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MINERAL POLLUTANTS TREATMENT IN PETROCHEMICAL INDUSTRY WASTEWATER

(Case Stady: Mobin petrochemical Co.)

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ABSTRACT

Industrial wastewaters are necessary to be seriously attended in the environmental point of view, due to the possible existence of chemical and toxic components, which are generated during different production process. The aim of the present study is to reduce the percentage of contaminants and mineral elements, in the wastewaters of Mobin petrochemical Co, through the assessment of proposed method. Therefore, sampling from wastewater and measure important contaminants up within a period of 3 months. The current filtration system in Mobin petrochemical CO, is standard active sludge. However, correct relatively output of this system, the percentage of some components and elements are significantly different from standards. The aim of the present study is to reduce the percentage of contaminants and mineral elements (such as nitrate, sulfate, phosphate and some heavy metals) Therefore, the proposed system (Membrane Bioreactor) is able to reduce and eliminate some of the contaminants, and in the optimum qualification and proper usage, it would eliminate most of the contaminants. Using the Taghuchi method, four parameters by four levels for each of them were specified. The effects of any parameters on contaminants elimination were assessed by statistic analyses, and the optimum qualification established. The following qualification is the best performance for elimination of contaminants: pH=8. Flow rate=20mg/liter. Hour. Subsist time=6 hours. Solvable oxygen = 3 mg/ liter. In this qualification, reducing and elimination of nitrate, sulfate, phosphate, iron, manganese and copper is possible based on the standards. However, Al^{+3} and Cr did not achieve to the standard levels, by any of experiments. It shows that increasing of output and efficiency, needs combinational and or supplemental methods.

Keywords: Industrial wastewaters, Petrochemical, Membrane Bioreactor, Active sludge, Taghuchi method

INTRODUCTION

Petrochemical complex is one of the most important and the biggest country production industries that required much water and is one of the biggest water consumers in big industries that in result of their activity produced much amounts of industrial wastewater [1]. In Iran first year 1343 Shamsy, national company of petrochemical industries dependent to national company of Iran oil formed and its activity initiated. Petrochemical industries in Iran have background about a half century [2].

Petrochemical industries with attention to entity of activities and accomplished processes and for production of effluent, diffusion of pollutant gases, dangerous wastewaters have bad effects on environment [3]. Different combinations are in wastewater of industries oil and/or effluents that used oil derivatives. Different methods employed for deletion of the pollutants that they mostly for their indecomposable and constant structure, recognized as environmental problem [4]. Today accompany with increase of use of oil derivations for preference of petrochemical industries and their penetration in all industries, content and quantity of petrochemical wastewater became different and has organic combinations like hydrocarbon combinations, Aniline, Nitrobenzene, Organochlorin, Phenol and ect, that everyday addicted to amount of entry of the oil combinations to environment [5].

Petrochemical wastewater has heterogeneous and complex combinations that even their low amounts are toxic and inhibited growth and activity of microorganisms in biological units [6]. Also discharge of wastewater of petrochemical industries with attention to entity of their combinations resulted in destruction of considerable part of biological elements. Major environmental problems of the industries especially in conditions of dissimilation of environmental standards caused hazardous consequences [7].

Consequences of this pollution especially heavy metals isn't limited to ecosystem vital performance but it is waved to humanely societies and affected on human healthy [8, 9]. Therefore, the study indicated that chemo physical methods like oxidation reduction, chemical sediment, filtration, electrochemical treatment, evaporation, ionic exchange and reverse osmosis process have limitations and aren't affordable commercially [10]. Petrochemical complex Mobin instituted in earth with width 84 hectare, and this company initiated its activity in year 1380. Products of the company included power, vapor, cooling water, drink water, boiler water, fresh water, water without solutions, competed air, azoth and oxygen that employed for servicing economical specific region of energy pars. Major target in the investigation is decrease of amount of pollutants and mineral combinations e.g. Nitrate, Sulfate, phosphate, heavy metals in output wastewater of petrochemical Mobin.

Introduction of unit effluent purification of petrochemical company Mobin:

Purification units of industrial wastewater and incinerator of petrochemical company Mobin instituted in southwest side specific region energy Pars. With initiation of purification unit of industrial wastewater, hygienic and chemical wastewater, petrochemical complexes placed in region like Ghadir (included photic, MEG).

Arya sasol, Pars, Ja, Zangros, Borzooyeh (included Pardis, Kavian, Morvarid, Mehr) collected by a tube 24 inch, Mixed and then entried to purification unit of petrochemical effluent Mobin [11]. Input wastewater to petrochemical complex Mobin after entries to complex in DAF buoyancy resource during coagulation and clotting stages, added chemical materials like chloropheric and polyelectrolyte and pollutions became as clot and then collected to figure of chemical sludge of on resource, to then burn in incinerators. Industrial wastewater after exited of chemical sludge laver, mixed with hygienic wastewater in 3 resources that this hygienic wastewater considered as resource of supply and nutrition of microorganisms.

In purification stage, sewage wastewater aerated and performed biological purification. In this part, soluble oxygen is about pH 5.5 and 6.5. Purified wastewater before final exit exposed gritty filters and active carbon beds that this practice is for clearing and decrease of suspended materials present in soluble and also performed for compensation of deficit of prior units. In finally, COD of output water reached to sub 100 and this water mixed with freshwater to ratio 1/3 output water of purification unit and 2/3 of fresh water and used for fire station.

Output water of purification wastewater is 220 meter square per hour. In stage related to biological purification in secondary precipitation laver, every week produced 2 ton biologic sludge. Biological and chemical sludge that formed sent to incinerator unit for burning. For this purpose, is used rotator incinerator for solid material with capacity 585 kilo per hour in temperature 700 degree siliceous and 2 static incinerator with capacity 3000 kilo per hour for liquid materials in temperature 900 degree siliceous [12].

MATERIALS AND METHODS

In this investigation, first analysis of input wastewater of each of petrochemical units and comparison with standards performed. For this purpose, wastewater for 3 months (Farvardin, Ordibehesht and Khordad) and every month 3 repeat and two shift of day and night measured. Then, purification method identified and output results analyzed.

Amount of heavy metals and mineral materials considered. Then, Suggested method examined in case of simulated wastewater and result compared with standards. In end, resulted sludge of process of suggested purification compared with resulted sludge of process in present conditions and analyzed.

All experiments performed on basis of standard instruction [13].

Suggested method is use of membranous bioreactor of dipping type. Effective agents in experiments divided to two groups on basis of statistically method Taguchi:

1- S: incontrollable agents

2- N: controllable agents (signal agents)

In this noise, method of analysis of ratio signal to noise for determination of the best performed of experiments or the best combination of levels of different agents for obtaining optimal response.

Since in this investigation, putative response is percent of deletion of mineral pollutants, thus by equation S/N, this ratio determinate:

$$S/N = -10\log\frac{y_1^{\frac{1}{2}+\frac{1}{2}+\cdots} y_2 y_n^{\frac{1}{2}}}{n}$$

Where *Yn* is amount of measured response for every experiment and n is number repeat of every experiment.

RESULTS AND DISCUSSION

In table 1, output wastewater of 4 sites (Arya sasool, Morvarid, Kavian and MEG) are with higher range pH of designed limit that indicated basophiling of wastewater.

Input wastewater to purification station Mobin also has pH 8-12. In output wastewater of purification station Mobin, amount of ion cl^- has fewer rates that determined limit. Input wastewater to biologic laver for COD and amoniacal nitrogen also has higher rate than designed rate. On basis of table 1, N_NH_3 also has high rate.

Table1. States of input wastewater to complex in months Farvardin (sample 1)

Wastewater COC	pars			Arias soul			jam		
	The design	Actual Value		The design	Actual Value		The design	Actual Value	
		8:00	22:00		8:00	22:00		8:00	22:00
Status Valve	o/c	#	#	o/c	0	0	o/c	#	#
COD(ppm)	--<4106			--<4106	263	248	--<4106		
TDS(ppm)	--<106			--<106	13/7	108	--<106		
TSS(ppm)	--<667			--<667	3/1	4/1	--<667		
N-NH3(ppm)	<50			<50	5/95	8/6	<50		
PH	6-8/5			6-8/5	8/8	8/8	6-8/5		
SO_4(ppm)	--<500			--<500			--<500		

MEG		Nori			Zagrous 1			Zagrous 2	
Actual Value		The design	Actual Value		The design	Actual Value		Actual Value	
8:00	22:00		8:00	22:00		8:00	22:00	8:00	22:00
0	0	o/c	#	#	o/c	c	c	c	c
529	769	--<4106			--<4106				
13/8	140	--<106			--<106				
0/55	1/8	--<667			--<667				
10/7	10/9	<50			<50				
9/2	9/3	6-8/5			6-8/5				
		--<500			--<500				

Wastewater COC	Pardis 1			Mehr			Morvarid		
	The design	Actual Value		The design	Actual Value		The design	Actual Value	
		8:00	22:00		8:00	22:00		8:00	22:00
Status Valve	o/c	c	c	o/c	0	0	o/c	0	0
COD(ppm)	--<4106			--<350	48	36	--<1000	220	208
TDS(ppm)	--<106			--<1500	610	773	--<800	2/5	80
TSS(ppm)	--<667			--<200	5/1	3/8	--<100	1/1	11/2
N-NH3(ppm)	<50			<49	0/26	1/01	<50	4/9	4/9
PH	6-8/5			6-10	8/2	8/6	6/5-7/5	9/1	8/1
SO_4(ppm)	--<500			--<500			--<500		

kavyan		
The design	Actual Value	
	8:00	22:00
o/c	0	#
--<1000	384	
--<6500	2377	
--<100	9/5	
<50	17/9	
6-8/5	12/1	
--<500		

Sanitary sewage entering the biological pond				
TEST SAMPLE	PH	COD PPM	Cond. Ms/cm	N-NH3 ppm
The design	6-8/5	--<430	--<3000	--<150
8:00	7/4	237	620	34/3
16:00	7/3	270	953	43/5
22:00	6/8	206	980	62/9

Mobin petrochemical wastewater entering the wastewater treatment unit			
	The design		
		8:00	22:00
PH	6-8/5	11/8	11/1
COD(ppm)	-<1260	315	384

TDS(ppm)	-<6500	702	3640
TSS(ppm)	-<90	6/9	8/3
N-NH3(ppm)	<50	7/95	28/9

Water purification Mobin petrochemical company												
TEST	PH	TSS	N-NO3	N-NH3	COD	Cl_2	Turbi	Color	Oil	Cr	SO_4	Fenol
SAMPLE		Ppm	Ppm	Ppm	ppm	Ppm	NTU	CU	ppm	Ppm	Ppm	Ppm
The design	6/5-8/5	-<50	-<50	-<2/5	-<100	0/1-0/2	-<50	-<75	-<5	-<600	-<500	-<1
Day	7/3	3/3	…	0/91	19	-<0/02	2/4	13/6		130		
Night	7/5	5/2	…	1/6	25	-<0/02	2/7	32/3	0/56	124		

Reported of status of recessive wastewater of petrochemical complexes of region of Asaluyeh and sewage productive service water of petrochemical Mobin

In table 2, is indicated presence of materials and combinations and mineral pollutants in compared with effluent output standard on basis of table present elements in petrochemical effluent Mobin are more of standard limit for different outputs. In result, with study of system of sewage purification in this complex distinguished that this system is good system and in case many of output coordinated with standards. But in mineral and heavy metals is not successful and much amount of heavy metals observed in system sludge and remainder observed in output. For this reason, is used suggested system (that used membranous bioreactor) for comparison?

Table2. Information related to analyze of biological sludge of petrochemical complex Mobin

Row	Element	Test Result (mg/l)	Effluent Standard Output (mg/l)		
			Discharge to Surface Waters	Drain on absorbent well	Agriculture and irrigation
1	NO_3^-	36	50	10	50
2	Fe	146	3	3	3
3	Po_4^{-3}	43	6	6	6
5	Al^{+3}	98	5	5	5
7	SO_4^{-2}	760	400	400	500
8	Mg	76	1	1	1
9	Cu^{+2}	35	1	1	0/2
10	Cr	77	2	2	2

Table 3 corresponded with designing of experiments on basis of model Taguchi, and number 16 experiments performed for determination of optimal limit for deletion heavy metals and mineral pollutants in suggested model.

Table 3: Results of experiments and amount of pollutants in output wastewater of suggested system

Number of tests	NO_3^- (mg/l)	Fe (mg/l)	PO_4^{-3} (mg/l)	Al^{+3} (mg/l)	So_4^{-2} (mg/l)	Mg (mg/l)	Cu^{+2} (mg/l)	Cr (mg/l)
1	65	188	91	106	1134	88	57	99
2	76	174	85	92	1005	79	50	93
3	55	191	87	121	878	102	60	100
4	51	164	76	90	776	3.8	1.3	83
5	19	7	6	13	423	2	0.26	6
6	31	29	10	20	490	3.1	0.4	6

7	**57**	**188**	**79**	**95**	**813**	**4.4**	**0.9**	**6**
8	**18**	**6**	**6**	**9**	**397**	**1.5**	**0.2**	**6**
9	**36**	**8**	**13**	**17**	**443**	**1.8**	**1.3**	**7.2**
10	**14**	**1.6**	**5**	**11**	**380**	**0.84**	**0.17**	**4.2**
11	**43**	**15**	**13**	**27**	**488**	**3**	**2**	**7.5**
12	**27**	**1.9**	**6**	**14**	**403**	**2.3**	**1.1**	**4.3**
13	**17**	**1.8**	**5**	**20**	**401**	**0.9**	**0.3**	**4.5**
14	**53**	**190**	**83**	**134**	**890**	**114**	**65**	**112**
15	**25**	**10**	**6**	**12**	**443**	**2.8**	**0.4**	**6**
16	**79**	**200**	**79**	**101**	**918**	**5**	**1.1**	**7**
	Similar to the Standard output indicator for agricultural and landscape irrigation							

Table4. Comparison of superior experiments in field of deletion of mineral pollutants

Number of tests	The initial soution pH	Flow rate (L/m^2h)	Hydrolic of Retention time (h)	DO (mg/l)	Remove Contaminants (Similar Standard)
8	7	30	9	4	NO_3^- ،PO_4^{-3} ،SO_4^{-2} ، Cu^{2+}
10	8	20	6	3	NO_3^- ،PO_4^{-3} ،SO_4^{-2} ، Cu^{2+} , Fe , Mg
12	8	30	9	1	NO_3^- ،PO_4^{-3} ،SO_4^{-2} , Fe
13	9	15	6	3	NO_3^- ،PO_4^{-3} ،SO_4^{-2} ، Cu^{2+} , Fe , Mg

In table 4, observed proper pH for successful deletion of putative pollutants, neutral and basophilic. Debby is variable of 15 to 30 liter per meter square in hour and indicated that in this cases one factor isn't major determining factors and than to other factors is less important proper it time is 6 to 9 hours and times 1 to 3 hours are not proper. Amount of proper soluble oxygen (Do) also is 3 mg/L.

CONCLUSION

With attention to that wastewater petrochemical industries have much amount of pollutants and for complex entity and diversity, many materials and combinations in production process entries and exited, necessary of accomplishment of standardization of wastewater is much important.

System of wastewater purification present in petrochemical complex Mobin is of type of common active sludge and used for agricultural irrigation and green space results indicated that wastewater output corresponded with much part of standards, but in case of some materials and elements, observed much different with standards.

Therefore, suggested system that is type of membranous bioreactor (MBR) has ability of decrease and deletion of the pollutants and if served correctly and in optimal conditions is able to deletion of much part of pollutants. Only with providing of conditions near to optimal, may possibility of deletion of pollutants and in all conditions, it not may. The best status for deletion of pollutants is:

pH=8m, Flow rate=20 mg/L/h. Retention time =6h, DO=3 mg/L.

In these conditions is possibility of deletion of Nitrate, Sulfate, Phosphate, Iron, Manganese, and Copper. But Aluminum don't reach in any of experiments to standard limit, that this indicated that for efficiency increase is necessary to served combinational and complementary methods in chemical purification. In appeared to in among of studied parameters (pH, flow rate, hydrolical retention time and DO in system), Flow rate parameter is less important than to other cases.

Recounting

[1]-(DAF):Dissolved Air Floatation

[2]-(DO): Dissolved Oxygen

[3]-(TDS): Total Dissolved Solid

[4] - Signal (S)

[5] - Noise (N)

[6] - S/N: Signal to Noise Ratio

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