

## **RESPONSE OF *CYPRINUS CARPIO* TO PHENOL AND FURFURAL SHOCK LOADS IN PACT SYSTEM**

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**Key words:** *Activated sludge, cyprinus carpio, PACT, oil refinery effluent, Shock load*

### **Abstract**

Treatment efficiency, design factors and kinetic coefficients were studied using two pilots of activated sludge (AS) and powdered activated carbon technology (PACT), for treating Tehran Oil Refinery effluent, in a duration of more than 12 months. In order to evaluate the performance of each system against growth inhibitor shock loads, different concentrations of phenol and furfural (10-300 mg/l) were applied, following a series of experiments in which, treated effluents from the two systems were used as influent water into two aquariums containing freshwater Common Carp (*Cyprinus carpio*) of 9-15g weight, 6-9 cm length and with a fish density of 5g/l. Results of fish fatal rates with 125 and 250 mg/l phenol, were 16% and 38% for AS system and 5.6% and 8% for PACT system, respectively. Changing the growth inhibitor to furfural, with a concentration of 100 mg/l, led to the fatal rates of 100% and 0% for AS and PACT systems, respectively. Increasing furfural load to 300 mg/l, destroyed only 20% of fish in PACT pilot.

### **Introduction**

Oil refinery effluents have complex qualities because of complicated processes in which water is in contact with different chemicals. Referring to the classification of oil refinery wastewaters(5) into the effluents of refining operations, water, electricity and steam generation and general services, final effluents in this industry are well diversified and besides degradable organic load, dissolved and suspended solids and oxygen demand, generally contain ammoniacal compounds, hydrogen sulfide, heavy metals, organic solvents and aromatics. Major methods of decreasing the contamination load of oil refinery effluents include process control, waste separation in different stages and final effluent treatment, using physical, chemical and biological systems.

Application of powdered activated carbon (PAC) in activated sludge treatment system, is proposed as a biological method for treating oil refinery effluents (PACT process). In 1977, results of the use of PACT process for the treatment of an oil refinery effluent, was compared with conventional activated

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sludge and GAC column leading to the choice of PACT system as the most appropriate (7). Following a series of experiments in the decade of 1980-1990, the PACT process was considered as an efficient method for controlling toxics, improving biological flocs and increasing degradable organics removal efficiency (6). Its ability in removing phenol from industrial effluents was also emphasized (8). Another study on oil refinery effluent treatment by this method (9) showed an increase in ammoniacal-nitrogen removal through nitrification and the improvement of final effluent quality based on COD and TOC. It was also confirmed that the sludge volume index (SVI) improves significantly in PACT process, comparing with conventional biological treatment methods.

Another survey on oil refinery effluent showed that the PACT system may increase ammoniacal-nitrogen removal efficiency and provide more resistance to toxic and organic shock loads, besides the increase of sludge retention time (SRT) (4). It was then confirmed that the application of PACT system for treating oil refinery effluents, may lead to significant decrease of toxics, comparing with AS system. Also, bioassay tests on 2 types of fish showed that after 96 hours of contact with treated effluents of PACT and AS systems, the fish fatal rates were 95% and 100%, respectively (10).

Tehran Oil Refinery is actually equipped with an activated sludge treatment system. Its rates of daily water use and wastewater production are 20,000 CM and 7000-8000 CM, respectively (1).

The work presented in this paper, investigates on the use of 2 pilots of AS and PACT for treating Tehran Oil Refinery effluent, in order to determine (i) organic removal efficiencies and (ii) responses to toxic compounds shock loads, for the two systems.

The principle objective of this research was to achieve and appropriate quality for treated effluent in order to reuse it as water supply in cooling towers or to discharge it into water resources.

#### Materials and methods

Two pilots, both equipped with: raw wastewater tank (primary settling tank), aerobic reactor with complete mixing (diffused aeration) and secondary settling tank, were designed and operated. One of them was connected to a tank filled with Iran manufactured PAC (mixed with water, as slurry). Phenol and furfural were fed to the aeration tank of both systems; treated effluents discharged from pilots were introduced to separate aquariums for bioassay tests.

Basic characteristics of the two pilots and their simple flowdiagram are demonstrated in Table 1 and Figure 1, respectively.

Raw effluent, after passing oil gravity separators was conducted to the raw effluent tank. Afterwards, it was fed to both AS and PACT systems. PAC manufactured in Iran was based on wood; its adsorptive characteristics and impurities were firstly determined (Table 2). Freshwater Common Carp (*Cyprinus carpio*), (with 6-9 cm length and 9-15 g weight) and a rate of 5 g fish/l (based on standards), were used for bioassay studies, which were conducted in three stages.

At the first stage, after the determination of optimum conditions of operation for AS and PACT pilots, with 2000 mg/l PAC and hydraulic retention time of 10.5 hours, the two treated effluents were conducted into the aquariums, in order to study the behavior of chosen fish. At the second and third stages, after applying shock loads of phenol (10,20,30,40,80, 175 and 250 mg/l) and furfural (50,100,150,200 and 300 mg/l), respectively, responses of *Cyprinus carpio* were investigated.

All of the experiments were performed based on (2) and (3). Furthermore all chemicals had laboratory grades and were manufactured.

#### Results

Results of the study on Tehran Oil Refinery effluent organic removal efficiencies by two pilots of AS and PACT, after providing optimum and stable conditions, are shown in Table 3, based on BOD<sub>5</sub>, COD and TSS.

In Table 4 and 5, COD and BOD<sub>5</sub> changes in treated effluents from AS and PACT pilots, a number of hours after shock loads of phenol and furfural, are demonstrated.

The fish fatal rates (expressed as weight percent), 24 to 96 hours after shock loads of phenol and furfural, are shown in Table 6.

#### Discussion

The data presented in Table 3 indicates that in optimum conditions, the PACT system has more capability in removing biodegradable organics and in decreasing chemical oxygen demands, compared with the AS system. On the other hand, subsequent experiments showed that the optimum hydraulic retention time (HRT) was 10.5 hours for both systems, optimum concentration of PAC addition in aeration tank was 2000 mg/l and optimum cellular retention time were 55 and 10 days, respectively for PACT and AS pilots.

Results in Tables 4 and 5 and the data demonstrated in Figures 2 and 3, indicate that the PACT system, present more resistance against the influent of different concentrations of phenol and furfural, besides their shock loads to the system. Furthermore, the recovery time after phenol and furfural shock loads, was significantly lower for the PACT system, comparing with the AS system.

This study showed that in the conditions of non-toxic loading, the fish in contact with the treated effluents of the two pilots, had zero fatal rate, even after a period of 21 days. But following phenol influent loading of maximum 250 mg/l, 38% of fish were killed in the AS system and only 8% in the PACT system. Also for furfural, 100% of fish were killed in the AS system with 100 mg/l toxic load, whereas only after the toxic load of 300 mg/l, the fatal rate in the PACT system reached to 20%.

Results of this investigation, confirmed completely the findings of former researchers about the role of PAC in activated sludge process, as for providing uniformity in the treatment, for decreasing toxic shock probability and also for adsorbing hard-degradable organics. Meanwhile, studying the results of PACT treatment system, indicated that its treated effluent may be reused as make-up in cooling towers, or may be discharged into surface of groundwater resources.

Table 1- Specifications of PACT and AS pilot plants

Unit No.	Unit Name	No. of Units	Unit Volume (L)
1	Combined stock and settling tank	1	1000
2	Aeration tank	2	275
3	Final clarifier	2	95
4	PAC container	1	20
5	Phenol and furfural container	2	3
6	Bioassay aquariums	2	28

Table 2- Specification of Iran's PAC compared with the Merck PAC

Parameter, Unit	Iran's PAC	Merck's PAC
Apparent density, g/cc	0.495	0.49
Ash, %W	4	3.9
Moisture, %W	2.8	1.9
pH	8.1	7.2
Water solubility, %W	0.37	0.3
Acid solubility, %W	1.2	1
Ethanol solubility, %W	0.26	0.2
Weight loss at 120°C, %W	2.8	0.5
Weight loss at 550°C, %W	7.1	1
Active surface area, m <sup>2</sup> /g	540	900
Iodine number, mg/g	500	720
Molasse number, mg/g	650	805

Table 3- Mean concentration of basic parameters in raw and treated effluents

Parameter	Raw wastewater	treated effluents	
		PACT	AS
BOD <sub>5</sub>	115.2	2.05	19.25
COD	198.23	3.75	33.34
TSS	162.48	2.86	30.43

Table 4- COD and BOD<sub>5</sub> changes in treated effluents from PACT and AS systems, hours after phenol shock load (250 mg/l), mg/l

Hours	Influent		Effluent			
	BOD <sub>5</sub>	COD	PACT		AS	
			BOD <sub>5</sub>	COD	BOD <sub>5</sub>	COD
0	135	215	2.75	4	23.5	36
3	-	270	-	15.75	-	83.75
6	-	270	-	12.5	-	84.5
9	-	270	-	12.5	-	86.5
12	-	215	-	8.25	-	65.8
24	130	215	4.5	6.5	40.5	65.5
48	125	205	2.6	3.5	37.5	61.5
72	120	230	2	3.5	36.25	66.25
120	115	200	2	2.75	29.5	54
168	120	210	1.9	3.25	27.5	48.76

Table 5- COD and BOD<sub>5</sub> changes in treated effluents from PACT and AS systems, hours after hours after furfural shock load (300 mg/l), mg/l

Hours	Influent		Effluent			
	BOD <sub>5</sub>	COD	PACT		AS	
			BOD <sub>5</sub>	COD	BOD <sub>5</sub>	COD
0	140	245	2.8	4.95	23.85	40
3	-	240	-	16.5	-	84
9	-	235	-	12.5	-	85.25
24	125	230	6.75	7.25	43.75	73
48	120	230	1.9	4.15	48.2	69.75
72	120	230	1.6	3.25	37.5	63.8
120	110	200	1.95	3	31.5	48.75
168	110	220	1.8	3.25	24.5	46.45

Table 6- Weight percent to fish killed, several hours after shock-loadings

Pilots	Phenol, mg/l					furfural, mg/l				
	10-40	80	125	175	250	50	100	150	200	300
PACT	0	0	0	0	8	0	0	10	17	20
AS	0	15.2	21.4	26.2	37.8	0	100	100	100	100

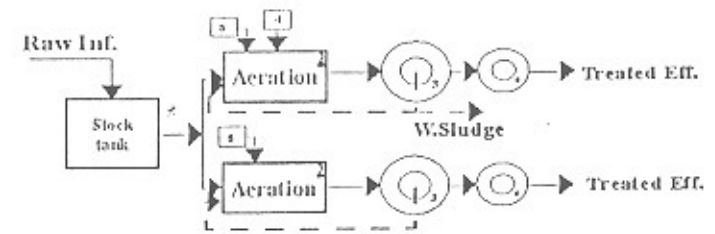


Fig. 1- The simple flowsheet of two pilot plants (AS and PACT)

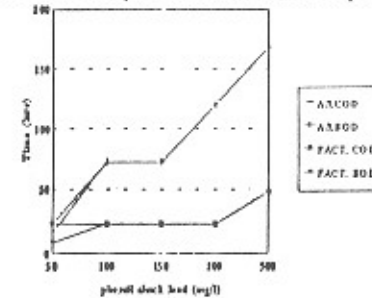


Fig. 2- Recovery time for two pilots after phenol shock loading by different concentrations

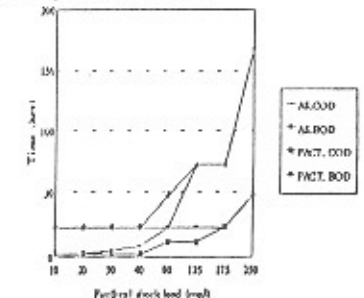


Fig. 3- Recovery time for two pilots after furfural shock loading by different concentrations

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