity of light scattered of a standard reference suspension (formazine) using turbidimeter.

### **3. Suspended Solids (S.S)**

The suspended solid was measured in collected water samples according to [Alpha et al., (1995)].

### **4. Dissolved oxygen**

Dissolved oxygen is carried out according to standard Winkler method which was modified by Strickland and Parson [Alpha et al., (1995)]. Where a 1 ml of  $MnSO_4$  solution in conical flask was added to the water sample (100ml) then 1ml of strong alkali-iodide-azide solution was added. The conical flask was stoppered carefully to exclude air bubble.

The mixture was mixed strongly and then 1-2 ml of concentrated sulphuric acid was added until the precipitate was dissolved. The liberated iodine was titrated against 0.025N sodium thiosulphate using starch solution as indicator.

### **5. Chemical oxygen demand (COD)**

Chemical oxygen demand was determined using closed reflux method [Alpha et al., (1995)]. The water sample was placed in culture tube and the digestion solution (potassium dichromate and sulphuric acid) was added, then add carefully sulphuric acid reagent (sulphuric acid and silver sulphate) was added carefully down inside of the tube. Tightly cap the tube, the solution was mixed completely, and then placed the tube in an electric oven preheated to  $150^{\circ}C$  for 2 hours. The mixture was cooled to room temperature and transferred its content to a conical flask for titration against 0.1N ferrous ammonium sulphate using ferrion as indicator.

### **6. Sulphate and sulphide**

Determination of Sulphide was carried out by adding excess of 0.025N iodine solution to (100ml) of the water sample. The mixture was treated with zinc acetate to produce zinc sulphide. The excess of iodine was back titrated with 0.025N sodium thiosulphate using starch solution as indicator [Alpha et al., (1995)]. While, sulphate was determined after make dilution to water sample with distilled water 100ml, then adding the condition reagent which it was prepared from (sodium chloride, hydrochloric acid, glycerol and ethyl alcohol) followed by adding barium

chloride and the solution turbidity was measured by spectrophotometer (Metertek SP-830) [Alpha et al., (1995)] at wave length 420 nm.

### 7. UV detection of organic compounds

The apparatus used for UV spectral analysis was double beam UV spectrophotometer (Perkins Elmer Lambda 38) with quartz cell, 1 cm width. Scanning was made between  $\lambda$  of 190nm and 400 nm of all these samples. The organic compounds were extracted from the water samples 11 using 50ml dichloro methane ( $\text{CH}_2\text{CL}_2$ Analar) as organic solvent and then were analyzed using UV technique.

The bands obtained for these extracted compounds were compared with those of standard organic compounds, which exist in the database of ultra violet spectrophotometer.

## III. RESULTS AND DISCUSSION

Data from UV spectra of the collected water samples of Suez oil processing company in summer 2003 are shown in Table 1. The spectrum of samples from inflow and outflow effluents samples 1,2 exhibit a band at 197 nm with absorbance value of 3.017 and 3.022 for Inflow and outflow effluent, which may be attributed to the presence of mercaptans compounds of type RSH [Shahine (2005)]. Also, there was an absorbance peak at 205nm with absorbance of 2.089 and 2.910 for the inflow and outflow effluent respectively which could be due to the presence of unsaturated organic acid of type(RCH=CHCOOH) [Shahine (2005)]. On the other hand, the spectrum of outflow effluent sample 4 exhibits UV bands at 197 and 205 nm (with absorbance of 3.187 and 2.971, respectively) in addition to a new band at 202 nm(with absorbance of 3.021) which may be related to the presence of acyclic disulphide and benzene compounds [Alpha et al., (1995)].

Table 1 collected the UV spectra of inflow of sample 5 and outflow of sample 6 during winter 2004. The outflow spectrum indicates the appearance of new bands at 210 and 219 nm (with absorbance 3.352 and 3.127) if compared to inflow water samples. The appearance of band at 210 nm is mainly due to the presence of phenolic compounds as shown in Table 1. While the band obtained at 219 nm is corresponding to acyclic compounds [Arora & Singh (1994)]. This interpretation was in harmony with the high turbidity reading and suspended solids value of 92.2 N.T.U and 923.7 mg/l, respectively recorded in the outflow effluent

in winter, as shown in Table 2. Such increase in turbidity reading and suspended solids value is most probably attributed to the discharge of huge amounts of suspended wastes from the dewaxing and coke distillation units which go directly into the outflow drain. As well as, oil-water separation systems can produce turbid water enriched in suspended solids. A through look at Table 1 it can be observed that, an increase in the absorbance of the broad band at 197 nm in winter 2004 for both inflow and outflow samples 5, 6 versus samples 3, 4 during autumn 2003. This is mainly attributed to the higher sulphide content 1.760 ppm and lower sulphate content 2527.5 ppm which were recorded in water samples 5,6 as shown in Table 3. Such increase in sulphide content is due to the reduction of sulphate ion under the effect of bacteria to sulphide ion [Shahine (2005)]. This explanation was supported by the characteristic odour of sulphide, which smelt during sampling from that site. However, the recorded data of sulphide content are within the permissible limits of Egyptian environmental law 4/1994 except those recorded in autumn 2003 and winter 2004 as shown in Table 3.

From the above results, the appearance of some petroleum compounds in the inflow water samples indicate the presence of petroleum wastes in the intake site. On the other side, the petroleum wastes were disappears from the intake of the Suez oil processing company during autumn and winter. This may be related to the biological degradation of organic compounds by microorganisms. This finding is in good agreement with the results of dissolved oxygen, where the higher concentrations of dissolved oxygen were recorded in the inflow water 5.0 and 5.1 ppm in autumn 2003 and winter 2004 respectively, as shown in Table 3. On the contrary, the chemical oxygen demand decreases to lower values of 180.0 and 187.0 mg O<sub>2</sub>/l in autumn 2003 and winter 2004 respectively. as clear from Table 3. Such drop in the values of chemical oxygen demand is mainly attributed to the decline in the biological degradation of hydrocarbons and Mercaptans compounds in the outflow effluent.



Table (2): The seasonal variation of turbidity (NTU) suspended solids (mg/L) of inflow water and outflow water of Suez oil processing company during 2003-2004.

Location	Inflow water		Outflow water	
	Turbidity NTU	Suspended solids mg/L	Turbidity NTU	Suspended solids mg/L
Spring 2003	21.03	422.95	50.65	645.20
Summer 2003	20.04	402.03	43.91	544.55
Autumn 2003	22.15	533.90	79.1	892.60
Winter 2004	21.26	450.30	92.2	923.70
Averages ± SD	21.12 0.751	452.3 50.13	66.46 19.88	751.51 144

Where SD represents standard deviation.

Table (3): The concentration of sulphate and sulphide (ppm) of the inflow water and outflow effluent of oil refinery during 2003-2004.

location	Inflow water		Outflow water		The maximum permissible limits of law 4/94
	Sulphate ppm	Sulphide ppm	Sulphate ppm	Sulphide ppm	
Spring2003	2515.5	0.604	2527.5	0.752	1.00 ppm
Summer2003	2864.0	0.880	4096.0	0.815	
Autumn2003	3190.0	0.554	5142.0	1.760	
Winter2004	2851.0	0.900	2925.0	1.025	
Averages± SD	2855.15 ±238.52	0.985 ±0.1566	3672.5 ±1025.7	1.088 ±0.401	

Where SD represents standard deviation

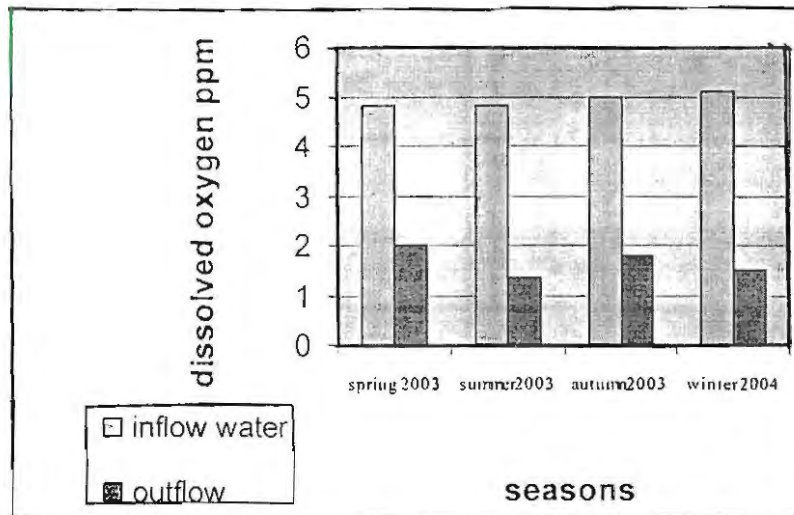


Fig.(1): Seasonal variation of dissolved oxygen in the inflow water and outflow water of oil refinery during 2003-2004.

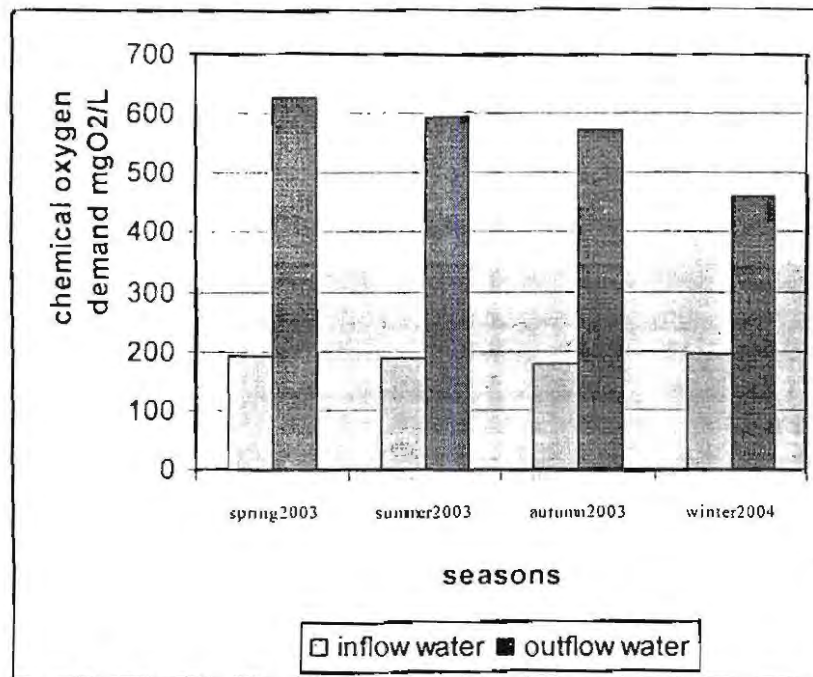


Fig.(2): Seasonal variation of chemical oxygen demand mg O<sub>2</sub>/L in the inflow and out flow water of oil refinery during 2003-2004



## CONCLUSION

In oil refiners boilers, heaters and other equipments are the sources of emission of particulates and volatile organic compounds. Ultra Violet Spectrophotometer performed the identification of organic compounds in the effluents of oil refinery. Where the following compounds were detected: Mercaptans (absorption band at 197nm), acyclic disulphide (absorption band at 202 nm, benzene (absorption band at 202 nm), acyclic compounds (absorption band at 219 nm) and unsaturated organic acid (absorption band at 205 nm). These organic compounds and sulphide ion potentially pose a major local environmental hazard. Finally, the following suggestions must be considered in the oil refiners to prevent and reduce water pollution which are: recycle oily wastes, regenerate and reuse spent solvents, recycle cooling water to minimize wastewater and prevent solid wastes from entering to drainage system.

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دراسة فزيائية- كيميائية للمخلفات السائلة التي تصرف من معمل  
تكرير البترول بمحافظة السويس

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تم تجميع عينات مختلفة من مدخل مخرج مياة لشركة السويس لتكرير البترول للتعرف على اى من المخلفات العضوية موجود فى العينات المخلفات السائلة تم استخدام تقنية الاشعة فوق بنفسجية. بينت اطياف الاشعة فوق بنفسجية للعينات التى تم تجميعها وجود المركبات (حزمة امتصاص عند ١٩٧ نانو متر)، مركب ثنائى الكبريتيد الحلقى (حزمة امتصاص عند ٢٠٢ نانو متر)، البنزين (حزمة امتصاص عند ٢٠٢ نانو متر)، مركبات حلقيه (حزمة امتصاص عند ٢١٩ نانو متر)، والأحماض العضوية الغير مشبعة (حزمة امتصاص عند ٢٠٥ نانو متر). علاوة على ذلك تم قياس المواد العلكة، العكارة، الكبريتاتو الكبريتيد فى عينات مياة الملوثة لشركة السويس لتكرير البترول والتى جأت متوافقة مع النتائج المتحصل عليها من اطياف الأشعة فوق بنفسجية. على أى حال فان القيم المرتفعة للمواد العلكة، الكبريتيد والعكارة فى الغالب ترجع الى القاء كميات هائلة من المخلفات العالقة من وحدة تصنيع الشمع وحدة تقطير الفحم مباشرة الى مصرف شركة السويس لتكرير البترول.

