1- Introduction

The degradation of the environment due to discharge of polluting effluent from industrial sources such as oil refinery effluents is a real problem in several countries. This situation is even worse in countries like Iraq where little or no treatment is carried out before disposals. It is a general knowledge that the activities of oil producing companies affect the environment and the health of the people living within the immediate vicinity of the crude oil processing plant. The attendant hazards may trigger processes that may have adverse effects on the ecosystem of such area (Reed and Johnsen, 1995).

The wastewater can contain physical, chemical and/or biological pollutants in any form or quantity and cannot adequately be quantified without actual measuring and testing. The degree of wastewater treatment varies, In some cases industrial wastewater either discharged directly into a receiving body of water or into the sewerage system of a municipality, or it will be reused or recycled, and major industrial facilities may have comprehensive in-plant treatment (Alley, 2006; Doorn *et al*.,2006).

Waste waters released by crude oil-processing and petrochemical industries are characterized by the presence of large quantities of crude oil products, polycyclic aromatic hydrocarbons, phenols, metal derivatives, surface-active substances, sulfides, naphthylenic acids and other chemicals (Suleimanov,1995). Due to the ineffectiveness of purification systems, wastewaters may become seriously dangerous, leading to the accumulation of toxic products in the receiving water bodies with potentially serious consequences on the ecosystem (Beg *et al* .,2003). Different studies were concerned about pollution by refineries discharge that alerts water quality leading to diverse effects on some organism (Namminga and Wilhm ,1976;Bleckmann *et al*.,1995;Asia *et al*,2006;Aziz *et al* .,2006;Al-Kazwini *et al*.,2009).

Basrah oil refinery is one of industrial plants that generate large quantities of wastewater vary in physiochemical characteristics .This refinery contain API separator in purpose to perform the initial separation of solids from liquids and oil from water .The wastewater discharged from the refinery ended in open area near Shatt Al-Basrah canal. Shatt Al-Basrah is artificial canal constructed for multi purposes ;total length of the canal 37 km .water speeds exceeds 2 m/s(Al-Bahili,1997).

This study aimed to: Assessment of Basrah oil refinery wastewater treatment system

2- Potential impact of refinery wastewater on Shatt Al-Basrah canal.

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Concentrations of some heavy elements in water, sediments and some aquatic plants in the Euphrates River in Al-Muthanna province- Iraq

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Abstract
The measurement of concentrations and accumulation of five heavy elements (lead, zinc, nickel, chromium, and cobalt) were performed in water, sediment, and two types of aquatic plants *Pharagmits australis* and *Ceratophyllum demersum.* The samples were collected during the Autumn 2017 from the Euphrates River from the borders of the entry of the Euphrates River to the city of Samawah until the exit of the river from the darraji side. The study showed that the concentration of elements in plants was higher than in sediments, and their concentration in sediments is higher than in the water. Their accumulation in *Phragmites australis* was higher than in the *Ceratophyllum demersum*. Through this study, it was found that these two types of plants could be used as a vital guide to the accumulation of heavy elements, as well as the concentration of heavy elements. The study samples were acceptable compared to global limits. The study showed that both plants could be used to remove this type of pollutant in the aquatic environment and could therefore be used for phytoremediation for this purpose.

Keywords: Heavy elements, aquatic plants, Euphrates River, Muthanna province.

Introduction

The development of human capacities and the misbehavior of water resources, particularly in recent decades, have led to the emergence of the problem of environmental pollution. It is increasing as water demand increases, and water pollution, particularly river and lake pollution, is one of the most serious types of pollution as it is the main source of water used for domestic use and agriculture. The main objective of the water quality assessment is to determine its suitability for various uses and the possibility of overcoming the problems that may occur and cause pollution to the environment. The study of the concentration of dissolved salts in water is an important topic for assessing the validity of water for irrigation and domestic use and its direct impact on soil salinization (Imadi et al., 2016). The course of water with pollutants such as heavy elements, chlorinated hydrocarbons, and oil is a serious problem of great urgency in modern society. Among different types of pollution, and the high pollution of the water system with toxic heavy elements is one of the main concern because these elements are not biodegradable and may be highly absorbed by crops as the food quality system has been affected mainly by natural inputs such as rock weathering and anthropogenic sources including urban, industrial, agricultural, groundwater run-off and wastewater disposal (Ali et al., 2019).

Aquatic plants are important components of many freshwater ecosystems (FAO, 2012)

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and the importance of aquatic plants in water bodies has been misunderstood as their presence in the environment is not a negative impact, but on the contrary, they have many benefits to the water ecosystem. They can be counted as an important food source for many animals as well as humans in some areas, and they regulate the reproduction and growth of aquatic organisms, as well as with other small organisms in the case of water bodies. With dense green cover, it also provides food sources for small-scale fish and amphibians (Lami and others, 2008) as well as its role, which is now known as plant processing and environmental clearance of pollutants. Concentrations of heavy elements have been studied in some aquatic plants and sediments. Sediments and plants have been further analyzed because they provide a clear indication of mineral inputs and accumulation in aquatic environments (Showqi et al., 2018).

2- Materials and Methods

Description of the study area

Basrah oil refinery : Basrah oil refinery located in the east of Basrah citiy ,Effluent discharge point near Shatt Al-Basrah canal was located 11.2km from the refinery (Fig .1). The sampling sites were divided into three stations consist of St1(API separator),St2(represent round basin for collecting wastewater from API separator) and St3 (large open basin that collecting and naturalized wastewater).

Shatt Al-Basrah canal : Three points in Shatt Al-Basrah canal were chosen in this station . Human activities like fishing were observed in this station ; also it received different diluted inputs of sewage from Hamdan station**.**

Sample collection and analysis

Samples of water from Shatt Al-Basrah canal and waste water from Basrah oil refinery that were collected monthly from the study stations during October 2009 and July 2010. Water samples were collected using glass and polyethylene containers capacity of 1 liter ,They were rinsed several times with water or effluent samples at the point of collection . Measurement of some physiochemical characteristics of water, including pH and Total Dissolved Solids were done using the Water quality multi meter (lovibond Sensodirect 150) . All samples were transported in ice chests and analyzed for pH and TDS within 12 hours of collection. Other physicochemical parameters were analyzed later using refrigerated samples. The procedures of sampling and measuring were done depending on APHA(2005).

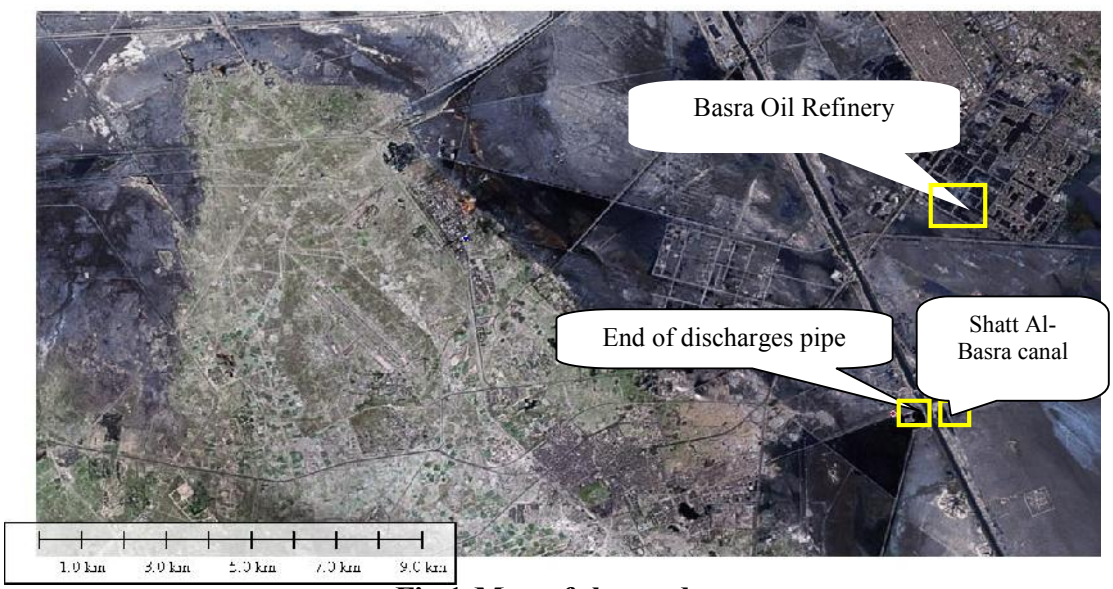

Fig.1:Map of the study area

Table 1: Mean of some physiochemical factors in wastewater samples from Basrah oil refinery wastewater system.

No.	Parameter	Station		
		1(input)	2	3(output)
1	Temperature(C°)	-	-	26.25
2	pH	8.2	7.9	7.65
3	Alkalinity (mg /L)	103	96	72
4	Turbidity (NTU)	-	-	23
5	TSS (mg /L)	31	30	20.5
6	TDS(mg /L)	4330	3562	3887
7	Sulphate (mg /L)	1806	1325	1544
8	Sulfide (mg /L)	20.7	22.6	21.3
9	Oil Grease(mg /L)	33.4	25.1	21.8
10	Phenols(mg /L)	0.81	0.77	0.62
11	Nitrate (µg /L)	24.1	24.2	22.3
12	Phosphate (µg /L)	1.1	2.1	3.2
13	BOD5 (mg /L)	-	-	23
14	COD(mg /L)	-	-	461.5
15	Pb(µg /L)	-	-	13.85
16	Cu (µg /L)	-	-	11.45
17	Zn (µg /L)	-	-	38.39
18	Cd (µg /L)	-	-	6.25

3- Results &Discussion

Assessment of Basrah oil refinery wastewater treatment system

The results of physiochemical factors of water in Basrah oil refinery showed the decrease in most of values of different factors throughout the treatment system.

All refineries employ some form of wastewater treatment so water effluents can safely be returned to the environment or re used in the refinery . the design of wastewater treatment plants is complicated by the diversity of refinery pollutants including oil, phenols, sulfides , dissolved solids, and toxic chemicals .Although the

treatment processes employed by refineries vary greatly ,Basrah oil refinery included neutralizers ,oil/water API separator ,settling chambers. Refinery water effluents collected from various processing unites and was conveyed through sewer and ditches to the treatment plant. Most of the treatment occurs in open ponds.

The results showed the ability of Basrah oil refinery treatment to reduce different types of pollutants except in some cases (Table 1 and figures 2 and 3).The highest values of some parameters like Turbidity ,TSS,TDS, Phenol ,Oil and Grease and Sulfide were during January 2010 that may also be attributed to the malfunction and sometimes blockage of the API unit and skimmers stop resulting in accumulation of these pollutants The variation in the pollutant concentration among months reflected continuous quantity of wastewater generated in the refinery. Variation in the values of the wastewater temperature degree was noted and ranged from 18.5- 34.5c° ,While the values were taken seasonal pattern during the study month .pH values were ranged from 5.6- 10.5 as shown in Fig (2). but, it were often alkaline direction ,with the exception of the change in the cases of failure and blockage of API unit led to the accumulation of discharge ,increasing in anaerobic digestion and the production of hydrogen sulfide ,which in turn operates to reduce the pH values (Fukui *et al*.,1990) . The study also showed that first station(API unit) had the highest values of pH compared to the other stations and that may be attributed to the receipted discharge with a high concentration of dissolved salts. Odjadjar and Okoh (2010) pointed out ,that high concentration of dissolved salts is working to raise the values of pH to alkaline direction. The concentrations of total alkalinity were fluctuated during the study period that varied among stations the lowest was in the third station, followed by the second station (fig.2) and that may be attributed to the lack of the receipted water except the third station as it receives additional quantities of water from other unites of the refinery ,which led to obtain dilution and thus lower the concentrations of alkalinity as well as low pH values Statistical analysis showed signification positive correlation between the values of pH and total alkalinity ($r=0.69;p<0.05$).

Turbidity values were high in the third stations all through the study period especially in cases of API unit blockage as it resulted in the accumulation of oils and grease. The values were ranged from 5.7-44.17 NTU, and the correlation was significance between the values of turbidity and oil and grease ($r=0.61;p<0.05$), and this is agreed with what El-Tohami(2009) found in his study of the impact of wastewater of the oil industry in Sudan .The study showed fluctuating in values of total suspended

solids during the study period ,first station had the highest values during January 2010 that may also be attributed to the blockage of API unit and may also due to the corrosion of metals within installation of pipes that transport effluents among stations, the statistical analysis showed differences in values of total dissolved solids that ranged from 1420-9130 mg/l during the months of the study ,as the highest values were in the first station during February 2010.Because of lack of oil refinery to integrated treatment unites, so this station receive continuous effluents after the separation process of oil from water only, as well as high concentrations of sulfates. Significance correlation was between total dissolved solids and sulfate concentrations ($r=00.96;<0.05$) and this is agreed with the results of Noaman(2008) in the effluents of northern Iraq refineries .A significant increase in the values of hydrogen sulfide in all stations during January and April 2010 and that may be attributed to stop of discharges pump resulting in the accumulation of wastewater containing high concentrations of suspended solids .As the material loose at the deposition a layer of mud (sludge) will be formed, which represents a suitable media for the reactions of anaerobic process as a result of organic compounds containment and lack of dissolved oxygen in water . These interactions led to the formation of sulfur ,phosphorus , and ammonia compounds (Galil and Rebhun,1990). Statistical analysis recorded a significant correlation between the concentrations of hydrogen sulfide and suspended solids . The results showed a clear variation in the values of sulfates for stations first station had the highest values during February 2010 that may be attributed to the blockage of API unit and accumulation of oily effluents containing a high concentrations of sulfates .Sulfur was one of oil components (GESAMP,1993), and this is agreed with the results of Noaman(2008).

As recorded, Nitrate concentrations were high in all stations in February 2010 as shown in Fig.(3) ,and that may be attributed to a malfunction of discharges pump which led to Nitrate accumulation as well as its derived from the sludge formed during the process of separating water from oil (Asia *et al*.,2006) ,which is not subject to any treatment in the Basrah oil refinery .Lower values in all stations were observed during March 2010 that may be due to continuous discharges of refinery effluents .No significant differences in phosphate concentration among months. The third station recorded the highest values in October 2009 compared with other stations ,this was due to the fact that the third receives additional discharge from the other

units of the refinery containing a high concentrations of waste cleaning equipment and devices ,which is consider as one of the main source of phosphorus compounds in the water (USEPA,1986;Abawi and Hassan,1990).

The results of statistical analysis showed significant differences in oil and grease concentrations among stations and months, as the highest values were the first station during October 2009 in and this may be due to malfunction of separation unit and accumulation of oil discharge in large quantities because of a blockage in the unit with no separation of water from oil. The second station recorded the lowest concentrations in October 2009 and that may be attributed to the lack of discharge access to this station through effluent carrying pipes among the wastewater treatment plant in the refinery. No significant differences in phenols concentrations were recorded among the stations ,but the study has recorded differences among months. The highest value recorded in January 2010 in third station and that may be attributed to the reason of fail of discharge pump and stop of skimmers ,which led to the accumulation of oil in the basin as well it is the main source of phenols in wastewater oil is one of thermal cracking of hydrocarbons incident during the refining and the liquidation of crude oil (Otokunefor and Obiukwu,2005).

We could not measure COD and BOD**5** in the first and second stations while, high values of COD and BOD**5** were showed in the third station through study period, which indicated the presence of high concentrations of organic materials such as oils and grease. organic wastes in high concentrations were decreased the values of dissolved oxygen as a result of microbial activity as well as it formed insulting layer led to prevent the exchange of gases and thus contributed to the high value of BOD**5** (Wake,2004) also high concentration of total dissolved solids and turbidity that recorded in the study may increase values of COD and BOD**5**. Statistical analysis showed significant differences among study months in the values of COD .

It's clear from pattern of monthly change in the study stations , the rates of oil and grease, total suspended solids , BOD**5**and COD were taken the same direction in most months of study and that is due to the lack of integrated treatment system in the refinery of Basrah that lesser concentrations of pollutants to the lowest levels . Different concentrations of metals were measured during the study (Fig.5), which included Lead, Copper, Zinc and Cadmium and this may be due to the lack of Basrah oil refinery treatment system. It can be seen from the results that the oily wastewater treatment system used in Basrah oil refinery was good in reducing the

concentrations of certain pollutants prior they release to the environment, which included pH and alkalinity and also there was a relative decrease in the concentration of oils and grease and suspended solids during the study period except cases of repeated failure of separation unit and discharge pump.

The potential impact Basrah oil refinery on Shatt Al-Basrah canal

There are two groups of results taken from the discharges of Basrah oil refinery (Appendix 1); first showed different physic-chemicals parameters that were within local permission limits .while other group was exceed it. The second group has potential impact on Shatt Al-Basrah canal. The results of the characterization carried out on water samples obtained from Shatt Al-Basrah canal are presented in Table 2. Variation in the values of water temperature of Shatt Al-Basrah canal was showed. temperatures values(23.8± 5.7) felt within the aquatic organism requirements in this region (Abaychi *et al*., 1991 and Al-Handal *et al*.,19910), while high values of temperature may be reduced the dissolved oxygen, affect on the level of dissolved salts concentration and on the interactions of chemical in aqueous media (Smith,2004).The pH value was 8.48±0.26 and this indicated that water of Shatt Al-Basrah canal was in alkaline direction and within local permission limits . This pH value play an important role in the chemical reactions occurring in aqueous media (Demirci *et al*.,1998;Abawi and Hassan,1990), while low pH is toxic to alkalinity values were appreciably low.

The total suspended solids were within local permission limits(<60 mg/l)..The main reasons of suspended solids presence in the water of Shatt Al-Basrha canal attributed to Basrah refinery discharges, rising of water table in addition to human activities in fishing and boat movement. However ,he values of H**2**S,SO**4**,NO**3** and PO**4** were lower than local permission limits. Sulfate significantly distributed in most of the industrial wastewater (Irshad *et al*.,1997) and approximately 80% of sulfate in some of the waste liquids were reduced by anaerobic bacteria and by presence of organic wastes turn to hydrogen sulfide ,which gives objectionable odor of water and cause corrosion to processing units(Fukui *et al*.,1999) .The sulfide is one of pollutants types generated in effluents of oil refineries resulted from sulfates reducing by sulfate reducing Bacteria(Fukui *et al*.,1999) . The main potential impact of high concentration of NO**3** and PO**4** were eutrophication.

Some heavy metals presence in different properties in the composition of crude oil included Nickel , Vanadium ,Lead, Iron,

Cobalt ,Cadmium ,Zinc and Copper (Concaw, 2004) . The values of all metals were within acceptable local permission limits .water analysis of Shatt Al-Basrah canal indicated the other group of results . Turbidity values for the station were higher than the local permission limits. The turbidity of 18±3.8 NTU showed that colloidal matter in the water was high and by implication the wastewater contained high solids concentration ,in addition to high concentrations of oil and grease (Ahmed, 2008).On the other hand ,TDS values of 3167±822 mg/l were generally high and suggest that the wastewater contain high concentration of ions which can be removed by coagulation and flocculation. Shatt Al-Basrah canal was subjected to Basrah oil refinery effluents in addition to natural process like evaporation in summer , as well as the high concentrations of nitrates and phosphates and sulfates, which sometimes combined with ions of some elements such as (Ca, Mg, Fe ,and K) composed ionized salts that rise the concentration of TDS(Al-Fhedawi,1999).

Oil and grease values of 22.3±3.6 mg/l were high when compared to local permission limits of 10 mg/l .These pollutants are known as a mixture of organic compound s ranging in molecular weights and include fatty acids, oils and fat. Fraction of these substance soluble in the water and other parts of them settle at the bottom after loss the volatile parts ,while the bulk of them was keeping floating on the surface of the water (Abawi and Hassan,1990),which will effect on different aquatic organisms .The phenol is one of the most dangerous persistent organic pollutants in water and the organisms are subjected to the formation of chlorophenols with a bad smell(Abawi and Hassan,1990) .The mean value of phenols was 0.3±0.1 mg/l that exceeded local permission limits. The values of COD and BOD**5** were quite high when compared to local permission limits and USEPA standard. This indicated strong pollution potential and therefore calls for treatment before disposal. The high COD values indicate the high potential of aqueous effluents to cause gross inorganic and organic pollution in receiving surface water bodies .This could cause a reduction on the population of fishes and other aquatic organism (Osibanjo,1992;Asia *et al*.,2006). The high values of COD (ranged 302-473 mg/l) may resulted from the nature of Basrah oil refinery discharges containing high concentration of oil and grease and dissolved salts that reduce dissolved oxygen (Lehatine ,1996).

Table 2: physico—chemical properties of Shatt Al-Basrah canal during study period

parameter	Unit	Max.	Min	Mean	± SD
W.T.	C°	30.0	17.8	23.8	5.7
pH	-	8.9	7.3	8.48	0.26
Alkalinity	mg /l	100.0	35.0	68.2	31.6
Turbidity	NTU	33.4	9.0	18.1	3.8
TSS	mg /l	39.0	20.0	29.0	7.8
TDS	mg /l	5010	1930.0	3167.0	822
Sulfate	mg /l	2102	1011.0	1569.0	450.0
Sulfide	mg /l	28.2	20.0	24.0	3.6
Oil &Grease	mg /l	43.0	5.0	22.3	3.6
Phenols	mg /l	0.4	0.3	0.3	0.1
Nitrate	mg /l	39.7	4.5	22.9	18.8
Phosphate	mg /l	4.4	0.8	2.2	1.6
BOD5	mg /l	22.0	12.0	17.0	4.4
COD	mg /l	473.0	302.0	368.5	56.5
Pb	mg /l	14.5	10.3	12.6	2.1
Cu	mg /l	11.8	11.1	11.5	0.3
Zn	mg /l	43.4	24.3	34.7	8.0
Cd	mg /l	4.4	3.8	4.5	0.7

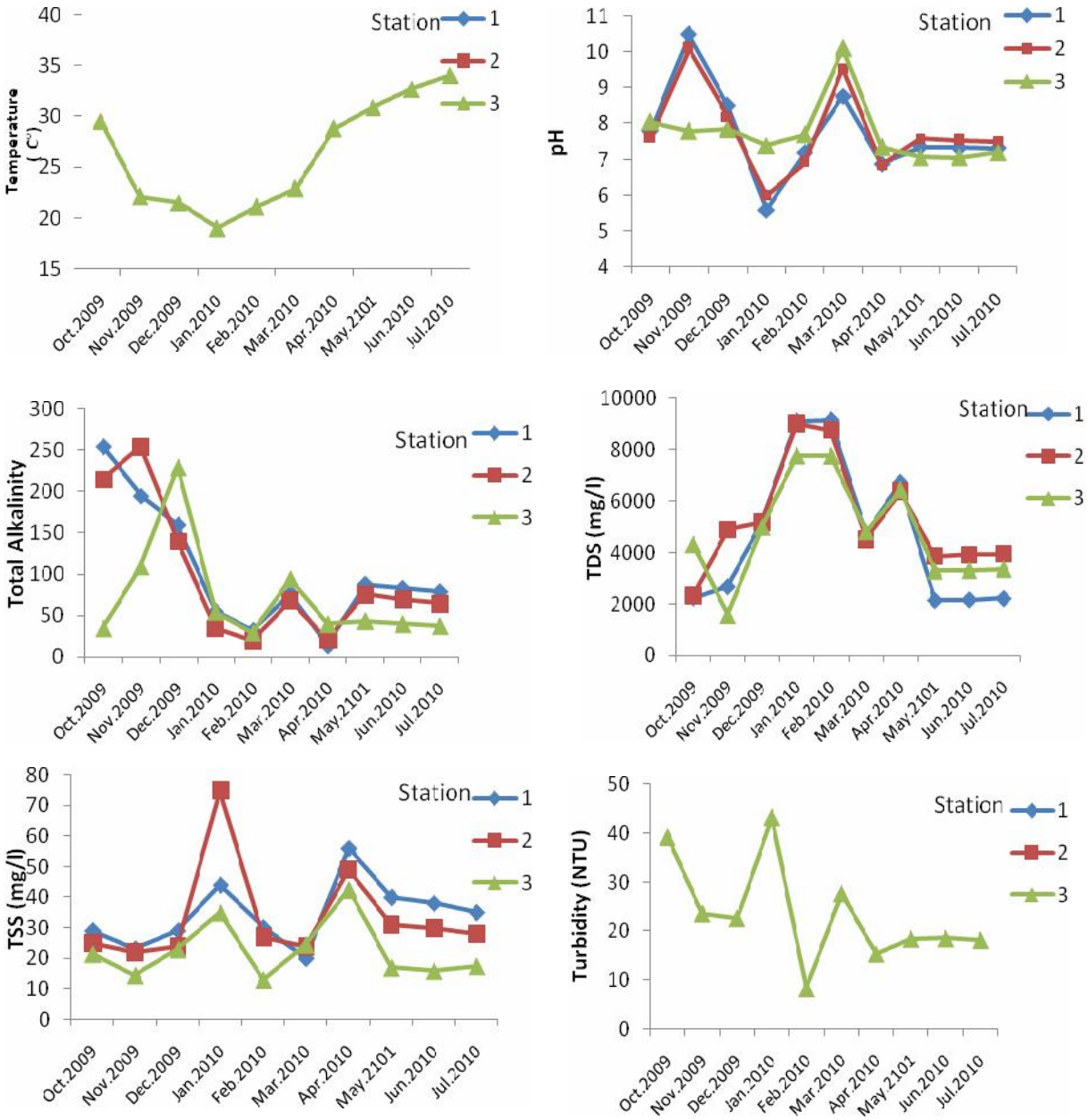

Fig.2: Monthly changes of some wastewater properties (Water temperature, pH, Alkalinity, TSS, TDS and turbidity) within Basra oil refinery treatment system

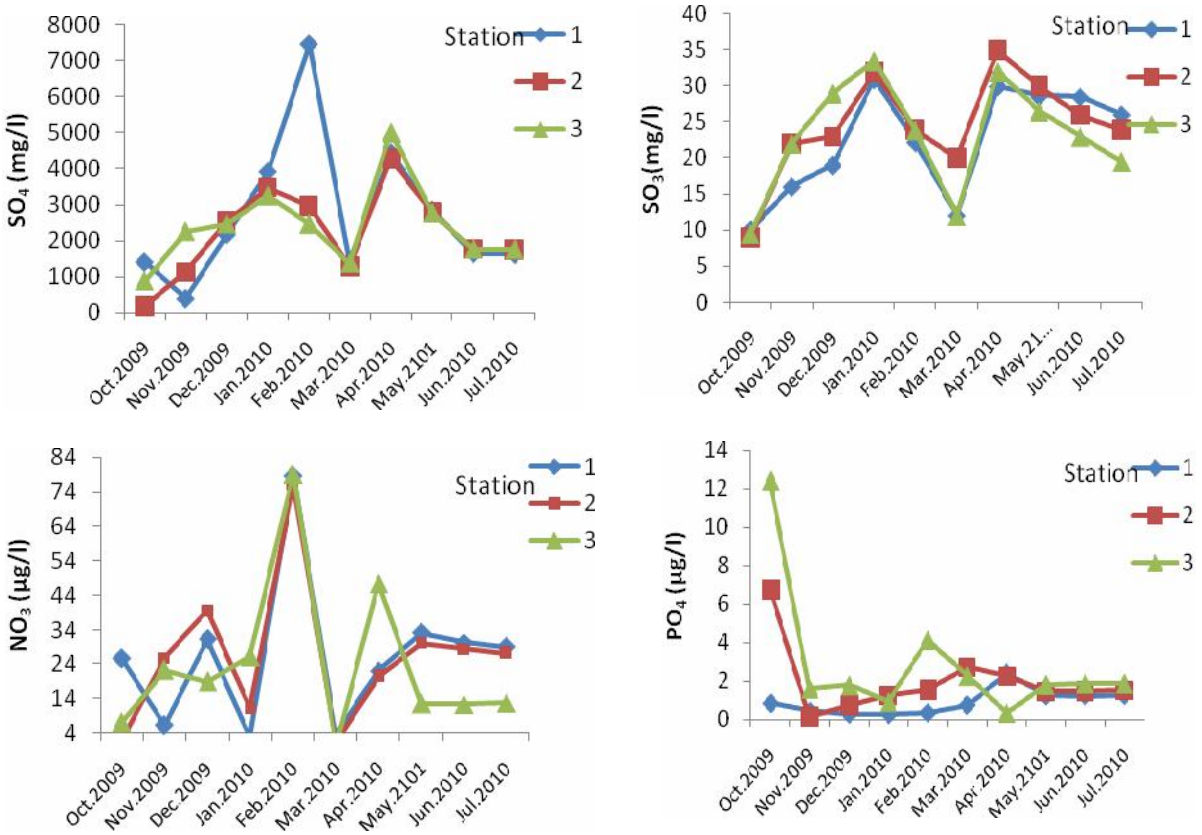

Fig.3: Monthly changes of some wastewater properties (SO_4, SO_3, NO_3, and PO_4) within Basra oil refinery treatment system

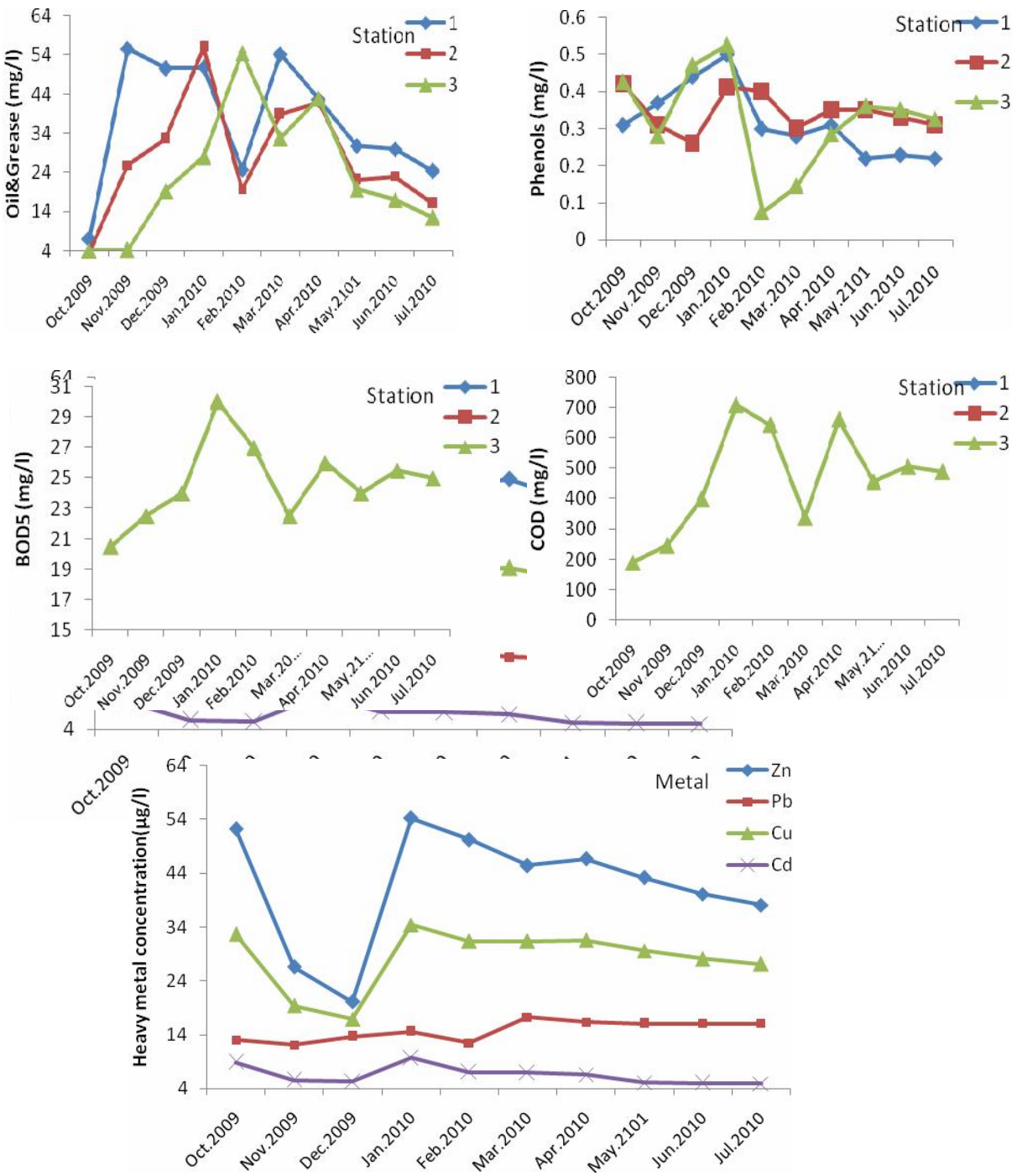

Fig.4: Monthly changes of some wastewater properties (Oil&grease, Phenols, BOD_5, and COD) within Basra oil refinery treatment system

4- Conclusion

It appears that there were potential impact of Basrah oil refinery discharge on Shatt Al-Basrah canal because of some problems in the treatment system that minimizes hazardous waste in the refinery .Improvement of operating procedures and more efficient equipment are two types of waste minimization practices that the refinery could adopt .It is necessary to work with individual facilities to determine the specific activities they engage in, to estimate the amount of waste they generate and how it is managed ,and to assess the current level of waste minimization practiced .

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Appendix 1:Comarison of wastewater in current study and Iraqi standard and USEPA limitation.

NO.	Physic-chemical properties	Current Study (Basrah oil refinery discharge)	Iraqi Standard limits (2009)	USEPA(2008)
1	Temperature(C°)	26	35	30
2	pH	9.02	6.5 – 9.5	6.5 – 8.5
3	Alkalinity (mg/L)	73	-	-
4	Turbidity (NTU)	25	10	-
5	TSS (mg/ L)	31	60	20
6	TDS (mg/ L)	4962	-	500
7	Sulphate (mg/ L)	1960	400	250
8	Sulfide (mg/ L)	29	-	0.5
9	Nitrate (mg / L)	0.02	50	10
10	Phosphate (mg / L)	0.0014	3	3
11	O&G (mg/ L)	27	10	5
12	Phenols (mg/ L)	0.4	0.05 – 0.01	0.35
13	BOD 5 (mg/ L)	24	40	15
14	COD(mg/ L)	721	100	125
15	Pb (mg/ L)	0.014	0.1	0.1
16	Cu (mg/ L)	0.012	0.2	1
17	Zn (mg/ L)	0.041	2	5
18	Cd (mg/ L)	0.0062	0.01	0.005

الخصائص الفيزيائية والكيميائية لمطروحات مصفى نفط البصرة و احتمالية تأثيرها في نوعية مياه شط البصرة

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الخلاصة

أجريت الدراسة للفترة من تشرين الأول 2009 إلى تموز 2010 وبمراقبة شهرية شملت 18 معياراً لنوعية المياه الناتجة عن مصفى نفط البصرة بهدف التعرف على مدى كفاءة نظام معالجة المياه العادمة داخل المصفى و التصاريف التي يطرحها عبر أنبوب التصريف الذي يصب بالقرب من قناة شط البصرة .تضمنت الدراسة قياس درجة الحرارة و الأس الهيدروجيني والقاعدية الكلية و الكدرة والمواد الصلبة الذائبة الكلية والمواد الصلبة العالقة الكلية والمتطلبين الحيوي والكيميائي للأوكسجين والزيوت والشحوم والفينولات وكبريتيد الهيدروجين والنترات والفوسفات والكبريتات وبعض المعادن الثقيلة (الرصاص والنحاس والكادميوم والخارصين).

سجل انخفاض في قيم بعض الخصائص الفيزيائية والكيميائية عند دخول المياه العادمة في وحدات المعالجة داخل المصفى وبين وصولها لمضخة التصريف كقيم الأس الهيدروجيني و القاعدية والمواد الصلبة العالقة الكلية والزيوت والشحوم والفينولات والنترات. أوضحت نتائج الدراسة موافقة في بعض خصائص مياه تصريف مصفى نفط البصرة مع المحددات العراقية ، إلا أن هناك تطرفا واضحا في قيم كل من الكدرة والمواد الصلبة الذائبة الكلية والكبريتات وكبريتيد الهيدروجين والفينولات والزيوت والشحوم وقيم المتطلب الكيميائي للأوكسجين. أثرت بعض المعايير المتطرفة من مطروحات المصفى على نوعية المياه في شط البصرة بشكل موسمي.

استنتج من الدراسة أن نظام معالجة المياه العادمة كان كفوءا نسبيا في تقليل تراكيز الزيوت والشحوم والمواد الصلبة العالقة الكلية ، لكنه يفتقر إلى وحدة معالجة متكاملة. يوجد تأثير كامن للتلوث في شط البصرة من مصفى النفط بفعل بعض المشاكل في نظام المعالجة التي تقلل من مستويات الخطر.