ENHANCEMENT OF PHENOL REMOVAL EFFICIENCY IN DORA REFINERY WASTEWATER TREATMENT PLANT

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ABSTRACT

Because the sanctions imposed on Iraq by the United Nations, programmed maintenance and wearing parts replacement has not been performed according to schedules in DORA Refinery Wastewater Unit, which resulted in higher phenol content and BOD_5 in effluents disposed to river. The investigations showed that two main reasons were behind this problem: Firstly, increased emissions of hydrocarbons in the complexity of refinery equipment and Secondly, the decreased efficiency of the aerators in the biological. During the last few months, phenol average concentration in the effluent, after biological treatment was found to be between 0.06-0.13 mg/L, while COD was exceeding 110 mg/L after treatment in the same period. Considerable enhancement, has been indicated recently, after the following performances: First: Recycling wastewater from some heat exchangers, and the segregation of low and high strength of wastewaters, Second: Minimizing emissions of hydrocarbons from fluid catalytic cracking and steam cracking, Third: Replacement of driving motors of the aerators in the biological treatment unit. After replacement of these units, a significant decrease in phenol concentration was obtained in purified water (0.03-0.05) mg/L and COD of 60 mg/L before the tertiary treatment. It is concluded that a better quality of effluents has been obtained after a series of emissions control and wastewater treatment unit equipment maintenance performances.

KEYWORDS

Waste water, aerator, phenolic compounds

INTRODUCTION

Dora refinery, which is situated in the mid of Greater Baghdad on the Tigris river western bank, underwent a period of considerable growth between (1954-1987). The capacity of processed crude oil has jumped from 25000 BPD to 100000 BPD (Barrel per Day).

The high authority in the Iraqi oil industry recognized since an early stage that a side effect of such development and location could increase pollution of the environment and more particularly of surface and ground waters. It therefore took steps to limit the impacts of its activities on the receiving water, more especially as since the discharging their effluent into Tigris river, the water which could immediately, be used for drinking or recreation.

To meet the much stringent standards for discharge into fresh water, the water management in Dora refinery was completely modified, aiming at:

- Reduction of water flow and pollutant load by reducing water consumption and by enhancing recirculation and re-use,
- Very efficient purification technique for high removal of suspended solids and oil and for reduction of the dissolved impurities that cause a high biochemical oxygen demand.

The success of the pollution abatement measures in Dora refinery is evident when one considers that, the refinery has been approximately 70% damaged and rebuilt during 1991-1992 and suffers from strict sanctions since that time. This paper will focus upon the case of phenol removal efficiency enhancement activities performed.

Phenol chemistry, degradation and relevant literature will be presented. A brief description of the treatment plant and effluent characteristics records for the last year with there analysis and conclusions will be included.

LETRATURE SURVEY

Phenols

Phenols are among the most important of the aromatics compounds. They are undesirable from many aspects. They impart an unpleasant medicinal taste and odder to drinking water which can be detected in the range of 50-100 ppb. If the drinking water is chlorinated, the phenols can be detected by taste in the range of about 5 ppb. Pure phenol has a theoretical oxygen demand (TOD) of 2,500,000 ppm. Thus, each 1 ppm. of phenol in a waste water may create 2.5 ppm. of ultimate BOD or about 1.7 ppm. of 5-day BOD, assuming that all of the TOD is biochemically oxidizable .

Phenol is powerful bactericidal and, because of this, it tends to interfere with the laboratory BOD test if present in very high concentrations. High shock concentrations (200 ppm. or more) can sometimes deactivate BOD treatment plants such as BOD trickle filters and activated sludge units by 'killing' the bacteria in these units. For this reason, municipal sewage systems may impose limits on phenol discharge. Phenol has been reported as toxic to fresh-water fish in concentrations raging from 1-10 ppm. A typical antipollution range of limits is 0.02-2 ppm. for phenol in waste streams discharged into natural waterways.

Biological Degradation of Phenols

As Compound with a basic aromatic structure, the behavior of phenols in biological degradation is fundamentally the same as that of aromatic hydrocarbons. The catabolism of aromatic substances takes place through the successive action of various enzymes (phenolases) which can easily be induced in some microorganisms through phenolated substrates. Phenol is firstly oxidized into a catechol by the creation of a second phenol function; then a break of the nucleus is observed, together with the formation of moronic acid which in its turn becomes β ceto-adipic acid. The latter hydrolyzes into acetic and succinic acids which are part of the regular metabolization cycle, (Fig. 1). Bacteria (Pseudomonas putida) and yeasts (Trichosporum cutaneum) rapidly degrade phenol at concentrations up to 100 mg/L without inhibition of metabolism, in a single –stage system. There are even species of bacteria that are highly specialized for the degradation of phenol (phenol bacteria) and, like Bacillus cereus, are able to tolerate concentrations up to 1000 mg/L without inhibition of phenol conversion (Radhakrishnan and Ray, 1974). At high phenol concentration, however, O_2 supply can become the rate- limiting factor. Up to 30-40 % of the phenol is utilized in energy metabolism and cell yields of 1.0 –1.3 g are observed per 1 g of phenol degraded[1]. The theoretical biochemical and scientific data concerning the degradability of phenols are fully confirmed by operating experience with biological sewage – treatment plants. For refinery wastes, phenol degrading is possible down to concentrations of 0.3 – 0.05 mg/L. Kostenbader and Fleckstein (1969) achieved degradation in the activated sludge process of 99.5% with phenol loading of 4.8 $kg/m^3.d$ and a residence time of only 1.6 h; the phenol loading was 0.86 kg/kg sludge /d. Above –average efficiency of the activated sludge process in the degradation of phenols was recorded in investigations by Adams (1974), who obtained effluent concentrations of less than 0.5 mg/L at input concentrations of 3270 mg/L. The BOD_5 sludge loading was 0.3 kg/kg total solids / day. On the whole it can be assumed that phenols, especially those of the monohydric type, generally belong to the class of easily biodegradable of their composition and concentration in refinery waste waters[1].

Recently more efficient tertiary treatments has been used to remove the remaining phenols combined with the bio-treatment such as enzymatic treatment[2], or any other chemical or physical treatment methods .

SITE WORK

Description of Dora Wastewaters Treatment Plant

Primarily fuels are produced through distillation at the refinery in Dora. In addition, production of various lubricants takes place. The refinery wastewater is purified in a central wastewater treatment plant dating from 1954. The wastewater is fed to the treatment plant from the individual production sites via a pipeline system. Specific partial flows are combined directly at the respective production facilities. In view of the possible necessity of partial flow treatment, this combining of partial wastewater flows is regarded as unfavorable. On partial flow is already fed to a preliminary treatment unit prior to being fed to the central treatment plant. The preliminary treatment unit consists of a gravity separator (API No. 2), in which primarily oil is removed from the wastewater. The partial flow treated here (approx. 200 m^3/h on average) comes from lubricating oil production line No.3. The discharge from this preliminary treatment stage flows to the central wastewater treatment plant.

The wastewater treatment plant comprises of the following purification stages:

a) Primary steps (physical/chemical):

1-Gravity separator API (a physical oil/water separation process has been approved by American Petroleum Institute which is most commonly used by petroleum industry) .

2- Preliminary settling tank.

3- Flocculation tank and reactor.

4- Flotation tank DAF (Dissolved Air Flotation).

b) Secondary steps:

1- Aeration tank (Biological) .

2- Final Clarifier.

c) Tertiary treatment:

- Filtration.

d) Sludge treatment:

1- Sludge storage.

2- Sludge incineration. .

The following schematic diagram shows the steps of Dora wastewater treatment plant

Compliance with the Required Discharge Levels

The required discharge levels must be complied with the national standards at the outlet to Tigris River. Mixing the treatment plant discharge with other partial non-polluted flows brings about dilution those results in a reduction in the discharge concentrations which is not accepted by the supervisory authorities, in some cases, that this will cause eventually high consumption in treated water. Table (1) shows that a proper treatment is necessary after the API treatment to met the required discharge levels.

Comparison Between Inlet Values and Design Values

In accordance with the design of the plant, certain inlet values must be met in order to comply with the previously indicated discharge levels. These values are compared with the measured values in Table (2). If one assumes that the factor for determining the BOD_5 results from the COD divided by 4 according to the treatment plant laboratory procedure[3] , the BOD_5 inlet concentration after API lies within a range of 70-100 mg/L. This is significantly below the design concentration. In the case of phenol, the inlet values are on the same order of magnitude as the design values[4].

Compliance with the Phenol Discharge Level

Phenol is a wastewater component that is fundamentally biodegradable. It must be noted that the discharge levels required for this parameter in Iraq (0.05 mg/L) have been tightened substantially in comparison to the values applying in Germany (0.3 or 0.2 mg/L)[5]. Although the phenol removal efficiency of the treatment plant is very good, the required discharge levels for this parameter cannot be met reliably.

The biodegradation could be improved if a higher proportion of phenol decomposing microorganisms present in the activated sludge remains the same and an increase in the total quantity of activated sludge corresponding to an increase in the volume of the aeration tank is necessary in order to increase the phenol-decomposing microorganisms.

BROCHIER[5] suggested that it is possible to install a separate treatment stage for phenol decomposition downstream from the biological stage. A process that works with immobilized microorganisms would be suitable here. For example, a submerged contact aerator or a submerged packed bed is conceivable.

While Dora Refinery, yet under UN sanction, a simple measures were taken to reduce phenols in the discharged effluents such as:

- Steps to reduce phenol discharge to partial wastewater from the source (Table 6).
- To enhance treatment prior to biological treatment unit (physical and chemical) .
- To improve oxygen supply by replacement of aerators drive motor to higher speed and power.

RESULTS AND DISCUSSION

A comprehensive investigations where performed by the researcher and refinery laboratory staff during the research work period. Tables 1-9 show the data been collected. Degradation of phenols, as illustrated in the literature is highly connected with the oxygen supply in the aerator. Investigations performed in the treatment plant laboratory indicate that considerable enhancement in phenol removal efficiency was obtained after improving aeration by increasing the speed and power of drive motors (Table 3). Fig.2-a and 2-b shows that dissolved oxygen was increased from 0.7-0.9 to 2-3 ppm with new aerators, which results in high phenol removal efficiency. Concentration of phenol and BOD_5 in wastewater discharged from Dora refinery, before and after treatment, is acceptable if compared with other countries concentration limit values.

CONCLUSIONS

Referring to the relevant literature and to the investigations carried out by Dora Refinery wastewater treatment plant and taking into account the report of inspection performed by BROCHIER Co. on Aug. 2000, it is concluded that:

1- Extensive preliminary physical and chemical treatment of the wastewater takes place through the existing plant technology.

2- The biodegradable wastewater components are extensively reduced in the aeration tank which was modified recently, they are subjected to :

- Low load inter the biox,
- Improving the aeration rate by aerators replacement which resulted in a

marked improvement in phenol removal efficiency,

- High attention has been paid to maintain dissolved oxygen in the range (2-3) ppm

3- To improve the discharge levels and to maintain stable operation of the aeration stage in Dora Refinery wastewater treatment plant , the following preliminary facilities are conceivable:

- Sulphate reduction.

- Furfural concentration control in the partial wastewater.

- Optimization measures are necessary such as partial and total flow meters and oxygen measurement.

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Table (1) Comparison between required levels and aeration outlet levels (after Brochier[(4)])

	COD (mg/L)	BOD_5 (mg/L)	Hydrocarbons (mg/L)	Phenol (mg/L)	Sulphate (mg/L)
Required discharge levels	4-5 ×BOD_5 =100	20	5	0.05	400
Aeration outlet					
16.08.2000 treatment plant laboratory	116	23.2)[1]	10	0.08	-
16.08.2000 Brochier	144	< 3	1.8	0.3	520
17.08.2000 Brochier	112	< 3	3.8	0.3 /< 0.02)[2]	480
Outlet to Tigris					
16.08.2000 treatment plant laboratory	36	7.2)[1]	5	0.022	-
16.08.2000 Brochier	79	< 3	1.6	< 0.1	590
17.08.2000 Brochier	64	< 3	-	0.1/< 0.02)[2]	510

[1]): The values are computed by the treatment plant laboratory from the COD (BOD_5 = COD /5).

[2)]: The first value indicated for phenol concentration was measured on site. The second value is from an analysis in Germany.

Table(2) Comparison between Operating State and design Parameters

	Inlet	COD	BOD_5	Hydrocarbons	Phenol	Sulphate
	[m^3/h]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]
Design parameters						
Normal operation	750		150	1000		
Design state	850		250	1500	0.9-1.2	312
Operating state / measurement results						
Mean conditions	Approx. 500					
After API 16.08.00 treatment plant laboratory		316	79)[1]	40	0.88	-
After API 16.08.00		334	-	12.4	1.44)[2]	460
After API 17.08.00 Brochier		338	-	-	1.2)[2]	820

1): The values are computed by the treatment plant laboratory from the COD

(BOD_5 = COD /4) ([6]).

2): The values were analyzed by Brochier(4) on site

Table(3) Average Phenol Concentration before and after Aerator Drive Motor replacement

Month	Phenol (ppm.) Before treatment	Phenol (ppm.) After treatment	Removal Efficiency %
Sept. 2002 Before D.M. Replacement	0.75	0.078	91
Oct. 2002 After D.M.Replac.	1.33	0.04	97

Table (4) Dora Refinery Industrial Water Investigations, (Average of daily Record- Aug. /2002)

Component ppm	Raw Water from Tigris river	Wastewater after API Pretreatment	Effluent after treatment	Local standard limits of treated effluent
Phenol	0.012	0.69	0.1	0.1
Oil	1.8	15.2	5.9	10
Susp. Solid	-	-	-	10
pH	7.5	7.3	7.4	-
B.O.D	5.8	48	92	20
C.O.D	29	193	18.4	4-5* B.O.D
Chloride as NaCL	188	334	264	-
Sulfate as SO_4^{-2}	248	595	578	-
Total Phosphate PO_4	0.08	1.5	Zero	-
Sulfide as S^{-2}	Nil	0.94	0.3	0.1
Turbidity (NTU)	7.8	26.5	30.7	-
T.D.S as $CaCO_3$	686	1111	1139	-
Calcium hardness as $CaCO_3$	223	268	263	-
Magnesium hardness as $CaCO_3$	152	108	115	-
M-alkalinity as HCO_3	142	121	121	-
Total hardness as $CaCO_3$	340	377	378	-
Conductivity $\mu s/cm$	1056	1709	1752	-

Phenol concentration in treated effluent still higher that required level before aeration drive motor replacement.

Table (5) Dora Refinery Industrial Water Investigations

(Average of daily record Oct. /2002)

Component Ppm	Raw Water from Tigris river	Wastewater after API Pretreatment	Effluent after treatment	Local standard limits of treated effluent
Phenol	Nil	1.0	0.039	0.1
Oil	2.8	21.4	6.5	10
Susp. Solid	-	29.0	24.6	10
pH	7.3	7.2	7.3	-
B.O.D	9.2	46	11.2	20
C.O.D	46	184	56	4-5* B.O.D
Chloride as NaCL	286	383	294	-
Sulfate as SO_4^{-2}	315	635	610	-
Total Phosphate PO_4	0.06	1.9	2.0	-
Sulfide as S^{-2}	NIL	0.32	0.12	0.1
Turbidity (NTU)	5.8	53.0	48.2	-
T.D.S as $CaCO_3$	809	1131	1075	-
Calcium hardness as $CaCO_3$	258	294	179	-
Magnesium hardness as $CaCO_3$	154	174	277	-
M-alkalinity as HCO_3	140	154	100	-
Total hardness as $CaCO_3$	412	468	456	-
Conductivity $\mu s / cm$	1246	1740	1655	--

Considerable enhancement of phenol removal efficiency after improvement of aeration rate.

Table (6) Phenol Concentration at the source of emission (mg/L) Compared with total processed Oil for 2002

Source Date of test	Light naphtha (1)	Light naphtha (2)	Heavy naphtha (2)	Crude Oil No. 2	Crude Oil No. 5
8/3/1999	9.0	9.0	-	-	-
9/3/1999	3.4	4.5	22.5	-	-
10/3/1999	0.0	0.0	19	-	-
11/3/1999	0.33	0.67	1.74	-	-
13/3/1999	8.5	10.0	22.5	-	-
16/8/2000	-	-	-	1.2	1.6
17/8/2000	-	-	-	0.8	2.8

Table(7) Typical Wastewater Flows* and Pollutant Loads in Established and Modern Refineries compared with Dora Refinery

	Established Refinery	Modern Refinery		Dora Refinery	
	Prior to Segregation	Before treatment	After treatment	Before	After
m^3 wastewater / ton Crude oil	14.5	0.2	0.2	1.17	1.17
Gm Oil in water/ ton crude Oil	170	5	0.4	33.93	7.6
Gm BOD in water/ton Crude	160	30	2	53.82	13.10
BOD in water mg/L	11.0	150	10	61.0	17.0

* Average raw water flowrate ≈ 1875 m^3/hr

Average wastewater flowrate ≈ 700 m^3/hr

Average crude oil processed ≈ 5 million ton /year ≈ 600 ton /hr

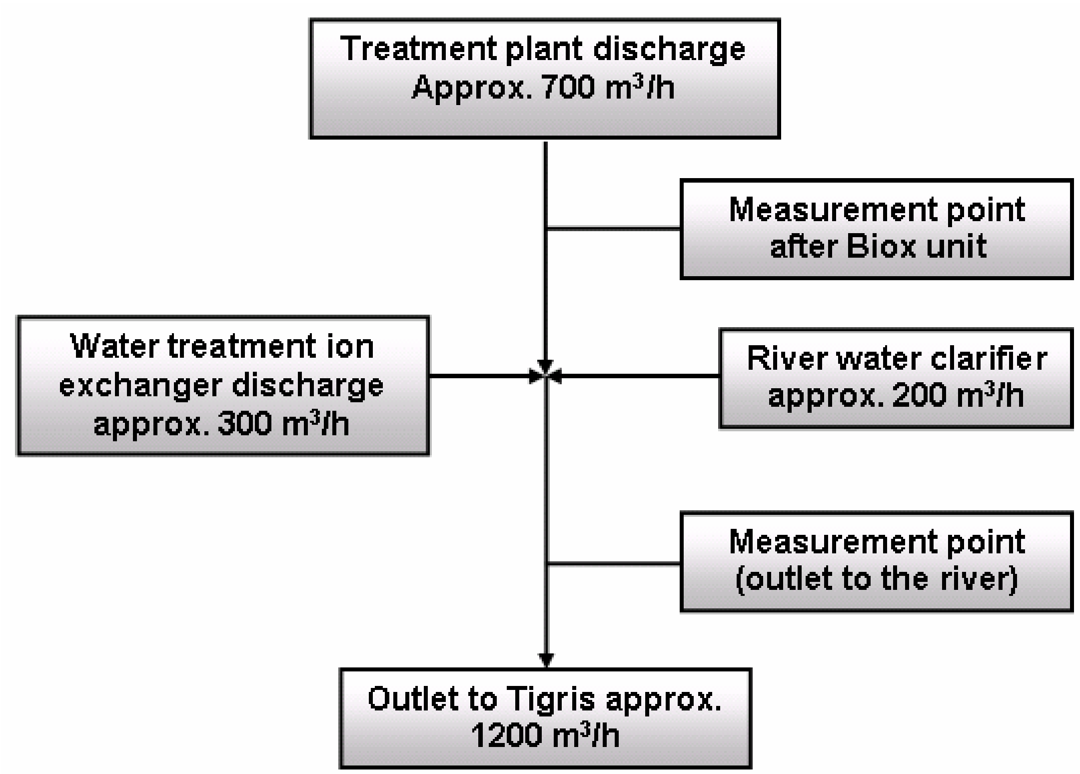
Table(8) Concentrations and Limit Values for wastewater in Europe and U.S.A (Concawe report n.5/79)

mg/L	Belgium	Denmark	Germany	United Kingdom	France	Italy	Ireland	Luxembourg	Netherlands	USA
BOD_5	35-70	20	20	20-400	30-40	40	-	-	-	15
COD	200-350	-	100	8-25	120-150	160	100	-	250	80-115
TOC	-	-	-	-	-	-	-	-	-	33
Oil, Hydrocarbon	20-30	5	2	20-50	$5/20^5$	5	-	-	20-30	5
Phenl	0.5.1	0.2	0.2	1-3	0.5-1	0.5	-	-	2.5	0.1

Table(9) Characteristics of Wastewater Before & After treatment In Dora Refinery (2002)

Month	pH		SO_4 (ppm)		COD (ppm)		BOD_5 (ppm)		Phenol (ppm)	
	Before	After	Before	After	Before	After	Before	After	Before	After
Jan.	-	7.66	511	590	406	49	101.5	9.8	1.02	0.04
Feb.	-	7.7	560	526	560	93	140	18.6	1.06	0.03
Mar.	-	7.7	520	557	194	58	48.6	11.6	1.01	0.025
Apr.	-	7.7	617	630	221	87..5	55.3	17.5	1.2	0.11
May	-	7.7	626	629	219	107	54	21	1.1	0.13
Jun.	-	7.7	460	490	146	71.9	36	14.3	0.64	0.09
Jul.	-	7.7	466	517	154	89	38.5	17.8	0.85	0.09
Aug.	7.2	7.6	595	578	193	92	48	18.9	0.69	0.1
Sep.	7.1	7.2	667	659	146	57.4	36.6	11.4	0.75	0.078
Oct.	7.4	7.5	635	610	184	56	46	11.2	1.0	0.039
Nov.*	7.9	7.7	432	484	271	116	67.3	23.2	1.33	1.28
Dec.*	7.7	7.8	415	470	254	160	63	32	1.3	1.3
Average	7.5	7.6	542	561	246	86.4	61	17	1.5	0.073

*** Shut down of biological treatment for maintenance**


Treatment plant discharge
Approx. 700 m³/h
Measurement point
after Biox unit
Water treatment ion
exchanger discharge
approx. 300 m³/h
River water clarifier
approx. 200 m³/h
Measurement point
(outlet to the river)
Outlet to Tigris approx.
1200 m³/h

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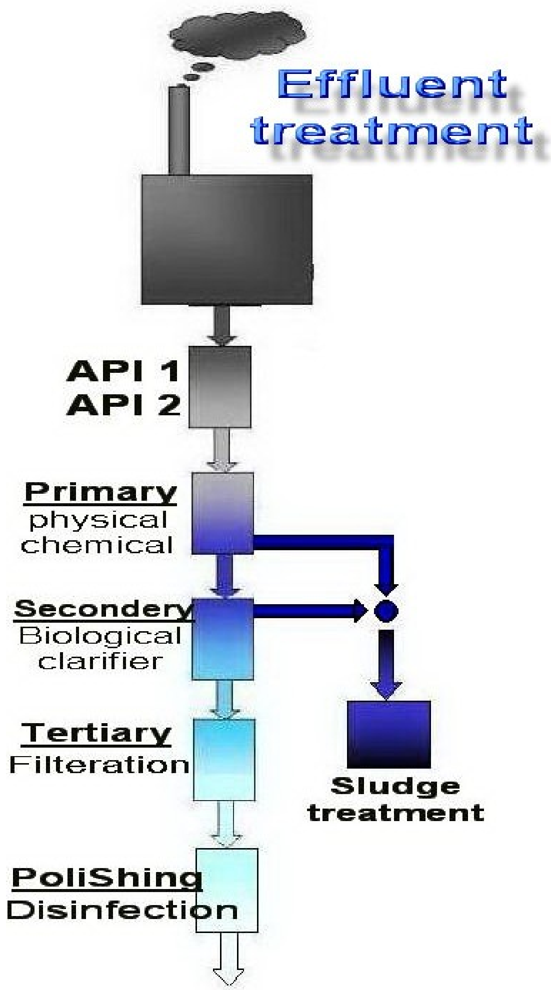
Effluent
treatment
API 1
API 2
Primary
physical
chemical
Secondery
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clarifier
Tertiary
Filteration
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PoliShing
Disinfection

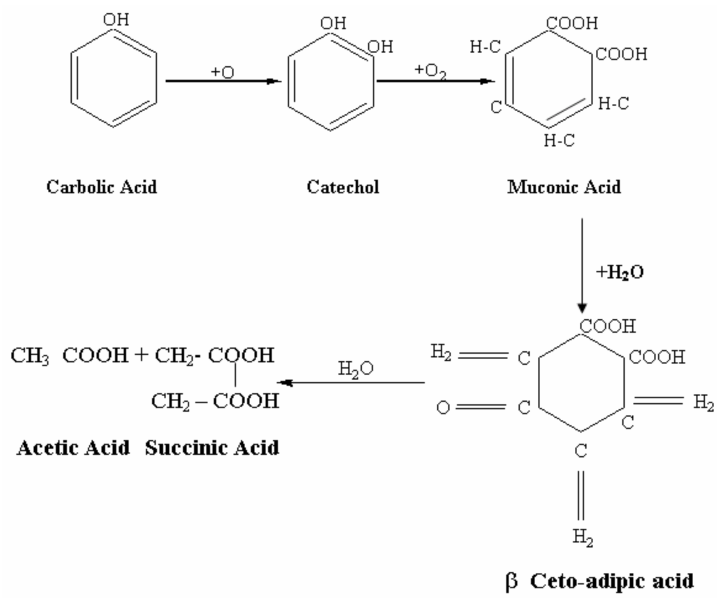

Fig. (1) The Behavior of Phenols in Biological Degradation

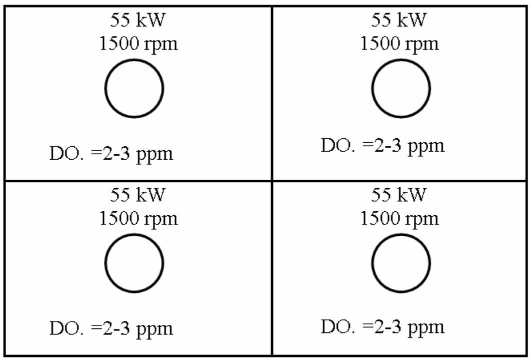

Fig. (2-a) Three Aerators in Aug. 2002, Max. Speed = 1000 rpm

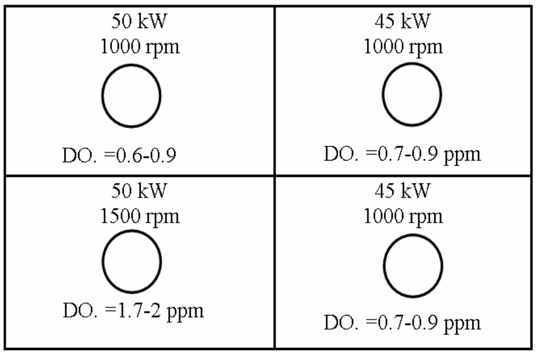

Fig. (2-b) Four Aerators in Oct. 2002 can Operate at Max. Speed =1500 rpm

Fig.(3) Low Mixing Rate with the Alternative Drive Motor of 1000 r.p.m. (after Brochier[4])

Fig. (4) High Mixing Rate With the New Drive Motors of 1500 r.p.m. 55 Kw. (after Brochier[4])

تحسين كفاءة إزالة الفينول في محطة معالجة المياه الثقيلة في مصفى الدورة

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الخلاصة

نتيجة للعقوبات المفروضة من قبل الأمم المتحدة على العراق،لم تتم عملية تبديل قطع الغيار والصيانة الدورية لوحدة معالجة المياه الثقيلة التابعة لمصفى الدورة مما تسبب في زيادة تراكيز الملوثات المطروحة من الفينولات والمتطلب الحيوي للأوكسجين (BOD_5) في المياه المطروحة للنهر. تم تشخيص سببين رئيسيين لهذا المشكل: السبب الأول، زيادة تراكيز الهايدروكاربونات المطروحة في مراحل تصفية الوقود في المصفى؛ السبب الثاني، انخفاض كفاءة المهويات في منظومة المعالجة البايولوجية. خلال فترة إجراء البحث، تراوحت قيم تراكيز الفينول بعد المعالجة البايولوجية بين (0.06-0.13) ملغم/لتر بينما كانت تراكيز المتطلب الكيميائي للأوكسجين (COD) تتجاوز 110 ملغم/لتر بعد نفس فترة المعالجة البايولوجية. تم تحسين كفاءة وحدة المعالجة بعد الإجراءات التالية: الأول، إعادة استخدام المياه الملوثة المطروحة من بعض المبادلات الحرارية ثم عملية فصل المياه الملوثة ذات الحمل العالي عن المياه الملوثة ذات الحمل الواطئ ؛ الثاني ، تقليل مطروحات الهايدروكاربونات المطروحة من الموائع المساعدة لعملية التكسير والتكسير باستعمال تقنية البخار؛ الثالث، تبديل محركات المهويات في المعالجة البايولوجية. بعد تبديل المحركات تم تقليل تراكيز الفينول في المياه المعالجة لتصل إلى (0.03-0.05) ملغم/لتر وقيمة المتطلب الكيماوي للأوكسجين (COD) إلى 60 ملغم/لتر قبل المعالجة التالية.