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The Survey of Phenol Removal from Oil Refinery Wastewater by Anaerobic Stabilization in High Temperature

[1]Abdollah Dargahi, [2]Zahra Atafar, [2]Mitra Mohammadi, [3]Ali Azizi,
[1]Khadijeh Shamsi and [2]Ali Almasi
[1]Department of Environmental Health Engineering, School of Health,
Hamadan University of Medical Sciences, Hamadan, Iran
[2]Department of Environmental Health Engineering, School of Health,
Kermanshah University of Medical Sciences, Kermanshah, Iran
[3]Department of Social Medicine Specialist, Faculty of Medicine,
Kermanshah University of Medical Sciences, Kermanshah, Iran

Abstract: Phenol is one of the most common organic pollutants which is toxic even at low concentrations. The main objective of this study was to survey the effect of phenol concentration on the anaerobic waste stabilization pond efficiency for the treatment of oil refinery wastewater in high temperature. In this study, phenol was added as the input for the WSP at various concentrations at high temperature. N-NH_3, phenol, COD, BOD and pH affecting the efficiency of anaerobic WSP were investigated which were utilized for the treatment of oil refinery waste water. The results obtained were indicating that the efficiency of anaerobic WSP increase when the concentration of phenol was decreasing (in temperature of 32°C). Also, the efficiency of the anaerobic WSP utilized for the treatment of oil refinery wastewater will be improved if temperature would be high and concentration of phenol would be low.

Key words: Anaerobic stabilization pond, phenol removal, oil refinery wastewater, temperature, phenol

INTRODUCTION

Phenol (C_6H_5OH) is one of the toxic aromatic hydrocarbons with molecular weight 94.11g mol^{-1}. The pure form of phenol in the solid is white but it is mostly colored due to the presence of impurities (Almasi *et al*., 2014). Phenol has a sweet taste, tar like odour and it is soluble in organic solvents such as alcohol, glycerol, petroleum etc however it is partially soluble in water (Basha *et al*., 2010). Phenol is one of the most common organic pollutants because it is toxic even at low concentrations (Almasi *et al*., 2014, 2012). Phenol and its derivatives are reported to be present in the effluent of many industries such as paper and pulp, pesticides, dyes and chemical manufacturing industries (Dargahi *et al*., 2014).

In addition to this, wastewater originating from other industries such as resin manufacturing, gas and coke manufacturing, tanning, textile, plastic, rubber, pharmaceutical, oil refineries, ceramic, steel, coal conversion processes, phenolic resin industries and petroleum also contains different form of phenols (Almasi *et al*., 2012; Dargahi *et al*., 2015; Bu *et al*., 2011). Phenols are also present in domestic effluents (Caetano *et al*., 2019). Therefore, wastewaters containing phenolic compounds can cause serious water pollution due to their poor biodegradability, high toxicity and ecological aspects (Almasi *et al*., 2012). Therefore, it is considered as a priority pollutant due to its adverse health effects even at low concentrations (Darhahi *et al*., 2014).

According to the World Health Organization regulation, maximum permissible concentration of phenol in potable water is 0.002 mg L^{-1}. The Environmental Protection Agency (EPA) has set that maximum permissible phenol content in wastewaters must be <1 mg L^{-1} (Almasi *et al*., 2012). That is why phenols and phenol compounds containing wastewaters must be treated before discharge into the aquatic environment (Reis *et al*., 2007).

Several technologies have widely been utilized for removing phenol and phenolic compounds from wastewaters such as physicochemical, biological, adsorption and chemical oxidation processes (Almasi *et al*., 2014, 2012). But such problems as high cost, low efficiency, formation of toxic by products and applicability to a limited concentration range are associated with the above methods.

On the other hand, biological processes have advantage over these methods which have little or no harmful effects on the environment because this techniques do not involve the use of harmful reagents (Jarboui *et al*., 2010). Among these biological treatment

Corresponding Author: Ali Almasi, Department of Social Medicine Specialist, Faculty of Medicine, Kermanshah University of Medical Sciences, Kermanshah, Iran

sysem Waste Stabilization Pond (WSPs) is useful for both industrial as well as municipal wastewater treatment. WSPs have been widely utilized in developing countries especially in rural areas (Corbitt, 1999; Beran and Kargi, 2005).

WSPs offer a cheap and attractive alternative to conventional processes in case adequate land is available (Almasi *et al*., 2013). Now a days, WSP has been used in many parts of the world as a series of anaerobic, facultative, maturation ponds (Ghazy *et al*., 2008; Naddafi *et al*., 2009; Dargahi *et al*., 2014; Mara, 2004).

In these systems, pollutants are removed from streams through settling operation or biological and chemical convert processes (Beran and Kargi, 2005; Almasi *et al*., 2013; Ghazy *et al*., 2008; Naddafi *et al*., 2009; Dargahi *et al*., 2014; Mara, 2004; Rajbhandari and Annachhatre, 2004). Anaerobic ponds are the smallest units in the series.

They are sized according to their volumetric organic loading which may receive volumetric organic loadings in the range 100-350 g BOD_5/m^3day, depending on the design temperature. The depth of anaerobic ponds is in the r ange 2-5 m and HRT are usually between 2 and 5 days (Varon and Mara, 2004). Anaerobic ponds work extremely well in warm climates: for example, a properly designed pond will achieve around 60% BOD_5 removal at 20°C and over 70% at 25°C and above (Almasi *et al*., 2013; Ghazy *et al*., 2008; Naddafi *et al*., 2009; Varon and Mara, 2004).

Literature survey revealed that there are no comprehensive reports on phenol removal from oil refinery wastewater by anaerobic WSP. Therefore, the main aim of present study was to design an anaerobic pond at pilot scale for treatment of Kermanshah oil refinery wastewater.

MATERIALS AND METHODS

This experimental study was carried out as fiberglass pilot scale. The dimensions of WSP were 0.2 m (width)×1 m (height)×1 m (length). The reactor was designed and launched in Kermanshah chemical laboratory of water and wastewater of Faculty of Health, Iran. Experiments were carried out at ambient air temperatures ranging from 35-42°C. Average temperature of pond was kept to 32±2°C. Hydraulic Retention Time (HRT) and hydraulic load was 5 days and 40 L day^{-1}, respectively.

The pond was loaded daily by the wastewater output of oil and grease separator unit of Kermanshah oil refinery. Kermanshah Oil Refinery raw wastewater containing: COD (Chemical Oxygen Demand) = 620 mg L^{-1}, BOD5 (Biochemical Oxygen Demand) = 200 mg L^{-1}, TSS (Total Suspended Solid) = 56 mg L^{-1}, VSS (Volatile Suspended Solid) = 44 mg L^{-1}, N-NH3 = 13 mg L^{-1}, phenol = 70 mg L^{-1} and pH = 8 At first, 1.5 L of sewage sludge added to 1 L oil refinery sludge in order to seeding. After three month, WSP was ready for launching. To adjust the anaerobic pond loading within the defined ranges and increasing the amount of phenol, the molasses was used. In present study was surveyed phenol various concentration (100, 200, 300 and 400 mg L^{-1}) in high temperature on pond efficiency. The parameters of NH_3, PO_4, COD, BOD, pH and phenol were measured according to standard method (APHA *et al*., 2005).

Oxidation and reduction potential of pool were measured to maintain and provide an anaerobic conditions. This parameter was determined using a Kent ORP meter (7020 model and with the Eil sensors). All of chemical was purchased from Merck CO., Germany. To clarify the phenol volatility theory, the pond's surface was isolated with a layer of paraffin and plastic cover and the system performance was evaluated. Three consecutive samples showed that the performance rate of the anaerobic pond is almost equal in both open and closed conditions. The removal efficiency of pollutants was calculated by using Eq. 1:

$$R\% = \left[\frac{C_i\text{-}C_e}{C_i}\right]\times 100$$

where, Ci and Ce were the initial and final concentrations of pollutants in the solution, respectively. Statistical analysis was performed by SPSS ver 12 (e.g., t-test and ANOVA). Operational conditions of anaerobic pond system are based on Almasi and Pescod experiments (Almasi and Pescod, 1996).

RESULTS AND DISCUSSION

Figure 1 shows the mean removal efficiency of measured parameters in different concentrations of phenol in anaerobic pond effluent of Kermanshah oil refinery. The anaerobic conditions during process were confirmed by oxidation-reduction potential (ORP = 246). In the system, loading volume in 32°C temperatures was 104.2,

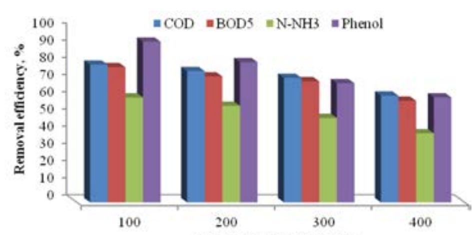

Fig. 1: Mean removal efficiency of measured parameters in different concentrations of phenol in anaerobic pond effluent of Kermanshah oil refinery

121.54, 136.01 and 148.12 $gBOD_5/m^3$.day for phenol concentrations of 100, 200, 300 and 400 mg L^{-1}, respectively.

Results indicated that the studied parameters have dramatically affected the WSP efficiency in oil refinery wastewater treatment (Table 1). The system performance was significantly increased with decreasing phenol concentration in 32°C ($p<0.001$). The performance of laboratory-scale anaerobic stabilization pond in removing the COD and BOD_5 is better than that of Papadopoulos *et al*. (2001) study results even in high phenol concentration. The results of current study showed that the removal efficiencies of BOD_5 and COD from the urban sewage by anaerobic WSP were 45 and 50%, respectively. COD/BOD ratio in the input and output of the system were 2.07 and 2.05, respectively (Papadopoulos *et al*., 2001).

Moreover, the WSP performance in treatment of the oil refinery wastewater with phenol different concentrations in input was better than that of Mahssen's study results. In the current study, the removal efficiencies of COD, BOD_5 and PO_4 by WSP were 28.89, 22.21 and 16.91%, respectively. In our study, the increase of COD removal compared with BOD removal can be attributed to the multiphase state of the oil wastewater in which its layers have been settled on the surface and there is the volatility potential for them. Moreover, some of the layers are separated from the liquid due to hydrophobic property and precipitate in the water column of the reactor or remain suspended in the liquid column. Another advantage of this system is biodegradation of resistant materials.

Due to the bacterial hydrolysis, these compounds were converted into catechol, aldehydes and acids and can be degraded by WSP. For this reason, besides the higher removal of COD in the reactor effluent compared with the BOD_5, the COD/BOD_5 ratio was identical in both input and output of the anaerobic bioreactor.

These results are consistent with the Papadopoulos study (Papadopoulos *et al*., 2001). Closeness of results in our study in BOD_5 and COD removal with the results of other researchers like Mara (1976), Oliveira (1990), Oswald *et al*. (1976) and Arceivala (1973) is evident. Their study showed that the removal efficiency of BOD5 from the wastewater in anaerobic ponds under 32°C conditions is 60-70%.

Also, it is consistent with the study undertaken by Almasi and pescod who used the anoxic pond for wastewater treatment in hot conditions with different volumetric organic loads (Almasi and Pescod, 1996). Almasi and Pescod have shown that the rate of BOD_5 and COD removal under the warm conditions by the anoxic pond system were 77 and 68.28%, respectively. The temperature effect on the speed of the biological reactions is an evident and proved fact. Ababa (2010) noted that anaerobic ponds are primarily a warm weather event and it has been proved that anaerobic ponds perform extremely well in hot weather conditions.

The results of Gao study showed that in domestic wastewater the COD removal efficiency decreased with decreasing temperature (Tyagi *et al*., 1993). Moreover, the result of Lotta Leven study on phenol removal at different temperatures under anaerobic conditions showed that the phenol removal increased in high temperature (Alemzadeh *et al*., 2002).

In recent years, research on various methods of biological treatment including biodegradation of oil refinery effluents in a pilot of Rotating Biological Contactor (RBC) type was performed. Results indicated that the TCOD removal efficiency by this system was 99% (Tyagi *et al*., 1993). Also results of the study by Alemzadeh *et al*. (2002) showed that phenol removal efficiency from the oil refinery effluent using the laboratory-scale RBC system was 99.9%.

On the other, Rahmani (2006)'s study results showed that the highest efficiency of removal of phenol with 50 mg L^{-1} initial concentration was obtained using the UV/TiO_2 process (80%). It's worth mentioning that the technology used in above study is expensive and requires specialized experts.

While the technology used in this study is the simplest and most flexible environmental technology. In a study undertaken by Ramos *et al*. (2005) using the laboratoryscale facultative stabilization pond in which wastewaters with high phenol content was used for

Table 1: Wastewater characteristics of influent and effluent of anaerobic stabilization poons in different concentrations of phenol in 32°C

Concentrations of phenol (mg L^{-1})								
400		300		200		100		
Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Parameters
7.2±0.33	7.9±0.38	7.13±0.3	7.85±0.33	7.09±0.2	7.91±0.35	7.09±0.3	7.93±0.41	pH
293.5±33.72	717.36±65.61	194.3±15.43	658.74±20.21	157.84±15.67	418.67±34.8	106.48±16.98	500.07±34.81	BOD5
900.67±124.8	2378.56±255.26	567.3±15.41	2061.85±63.26	440.38±43.74	1873.49±69.18	316.32±69.42	1586.06±199.6	COD
11.45±2.14	19.33±3.83	10.08±2.24	20.19±4.4	9.04±2.01	20.7±3.01	6.39±1.06	16.38±2.18	$N-NH_3$ (mg L^{-1})
180.5±10.5	464.42±15.44	113.05±11.17	369.38±14.3	48.9±13.37	266.44±9.65	11.01±1.8	171.71±12.39	Phenol (mg L^{-1})
-	143.48	-	131.74	-	118.55	-	100	Volumetric
3.07	3.31	2.92	3.13	2.8	4.48	2.98	3.172	TCOD/TBOD

removal of phenol with different concentrations, the results showed that the highest and lowest rate of phenol removal relates to 1000 mg L^{-1} (92%) and 4000 (22%) mg L^{-1} concentrations, respectively (Ramos *et al*., 2005) but for the anaerobic pond for phenol removal no independent study was found. Results of the study by Nahid and Kazemi (2004) showed that by the increase in concentration of phenol within the range 0-200 mg L^{-1}, the COD removal rate is reduced due to the phenol toxicity effect on the microbial mass activity.

The study results carried out by Gonzalo *et al*. (2007) showed that the phenol removal efficiency from the synthetic wastewater by the anaerobic continuous fluidized-bed bioreactor with retention time of 6 h has been 85-96%.

Avelar *et al*. (2001) showed that by increasing the concentration of phenol in influent wastewater, the efficiency of removal by the pond is reduced.

Optimal conditions resulting from this study was evaluated considering the performance of anaerobic pond in oil wastewater treatment and the decrease in the phenol concentration in the output. The highest efficiency of phenol removal in this study was obtained in phenol concentration of 100 mg L^{-1} (93.58%) after 5 days which is more than phenol removal by the UV/TiO_2 process and <RBC biological system. Considering the fact that the anaerobic ponds in all different phenol concentrations (except 100 mg L^{-1}) is not by itself capable of removing the organic pollutants up to permissible standards of discharge into the environment it must be employed as pre-treatment and subsequently the anoxic and facultative stabilization pond must be used.

Recent research by the DOW chemical company in Midland, Michigan and elsewhere has shown that phenol can be used as nutrient by the bacteria (without having toxic effects on bacteria up to 500 mg L^{-1} concentration). Studies with this compound and also with formaldehyde have already determined the toxicity threshold limit for the mentioned bacteria.

In concentration limits lower than the toxicity threshold, the bacteria use phenols as nutrient while in limits above the toxicity threshold level, phenol entails extremely toxic effect on them and adapted microorganisms should be used (Sawyer *et al*., 2003).

According to the results we can conclude that with the increase in phenol concentration, the anaerobic stabilization pond system performance is reduced due to the increased toxicity of phenol on bacteria treating of oil refinery wastewater.

Phenol as part of organic compounds forming BOD_5 and COD is dissolved into solution and lacks the potential of sedimentation in anaerobic pond; this finding is consistent with the Saqqar and Pescod study (Saqqar and Pescod, 1993). On the whole it can be concluded that anaerobic stabilization ponds, if properly operated, show favorable performance in removing the organic compounds at different concentrations of phenol in warm temperatures.

CONCLUSION

Considering advantages of WSP system such as flexibility, simplicity of operation and relatively high efficiency, it can be used as a better alternative in comparison of expensive and complex systems. Since, the WSP efficiency for removing phenol and phenolic compounds was better in comparison to conventional biological treatment method, it can be conclude that the anaerobic pond system as an option with proper cost-effectiveness can be employed for treatment of petrochemicals and oil refinery wastewaters containing phenol.

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