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Petrochemical Wastewater Treatment Using an Anaerobic Hybrid Reactor

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Abstract: Performance of an anaerobic hybrid reactor (UASB/Filter) treating petrochemical wastewater at mesophilic condition was investigated. The reactor was seeded with flocculent sludge from a UASB plant treating dairy wastewater. The sludge was acclimatized to petrochemical wastewater in two-stage operation. After 39 weeks, a COD reduction of 70.3% was obtained at OLR = 2.0 kg m^{-3}.day and HRT = 18 h. During the reactor operation, the influent COD concentration was kept between 1000-4000 mg L^{-1} range and the organic loading rates and hydraulic retention times ranging between 0.5-24.0 kg COD m^{-3} day, respectively. The performance of the different sections of the reactor (sludge bed and fixed bed) was evaluated and is presented separately. The minimum and maximum COD reduction of the overall reactor were 42.1 and 85.9% at influent COD concentration of 3000 mg L^{-1} and 4000 mg L^{-1}, HRT = 24 h and 4h, and OLR = 3.0 kg m^{-3} day and OLR = 24.0 kg m^{-3} day, respectively.

Key words: Anaerobic treatment, hybrid, petrochemical, wastewater

INTRODUCTION

Due to the development of high-rate reactors, such as anaerobic filter (Young and McCarty, 1969) and up flow anaerobic sludge blanket (UASB) reactor (Lettinga *et al*., 1980) and a better understanding of microbiology, anaerobic technology has advanced considerably to become viable in industrial wastewater treatment (Speece, 1983). The anaerobic hybrid reactor, which operates with a sludge blanket in the lower zone and packing media forming a filter in the upper zone, was first developed in 1981 (Maxham and Wakamiya, 1981). Since then, much work has been carried out on both laboratory and full-scale reactors in order to optimize the design and operation parameters (Change, 1989; Harris *et al*., 1992; Hawkes *et al*., 1995; Tur and Huang, 1997). Some researchers showed that the hydraulic retention time (HRT) and organic loading rate are the more important parameters on reactor performance (Young, 1991). Also, some studies has been carried out for treatment of petrochemical wastes by hybrid reactor (Kleerebezem *et al*., 1997; Macarie, 2000, Montenegro *et al*., 2001, Page *et al*., 1998, 1999; Young *et al*., 2000).

Increase in yearly production capacity from 5.9 million tons in 1990 to 42.2 million tons until 2006, either due to construction of new plants or expansion of existing petrochemical plants in Iran, resulted in more quantity and higher strength of wastewater. The type of wastewaters treated by anaerobic technology in the world is completely different from wastewater produced by petrochemical industries in Iran. The reactor feed substrate is considered to be an important parameter for anaerobic reactors. So that the major part of studies on anaerobic treatment or constructed anaerobic plants for petrochemical wastewater focused on PET or PTA plants but there is only one plant in Iran that produce PET and PTA. On the other hand some petrochemical complexes are concentrated in a region named petrochemical zones that the wastewater from all complexes will be treated at one common wastewater treatment plant. This will result in more difference between the qualities and compounds of wastewater treated by anaerobic technology in here and that in other countries. In this study, the treatment of wastewater from some plants by an anaerobic hybrid reactor is studied for determining the effects of HRT and OLR on reactor performance.

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MATERIALS AND METHODS

Location: This study was conducted from October 2002 to September 2005 in ARAK petrochemical company in center of IRAN. In this complex, variety of products including chemicals and polymers are produced. Some products of this complex are: Ethylene; Propylene; C4; Pyrolize Benzene; Crude Oil; Polypropylene; High and Low Density polyethylene (HDPE and LDPE); 1-Butane; 1,3-Butadyane; Poly Butadiene; rubber; Ethylene oxide; Mono, Di and Tri Ethanol Amine; Acetic Acid; Mono, Di and Tri Ethylene Glycol; Vinyl Acetate; 2-ethyl Hexanol; Normal Butanol and Chloro Acetyl Chloride.

Model reactor: In this study, a Plexiglas column (15 cm in diameter and 120 cm in height) was used as the anaerobic hybrid reactor in this study. The upper 20 cm of the reactor was operated with fixed bed of corrugated plastic sheet with 170 m^2 m^{-3} specific surface areas. The total volume of the reactor was 18.5 L and the volume of liquid was 15.4 L. Recycle, being designed only for emergency conditions, such as clogging of the distribution system, was not used continuously during the experimental study. There aren't any solids/liquid/gas separation devices in the reactor. The schematic diagram of the model reactor is given in Fig.1.

The reactor was operated under mesophilic conditions and temperature of the influent flow was adjusted to 35°C by a heat exchanger before entering to the reactor. Also two automatically adjustable heating devices placed in the bottom and middle of the reactor adjusted the temperature of the liquid inside the reactor.

Influent wastewater to the reactor: There is an existing wastewater treatment plant in ARAK petrochemical complex. This WTP consists of some physicochemical units followed by an activated sludge system for treatment of wastewater. The output of API oil separator entered to the reactor. Because of increase in the production capacity of the existing plants, the flow and strength of wastewater was increased more than the WTP design criteria. Basic composition of wastewater is presented in Table 1.

Biological treatment processes require macronutrients such as nitrogen as nitrate or ammonium salts and phosphorous as phosphorous salts for bacterial metabolism, growth, activity and stability of process. Also, all methanogens use ammonia as nitrogen source (Singh *et al*., 1999). The COD_{tot} : N : P ratio of the wastewater is 1726:45.2:1.5 or 700:18.33:0.61. But the suitable COD_{tot}:N:P ratio for anaerobic treatment is about 700:5:1. (Bitton, 1999). The comparison of these two ratios shows that the amount of phosphorous is low. Thus phosphoric acid is added to wastewater for compensating phosphorous.

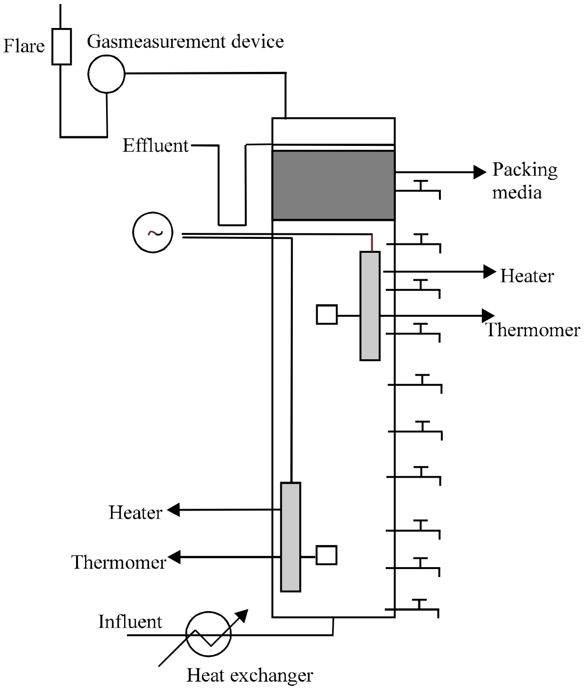

Fig. 1: Schematic diagram of the hybrid model reactor

Table 1: Basic composition of wastewater from ARAK petrochemical complex

Parameter	Range	Average	SD	No. of samples
pH	4.2-12.8	6.12	3.46	590
T,(°C)	33-36	34.5	1.19	145
*COD_{tot} ,(mg L^{-1})	600-4900	2075	1075	590
COD_{tot} , (mg L^{-1})	600-3900	1726	846	590
COD_{SUS}/COD_{tot}	0.55-0.972	0.856	0.102	53
BOD_5 /COD	0.633-0.749	0.684	0.107	19
BOD_{20} /COD	0.913-1.234	0.776	0.123	19
TDS, (mg L^{-1})	300-1070	672	232.5	53
TKN, (mg L^{-1})	6.1-148	45.2	34.8	53
TP, (mg L^{-1})	0.03-5.2	1.5	1.25	53
Alkalinity, (mg L^{-1})	240-440	366	56.4	53

*Before API separator unit, SD: Standard Deviation

Seeding: The use of appropriate seed is very important at the start up of the reactor. Because sufficient seed quality will result in process stability and minimize the start up period (Lettinga and van Lier, 2005). In Iran, anaerobic treatment process is nowhere used to treat petrochemical waste. Hence, there is no seed culture that is acclimatized to this type of wastewater. Therefore the reactor was seeded with flocculent sludge from a UASB Plant treating dairy wastewater.

Start up: The results of BOD tests at different dilutions and comparing the curves with typical BOD curves showed that there is a lag period and increase in the toxicity to bacteria to degrade petrochemical wastes, thus it is necessary to adapt the microbial cells to these wastes.

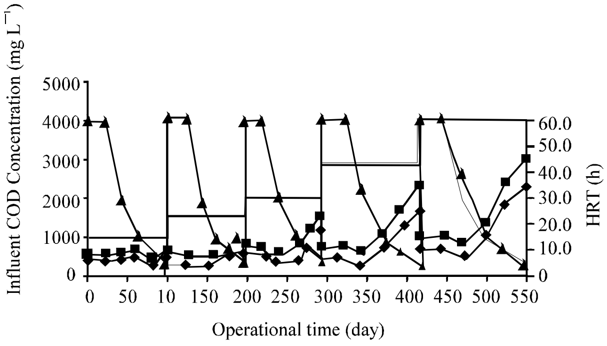

Fig. 2. Influent and effluent COD concentration among the reactor operation time

At the beginning of this study (Before measuring of BOD values), the reactor was run for 5 months without adaptation but it was unsuccessful. So it was considered to adapt the sludge in two stages. In first stage, the synthetic wastewater made from dry milk was fed to the reactor. Then in second stage, concentration of COD was increased in the feed at 10% increment per cycle till it reached 100%. After 30 weeks, a COD removal of 70.3% was obtained at OLR = 2.0 kg m^{-3} day and HRT = 18 h.

Concentration, HRT and OLR changing scheme: After successful start-up was completed on week 40, the influent COD concentration changed stepwise from 1000 to 4000 mg L^{-1}. At each COD changing steps, the HRT of the reactor changed from 48 to 24, 12, 8 and 4 h, respectively that resulted in different OLRs. By changing the hydraulic retention time and influent COD concentrations, 25 different operational conditions were applied and COD removal efficiencies measured after reaching to hydraulically steady state conditions. When hydraulically steady state conditions were reached changing to different HRTs were tried. The influent and effluent COD concentration among the reactor operation time are shown in Fig 2.

The criteria for hydraulic steady state were the following: (a) an operation period of more than 10 times the HRT (and more than 2 weeks) (Noyola *et al*., 1988); and (b) variations in effluent concentration less than± 10% (Polprasert *et al*., 1992). Elmitwalli (2000) and Mahmoud (2002) also considered these criteria satisfactory. A real steady state would only be achieved in the sludge bed and consequently in the reactor, if the operation period is at least three times SRTs (Van Haandel and Lettinga, 1994).

Analytical procedures: Samples of the influent and effluent of the model reactor were taken and analyzed according to APHA (1995). pH, COD, alkalinity and biogas volume were measured daily. The COD concentration was determined by the colorimetric method, using a spectrophotometer Hacth DR2010 at wavelength 640 nm. The pH value was measured with 692 pH-meter metrohm. A gas/liquid displacement device measured the volume of biogas.

RESULTS AND DISCUSSION

The COD reduction of the system ranging from 42.1 to 85.9% was achieved. The maximum COD reduction is obtained at influent COD concentration of 3000 mg L^{-1}, HRT = 24 h and OLR = 3.00 kg m^{-3} day. The minimum COD reduction is obtained at influent COD concentration of 4000 mg L^{-1}, HRT = 4 h and OLR = 24 kg m^{-3}.day. The COD reduction at about average COD concentration of this petrochemical complex (1726 mg L^{-1}) was ranging between 43.4-80.9% depends on operational conditions (Table 2).

The results of sludge bed region performance at different HRTs (Fig. 3) showed that the reactor performance decrease hardly if the HRT decrease to less than about 10 h, because of increase of up flow velocity that resulted in wash out of biomass. Also, increase of HRT to more than 16 h, has not significant improvement on reduction performance. This noted that the optimum HRT is about 10-16 h. Also, the obtained results at fixed bed region (Fig. 4) showed that the optimum HRT value is about 5 h.

The results of overall reactor performance versus HRT (Fig. 5) showed that the reduction of COD reached to a maximum at HRT = 24 h and then decreased gradually with increase of HRT. It can be the result of decrease in biogas production and up flow velocities that resulted in lower mixing and contact between substrate and biomass.

The tests conducted by some investigators were used to make a statistical screening ranking of parameters affecting anaerobic filter performance (Yang *et al*., 1987). This Screening showed that HRT was the most important parameter affecting COD removal performance (Young, 1991). When HRT was considered to be the sole parameter affecting efficiency, the relationship indicated that doubling the HRT would change the COD removal efficiency by about 5-44% (average 25%). Young (1991) found this value by about 12-17% for anaerobic filters.

The results of sludge bed region performance at different OLRs (Fig. 6) showed that the reactor performance increase gradually by increasing of OLR to a specific value. As shown in Fig. 6 the reduction performance increase to about 70-80% by increasing the OLR to about 5.0 kg m^{-3} day. The increase of OLR (to more than 5 kg m^{-3} day) by decrease in HRT resulted in reduced performance because of high up flow velocity resulted in biomass wash out which agrees with

Table 2: The operational condition and performance of the reactor during the experimental study

Operational conditions							
C_0 mg L^{-1}	HRT (h)	OLR kg m^{-3} day	Eff. COD (SBR)mg L^{-1}	Eff. COD (FBR)mg L^{-1}	COD Red. (SBR)mg L^{-1}	COD Red. (FBR)%	COD Red. (Total) %
1000	48	0.50	514	381	48.6	25.9	61.9
	24	1.00	654	448	34.6	31.5	55.2
	12	2.00	546	423	45.4	22.5	57.7
	8	3.00	556	396	44.4	28.8	60.4
	4	6.00	650	568	35.0	12.6	43.2
1500	48	0.75	568	385	62.1	32.2	74.3
	24	1.50	524	353	65.1	32.6	76.5
	12	3.00	498	398	66.8	20.1	73.5
	8	4.50	589	408	60.7	30.7	72.8
	4	9.00	957	675	36.2	29.5	55.0
2000	48	1.00	650	456	67.5	29.9	77.2
	24	2.00	643	418	67.9	35.0	79.1
	12	4.00	546	383	72.7	29.9	80.9
	8	6.00	1124	756	43.8	32.7	62.2
	4	12.00	1540	1133	23.0	26.4	43.4
3000	48	1.50	720	493	76.0	31.5	83.6
	24	3.00	672	423	77.6	37.1	85.9
	12	6.00	987	681	67.1	31.0	77.3
	8	`9.00	1753	1248	41.6	28.8	58.4
	4	18.00	2143	1614	28.6	24.7	46.2
4000	48	2.00	987	669	75.3	32.2	83.3
	24	4.00	893	608	77.7	31.9	84.8
	12	8.00	1389	965	65.3	30.5	85.0
	8	12.00	2512	1822	37.2	27.5	54.5
	4	24.00	2989	2316	25.3	22.5	42.1

(SBR) = Sludge Bed Region, (FBR) = Fixed Bed Region

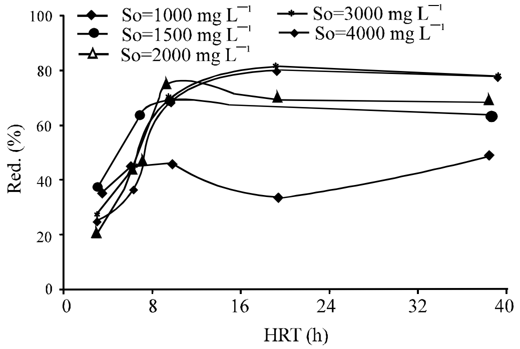

Fig. 3: Sludge bed region performance vs. HRT at different influent substrate concentrations

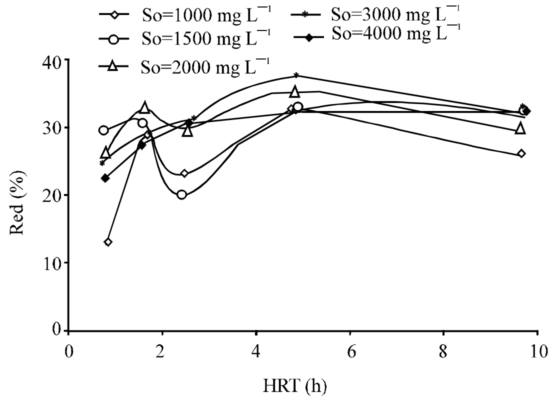

Fig. 4: Fixed bed region performance vs. HRT at different influent substrate concentrations

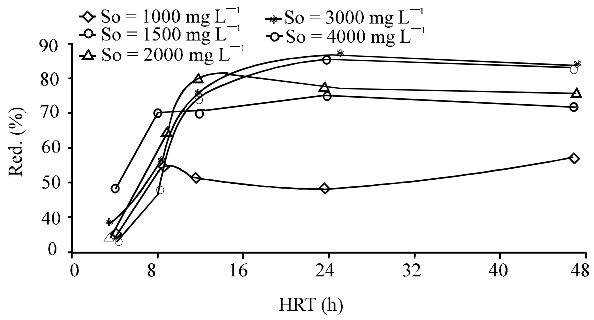

Fig. 5: Total reactor performance vs. HRT at different influent substrate concentrations

Sayed (1987), Ruiz *et al.* (1997) and Kalyuzhnyi *et al.* (1998).

Also, the results of fixed bed region (Fig. 7) showed that performance of this region will gradually decrease at OLR more than 9.0 kg m^{-3} day. The reason is decreasing of HRT to less than 2.4 h that resulted in more up flow velocity and biomass wash out. As shown in Fig. 7, the maximum applicable organic load to fixed bed region in order to reach a maximum sustain performance at influent concentration of 1000, 1500, 2000, 3000 and 4000 mg L^{-1} are 8.29, 8.78, 5.00, 9.81 and 13.8 kg m^{-3} day that resulted in 28.8, 30,73, 30.00, 31.00 and 27.5 % reduction, respectively. It can be concluded that substrate in this region is not biologically degradable or recalcitrant that resulted in lower performance (about 30%) in this region.

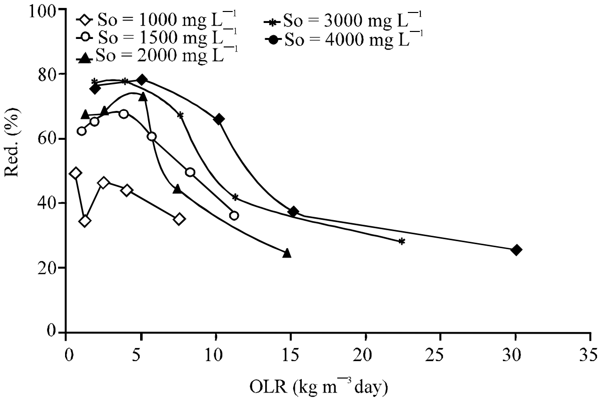

Fig. 6: Sludge bed region performance vs. OLR at different influent substrate concentrations

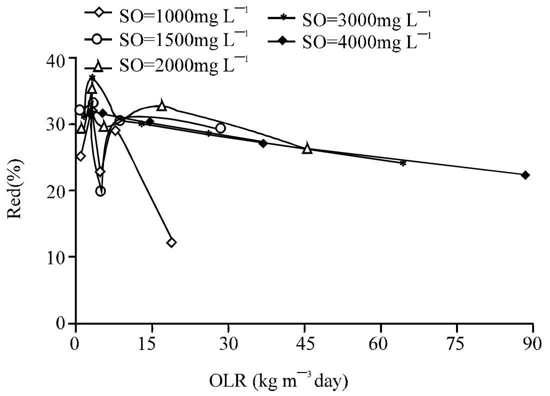

Fig. 7: Fixed bed region performance vs. OLR at different influent substrate concentrations

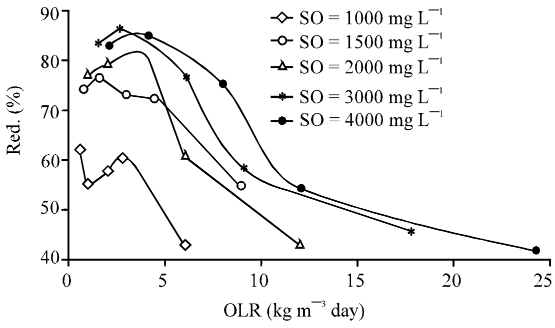

Fig. 8: Total reactor performance vs. OLR at different influent substrate concentrations

The investigation of Fig. 8 and comparing with Fig. 6 shows that the overall reactor performance depends hardly on sludge bed region performance because the major part of COD reduced in sludge bed region and performance of fixed bed is about constant. These results showed that the role of sludge bed region is about 70-85% that is very much higher than fixed bed region.

The applied organic loading rate is related to the HRT and influent COD concentration. Using applied loading rate alone as a process parameter, by doubling the OLR while holding the influent concentration constant, would be expected to decrease efficiency by -5 to 43%. Young (1991) found this value by about-8 to 15%.

CONCLUSIONS

It is necessary to adapt the seed sludge to petrochemical wastes for smooth start-up.

The start up period to achieve hydraulic steady state conditions took 9 months and the COD reduction at OLR = 2.0 kg m^{-3} day and HRT = 18 h reached to 70% at the end of start up period.

The results showed that the minimum required HRT for sludge bed region is 10 h and increase of HRT to more than 16 h has no significant effect on performance reduction. The performance of this region increased to about 70-80% by increasing the OLR to about 5.0 kg m^{-3} day. At OLR more than 5.0 kg m^{-3} day, the performance will decrease gradually.

In fixed bed region, HRT of 5 h resulted in maximum reduction and increasing of HRT to more than 5 h has not significant effect on reduction performance. The performance of this region will gradually decrease at OLR more than 9.0 kg m^{-3} day because of decreasing of HRT to less than 2.4 h. The maximum applicable organic load in order to reach a sustain performance are about 8.3-13.8 kg m^{-3} day for influent COD concentration ranging from 1000 to 4000 mg L^{-1}.

The obtained results for overall reactor showed that the performance would increase only 10% if the HRT is increased from 12 to 24 h doubles the reactor volume. The results show that the overall reactor performance according to OLR depends hardly on sludge bed region performance.

By doubling the HRT, the COD removal efficiency would change by about 5-44%. Also, by doubling the OLR, the COD removal efficiency will decrease-5 to 43%.

Finally, it can be concluded that it is possible to treat petrochemical wastes by an anaerobic hybrid reactor.

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