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Short Communication

Studying the efficiency of anaerobic stabilization pond on removing BOD and COD and changing the sulfur compounds in wastewater of Oil Refine

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ABSTRACT

Oil refinery wastewater as the most polluting industrial wastewater contain various hydrocarbons and sulfur with its derivatives and can cause problems in biological systems by the production of sulfuric acid. Variations of amount of sulfur depending on bioreactor condition such as temperature, pH, microbial activity and other factors. This study focused on determining variations of sulfur in anaerobic ponds for treatment of oil refinery wastewater. Samples were taken every 6 days during eight consecutive months and the type of sampling was 24-hour composite. This means that each sample is composed of 12 samples in 24 hours. 40 samples were taken from inlet and outlet of anaerobic stabilization pond for measuring sulfate, sulfide and sulfur, so a total of 240 samples were analyzed in this study. The results of the study showed that removal efficiency of COD and BOD were obtained 43 % and 24 %, respectively. Variations of sulfide and sulfur were obtained 4 % and 44 %, which increase respectively, but for sulfate have shown 15.8 % reduction. It can be said that sulfate-reducing bacteria have had significant activity to produce sulfide and sulfur form and decrease of the amount of sulfate in bioreactor.

1. Introduction

The growing process of population and therefore the growth of urbanization and industrialization of societies has affected on the water resources quantitatively and qualitatively) Rajkumar and Palanivelu. 2004). The development of major industries such as Oil Refinery and also related industries which their control of exit pollutant isn't in appropriate method increases the risk of oil pollution in the nature) Zouboulis and Avranas 2000). Among the mentioned industries, the wastewater of Oil Refinery has especial importance, because they have large amounts of oil and fat in the form of particulates, hydrocarbons, phenol and other organic materials (kiely 1998; Tchobanoglous and Burton 2003). Most of these materials have undesirable properties such as toxicity, mutagen or carcinogenesis and their disposal or evacuation in the environment have many problems, therefore they are considered as the most important environmental pollutants (Sudip et al. 2002). Because of above effects treatment and disposal of these toxic chemicals is very important (Laor et al. 1999). In addition the oil products contain sulfur and its derivatives (Solberg and Wagberg. 1999). The presence of hydrogen sulfide, sulfate and sulfur in the wastewater of industries caused problems in the environment. It can be said that the presence and abundance of sulfur and its derivatives cause overcome to the population of sulphate reducing bacteria (SRB) and producing sulfide hydrogen in oil wastewater. That is why in the process of oil wastewater, different physical, chemical and biological methods are used in order to remove these compounds (Singh. 1976). Spreading the reduced sulfur compounds in the environment can cause corrosion, toxicity and producing smell in the environment. That's why it would have inappropriate effects on the environment and therefore these effects should be controlled (Janssen et al. 2001). Different methods have been proposed in order to remove these compounds in the aquatic environment. The physical and chemical methods are typically expensive and have lots of limitations. Many researches were conducted on the biodegradation of petroleum compounds and they showed that this method is perfectly possible and can be one of the most economical and most effective methods in removing petroleum compounds (Lakha et al. 2005).

Also in this method no harmful chemicals for the environment are used. So wastewater and sludge disposal from these processes has fewer adverse effects than the chemical processes in the receiver resources (Bielicka et al. 2002). The stabilization ponds are considered as the simplest methods and in comparison with other methods they have high efficiency against toxins and organic loads (Reed et al. 1995).

In addition the anaerobic processes play an important role in reducing sulfuric compounds (White et al. 1997). According to the irreparable effects of the organic and sulfuric compounds of the wastewater of oil refinery on the environment and public health, this study aims to evaluate the efficiency of anaerobic stabilization ponds on removing organic compounds and also on changing the sulfuric compounds.

2. Materials and methods

2.1. Anaerobic stabilization pond

This study is a descriptive – analytical study which dealt with changing COD, BOD, sulphate, sulfide and sulfur in the wastewater of Kermanshah Oil Refinery in an anaerobic stabilization pond. The useful depth and hydraulic retention time of this pond are respectively 5 meters and 6 days. Also the entrance of the anaerobic stabilization pond was embedded in 30 cm above the bottom of the pond.

2.2. Sampling

In this study, after launching an anaerobic stabilization pond in order to treat the oil wastewater of Oil Refineries, daily sampling have

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been conducted from the inlet and outlet of pond. Sampling was done during 8 consecutive months as 24-hours compounds. This means that each sample is the result of combining 24-hours samples. The parameters such as pH and temperature were measured in sampling site. The samples then were transferred to the laboratories and the experiments were conducted.

2.3. Analytical methods

Several test such as BOD, COD, sulphate, sulfide, sulfur and alkalinity were done in order to get information about system efficiency from inlet and outlet of pond. Sulphate concentration was determined using turbidity test and by spectrophotometer model Jenway 6305. Sulfide and sulfur were determined by colorimetric method, and methylene blue method (APHA, AWWA, and WEF. 1998). The pH was measured using pH meter (Swiss MADC). The pH adjustment carried out by sulfuric acid 0.1 N and sodium hydroxide 0.1 N. In order to maintain and achieve to anaerobic conditions, the power of oxidation and reducing of the pond were measured using Kent ORP meter, model 7020 with sensors model Eli.

3. Results and discussion

In this study COD and BOD were measured by their biological performances to ensure the desirable conditions and to maintain the performance of the anaerobic stabilization pond. According to the results, the average COD in the inlet and outlet of the anaerobic stabilization pond was respectively 1185.82 and 652.53 mg/l which it shows 43% reduction. Also the average BOD in the inlet and outlet of system was respectively 150.22 and 113.85 mg/l which show 24 % reduction on average (Table 1). The removal of organic materials as BOD and COD take place in the deeper parts of the pond by methanation processThe amount of sulphate in inlet and outlet of stabilization anaerobic pond is respectively 358.48 and 318.49 mg/l which reduced 15.8% on average (Table 1). These changes of sulfuric compound are resulting from the biological activity of microorganisms in ponds, which includes reducing cycle and oxidation. This biological system has tremendous impact on its transformation (Robertson and kuenen xii. 2006). Since the stabilization loaded pond has low ranges in terms of organic loading, the activity of reducing bacteria of sulphate is dominant over other bacteria. For this reason, reducing sulphate in such conditions by sulphate reducer bacteria (SBR) reduces the amount of sulphate (Bak and Pfennig 1987). The amount of sulphate in the inlet and outlet is respectively 169.58 and 177.00 mg/l which show an increase of 4 %. The amount of sulfide in entrance and exit of the anaerobic stabilization pond is respectively 50.04 and 72.28 mg/l which had an average increase of 44 %. The increase of sulfide and sulfur in anaerobic ponds was respectively 44 % and 4 %. Sulfide can be produced using the anaerobic decomposition of microorganisms by breaking down proteins into amino acids and then decomposition of amino acid into sulfide or using direct reducing of sulphate by sulphate reducer bacteria (Postgate. 1984). Another reason for decreasing the amount of sulphate and increasing the amount of sulfide is that reducing sulphate can be conducted in 2 methods, dissimilatory and assimilatory. Assimilatory is a method in which the sulfur compounds are reduced in the biochemical reactions of amino acids and proteins, but they are not directly converted into sulfide. The sulphate reducing reaction in both methods of dissimilatory and assimilatory is produced by adenosine triphosphate. So at the beginning the adenosine triphosphate sulfurizing enzyme leads to produce adenosine phosphate sulphate. In dissimilatory, a part of sulphate is converted into sulphate using reducing enzyme APS and sulfite is converted into sulfide by reducing enzyme of sulphate. But in assimilatory some phosphorus atoms will be added to adenosine phosphate sulphate and phosphate adenosine phosphate sulphate is produced and first it converted into sulfite using reducing sulfide enzymes and then converted into sulfide (Madigan et al. 2006). The studies of Liam Lee and Nachatra showed that the final product of refinement of sulphate – containing wastewater is hydrogen sulfide. Its relative reduction is due to the lack of sufficient electron donor organic material like ethanol, methanol, acetate, and butyrate and so on. The results of this study are consistent with the present study (Liamleam and Annachhatre. 2007). Another reason for increasing sulfur is that the produced sulfide can be oxidized and be converted into elemental sulfur. Another reason for increasing sulfur is that the oxidizing photoautotrophic and chemolothotrophic microorganisms of sulfide use sulfide and electron donors and it converted them into sulfur and sulphate. The results of study showed that the elemental sulfur in increased. The reason of this increase can be related to the oxidation by photoautotrophic and chemolothotrophic which uses H_2S as an electron donor and oxidize the H_2S to S. On the other hand according to the negligible increase of sulfur, it can be pointed out that although the elemental sulfur can be produced by some of the mentioned microorganisms, but in anaerobic conditions, H_2S can be converted into elemental sulfur as an electron donor and can be stored inside of the chromatiase cells in amethyst sulfur bacteria or outside of the chrobiase cells in green sulfur bacteria. Also the string sulfur bacteria such as Bagzhiatova and Tthrikotris can oxidize H_2S to elemental sulfur and store them in sulfur granules (Madigan et al. 2006). The studies of Jenuic Leo Acharin and Ajit Anach Hotter which were done in a bioreactor with 0.2 to 1 mg/l of dissolved oxygen showed that in a bioreactor 90% of sulfide is converted into elemental sulfur (Lohwacharin and Annachhatre. 2009). The studies of Kim Berli Tang et al in 2009 about microorganisms showed that the sulfur oxidizing bacteria and sulphate reducing bacteria have a very important role in the cycle of sulfur in the oil industry (Tang et al. 2009). Temperature and pH are two effective parameters on the reaction. Measuring the abovementioned parameters showed that the temperature changes in entrance and exit of pond were respectively 28.9 and 29.1˚c. Another reason for changing sulfur compounds is the available microorganisms including the wide range of mesophilic and thermophilic bacteria and the growth and reduction of sulphate depends on the temperature of reaction (Houten et al. 1997; Weijma et al. 2000). The studied of Moses et al (2005) showed that increasing temperature from 20 to 35 increases sulphate reduction and increasing temperature to more than 40 ˚c decreases the reaction. The colored sulfur bacteria have a wide range and their growth depends on PH and temperature. It is reported that their growth has a wide range of pH (1 – 9) while the temperature is 4 to 90 ˚C (Hasany et al. 2005). The alkalinity of calcium carbonate in the entrance and exit of anaerobic stabilization pond was respectively 323.93 and 577.46 mg/l and on average it increased 93% (Table 1). Another effective parameter in this study was pH and its value in the entrance and exit of the anaerobic stabilization pond is respectively 7.6 and 7.52. So the activities of reactions in the outside of the range of 5 – 9 show the decrease (Mihaela et al. 2005). The study of Visser et al (2001) showed that sulphate reduction in anaerobic reactor has the highest value in the pH of 6.9 – 8.5) Kolmert and Johnson. 2001). Also the study of Frotin et al (1996) showed that the reaction of sulphate reduction was unsuccessful when the pH was less than 5.5 (Fortin et al. 1996).

Table 1. The results of Oil refinery treatment using anaerobic stabilization pond.

Sample Location	COD (mg/l)	BOD (mg/l)	Sulfur (mg/l)	Sulfide (mg/l)	Sulfate (mg/l)	Alkalinity (mg/l)	pH		T °c
Input	1185.82±80	150.22±15	169.58±21	50.04±11	358.48±47	323.93±42	7.6		28.9
Output	652.53±34	113.85±11	177±15	72.28±23	318.49±32	577.46±48	7.52		29.1
%	-%43	-%24	+%4	+%44	-%15.8	+%93	-	-	

+ Icrease; - Decrease

4. Conclusions

In this study according to the stabilization function of anaerobic stabilization pond and relatively favorable removal of organic material, the changes of sulfur were studied. The results of this study showed that the anaerobic stabilization pond in the wastewater of oil refineries changes the amount of sulfuric compounds and organic materials. The reduction of theconsequently converting it into hydrogen sulfide, it is suggested to control sulphate at the range of less than 500 mg/l.

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