COUPLED ANAEROBIC BAFFLED REACTOR (ABR)/ACTIVATED SLUDGE TREATMENT OF SYNTHETIC WASTEWATER WITH HIGH CONCENTRATION OF SULFATE AND COD

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Abstract A synthetic wastewater with high concentration of sulfate and COD was treated in anaerobic baffled reactor (ABR) coupled with an activated sludge. The work was accomplished in two phases .In the first phase, the concentration of sulfate was kept constant at 500mg/l, but COD concentration was increased from (3000mg/l to 6000mg/l), consequently, COD and sulfate removal in ABR reached to 80% and 95%, respectively. Some of produced sulfide in ABR converted to sulfur by photosynthetic bacteria which appeared on the top of the ABR. Effluent from the ABR entered to activated sludge where COD removal reached 60%, but some of sulfide converted to sulfate. In the second phase, at constant concentration of COD, when sulfate concentration was increased from 500mg/l to 1750 mg/l by steps about 250mg/l, inhibition was not observed. When effluent of this second phase was entered in activated sludge, COD removal was decreased, and sulfide cause bulking in activated sludge. The ABR and activated sludge were worked with hydraulic retention time (HRT) about 24 hours and 15 hours, respectively. The temperature of ABR system was maintained at 35ºC.

Key Words Anaerobic Baffled, Activated Sludge, COD Removal, Sulfide, Sulfate Removal

چکیده تصفیه یک پساب ساختگی (سنتیتیک) با غلظت بالایی از COD و سولفات توسط سری راکتور غیر هوازی بافل دار و راکتور لجن فعال بررسی شده است. در اولین مرحله از این کار غلظت COD از ۳۰۰۰ به ٦۰۰۰ میلی گرم در لیتر در غلظت ثابتی از سولفات برابر ۵۰۰ میلی گرم در لیتر افزایش یافته است. بازده زدودن COD در راکتور غیر هوازی بافل دار به ۸۰٪ و بازده زدودن سولفات به ۹۵٪ رسیده است. بازده زدودن COD از خروجی راکتور غیر هوازی در راکتور لجن فعال ٦۰٪ می باشد. در دومین مرحله کاری هنگام افزایش سولفات از ۵۰۰ میلی گرم در لیتر به ۱۷۵۰ میلی گرم در لیتر در غلظت ثابتی از COD برابر ٦۰۰۰ میلی گرم در لیتر بازده زدودن COD تقریبا کاهش نیافته است. مقداری از سولفید در راکتور غیر هوازی به عنصر سولفور تبدیل شده است. همچنین در هر دو مرحله مقداری از سولفید در راکتور لجن فعال به سولفات تبدیل شده است. زمان ماند هیدرولیکی در راکتور غیر هوازی و لجن فعال به ترتیب ٢٤ و ۱۵ ساعت بوده است و دمای راکتور غیر هوازی در ۳۵ درجه سانتیگراد ثابت نگهداشته شده بود.

1. INTRODUCTION

Wastewater effluent from alcohol distillery, pharmaceutical, textile and pulp and paper mill, may have high concentration of COD and sulfate, or a complex substrate. Under the mentioned condition only one treatment system like anaerobic or aerobic treatment could not treat strength wastewater; therefore, anaerobic –aerobic system is the best alternative for strength wastewater. In this system less excess sludge will be produced and less energy will be consumed in the case of minimal COD removal in the anaerobic reactor [1]. Anaerobic process has had wide application in the treatment of sewage sludge and high strength industrial wastewaters. The anaerobic baffled reactor (ABR) has been described as a series of UASBs , which does not require granulation for operation [2]. This design consists of vertical baffles, which force the wastewater to flow under and over them as it passes from the inlet to the outlet. The bacteria tend to rise and settle with gas production in each compartment, but they move horizontally down the reactor at a relatively slow rate giving rise to cell retention times (CRT) of 100days at 20-h hydraulic retention time (HRT) [3]. Wastewaters from oil refineries, gas manufacturing, pulp and paper mills, and pharmaceutical industries may have high concentration of sulfate. It has not been possible, as yet, to avoid biological sulfate removal. When Hilton and Archer (1988) added Na_2MoO_4 for inhibition of sulfate-reducing bacteria, the methane production decreased as a consequence [4]. The presence of sulfate could cause several problems in the anaerobic treatment process for the following reasons (a) sulfate is reduced to hydrogen sulfide which is a strong inhibitor of methanogenesis (b) sulfide is malodorous and exerts a high oxygen demand (c) hydrogen sulfide released to the biogas causes corrosion down the stream and (d) sulfate reducing bacteria (SRB) compete with other bacteria associated with methane production for substrate, and high sulfide concentration can inhibit methanogenesis and can precipitate nutrients essential to methanogenesis. It is commonly believed that in the sulfate –rich condition, SRB can out-compete MPB for hydrogen and acetate. However, Isa et al., reported that SRB did not completely out-compete MPB in high-rate anaerobic reactors [5].

Biological sulfide oxidation has been used to remove sulfide in anaerobic effluent. The advantages of biological sulfide removal are: (a) no catalyst or oxidant (except air) is required, (b) no chemical sludge is disposed and (c) no high energy is consumed. A promising new process entails the biological reduction of sulfate to sulfide by the bacterium desufovibrio desulfuricans [6]. Sulfide can, in turn, be removed by photooxidation to sulfur. A possible way to avoid sulfide inhibition is converting sulfide to elemental sulfur by photosynthetic bacteria. Sulfide can be oxidized to sulfur by the photosynthetic green sulfur bacterium chlorobium, which is capable of growing at very low light intensities [7]. In addition, the presence of hydrogen sulfide (H_2S) in the influent to activated sludge treatment plant is known to create problems with solid –liquid separation [8].

Bulking or poor settling properties are usually the reasons when excessive growth of some types of sulfide oxidizing filamentous microorganisms cause the settling properties to deteriorate. Because of the variable nature of industrial wastes, reactor stability to organic and sulfate shock loads is the most important aspect of reactor design. The ABR is extremely stable at constant HRTs to step change in feed COD and it retains high degree of removal (>90%), weeks after a large shock. Hence, it appears that the ABR would be appropriate for industry [9]. In sum, the general response of anaerobic processes to an organic shock can be characterized by the following: an increase in volatile fatty acids (VFAs), a decrease in removal efficiency, a decrease in methane content, an increase in effluent suspended solids, and an increase in sludge volume index [10,11,14]. In this paper, effects of increasing COD and SO_4 step shocks were investigated. The goal of this work was to study the responsibility of anaerobic baffled reactor coupled with an activated sludge system ratio to high sulfate synthetic wastewater. The research was established in two phases. In the first phase, at constant concentration of sulfate, COD was increased, then effluent from anaerobic reactor was entered to activated sludge .In the second phase, at constant concentration of COD, sulfate concentration was increased and the abilities of activated sludge and ABR system were investigated.

2. MATERIALS AND METHOD

Media Diluted molasses, before alcohol fermentation, was used as carbon source. Sulfate sodium10H_2O was added as sulfur source and nitrogen and phosphorous were added in the forms of urea (0.007g/g of COD) and phosphate dehydrogen potassium (0.0006g/g of COD), respectively. Characteristic of diluted molasses are shown in Table 1. The pH was adjusted to 7±0.3.

Sampling and Monitoring Analysis of chemical oxygen demand (COD), sulfate, suspended solids (SS), were measured every other day. The samples for COD were acidified and stirred until sulfide was removed in the form of H_2S. Temperature and pH were monitored every day. All analyses were carried out according to the standard methods (AHPA, 1986).

Seed Materials The seed material for anaerobic baffled reactor (ABR) was obtained from the

TABLE 1. Analyses of 1 g/l Molasses.

Compound	Average Concentration (mg/l)
Biochemical oxygen demand (BOD)	488
Chemical oxygen demand (COD)	710
Total kjeldahl nitrogen (TKN)	10.25
Total sugar	510
Protein	65.4
Ash	83.5
Sulfate	4.04
Zinc	0.05
Iron	0.205
Nickel	0.083
Manganese	0.042
Potassium	24
Calcium	20.5
Magnesium	10
Sodium	9.2

previous anaerobic reactor. The sludge that was screened for many times and adapted with sulfate was used for this work. The anaerobic baffled reactor was inoculated with 25g /L MLSS. Since this sludge has sulphidogenic and methanogenic bacteria, it was a good seed for ABR.

The seed sludge for activated sludge system was collected from activated sludge plant of the Tehran refinery. This system was inoculated with 2.5 g /L MLSS.

3. EXPERIMENTAL SET UP

The activated sludge and anaerobic baffled reactor (ABR) used for carrying out the experimental work are shown in Figure 1. Both systems are made of plexiglass. The working volume of the activated

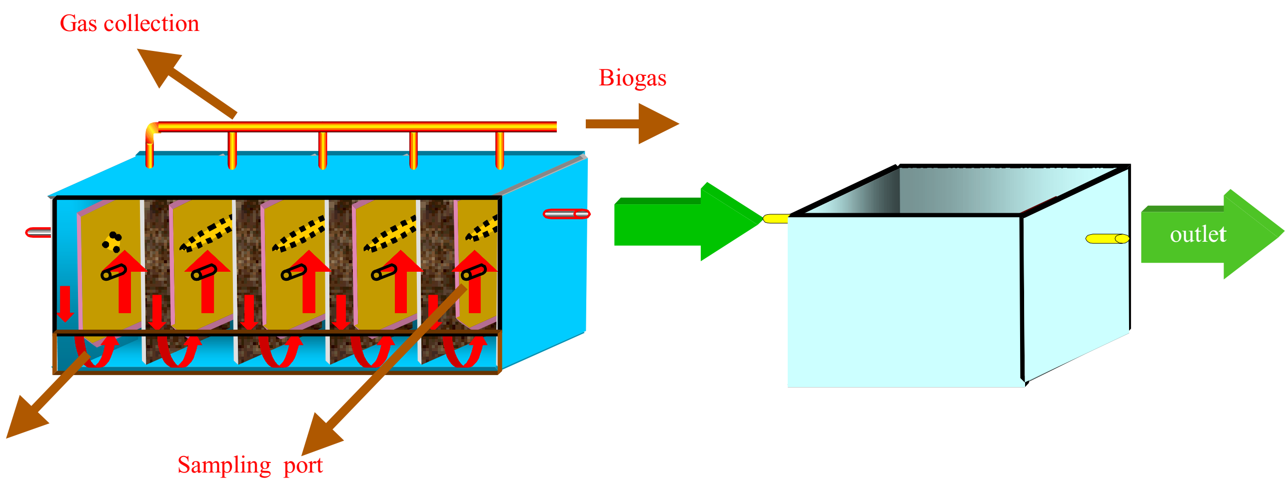

Figure 1. Schematic of anaerobic baffled reactor coupled with activated sludge reactor.

sludge was 7 liters (length: 25 cm, width: 16 cm, height: 20 cm), of which one-liter was considered as settling tank. The ABR system consisted of five compartments each of which separated by a vertical baffle. The working volume of this reactor was 10 liters (length: 50 cm, width: 15cm, height: 30cm), the active volume of each compartment was 2L, the sampling ports located at 8 cm from the bed of each compartment and the width of riser (up comer) was 2.4 times of the width of the down corner. All experiments for ABR were conducted in a control bath at 35ºC, but the activated sludge worked at ambient temperature. Since ABR's seed sludge was acclimatized with sulfide and molasses as COD, this reactor started with organic loading rate (OLR = 3 kg-COD/m^3.day) and sulfate loading rate (SLR = 0.5 Kg-SO_4/m^3.day) at constant hydraulic retention time (HRT) of 24h. The influent COD and sulfate concentration varied as a function of organic loading rate, between 3000 to 6000 mg/l and 500 to 1750 mg/l for COD and sulfate, respectively.

4. RESULTS AND DISCUSSION

Figure 2 Shows the profiles of COD in each compartment of ABR and influent over time during the step shocks from 3000 to 6000mg/l COD in the feed at an HRT of 24h. At these periods when COD increased at a constant concentration of sulfate, effluent COD almost did not change. In addition, about 65% to 75% of COD removal occurred in the first compartment. This means that the ABR was able to adapt itself to a new higher feed concentration in first days. It may be concluded that ABR system was stabilized when COD concentration in influent was doubled. When COD level in influent was reached to 5500mg/l with step about 500mg/l, the COD level in first compartment was increased but COD level in effluent was not increased because another compartment caused COD conversion. Since almost 75% of COD removal occurred in the first compartment, the rate of OLR in the first compartment in this period reached to about 20 kg-COD/m^3.day. This phenomenon shows that about 4.8 hours is sufficient for 75% of COD removal. Figure 3.shows the SO_4 profile in all compartments of ABR, when COD concentration increased from 3000 to 6000 mg/l. It can be observed that about 72% to 84% of SO_4 removal occurred in the first compartment and finally overall removal efficiency reached 94 to 96%. One important observation was that when COD increased in influent, SO_4 removal in the

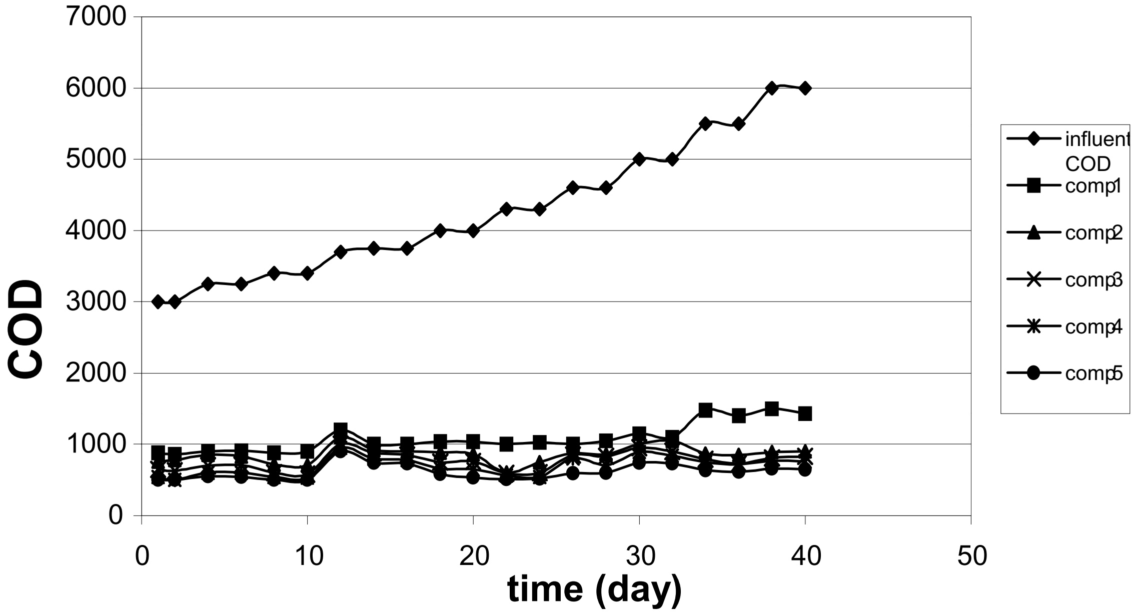

Figure 2. COD profiles in all compartment during the step organic shocks.

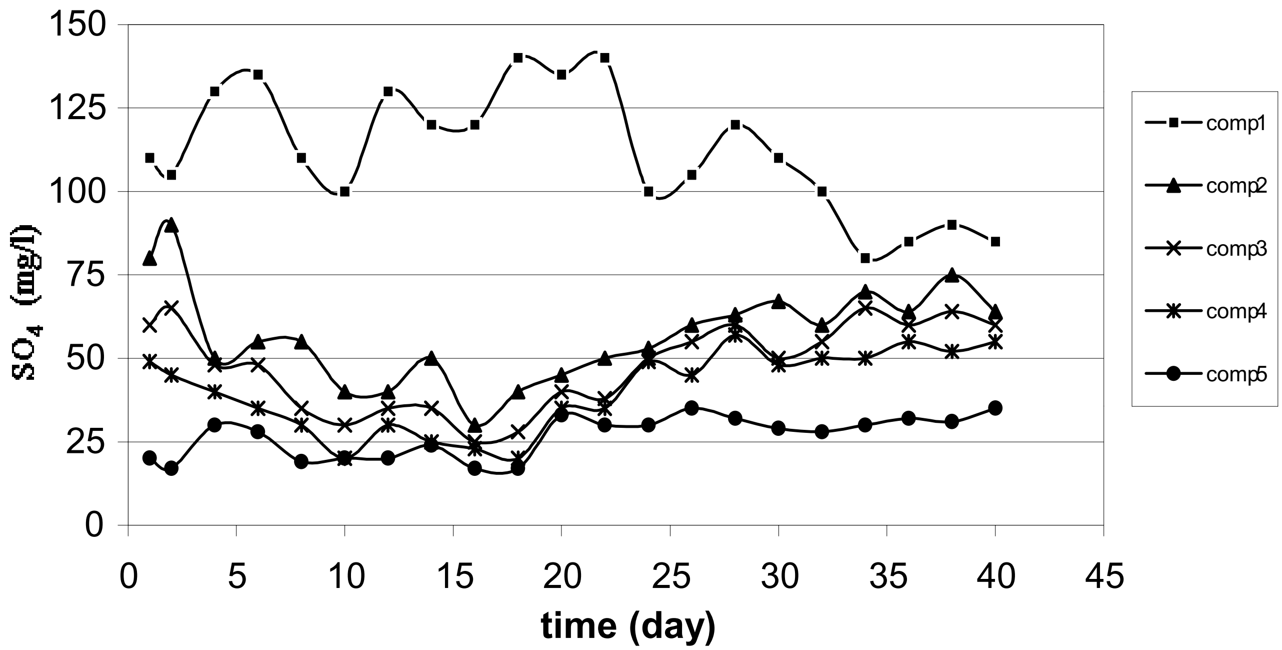

Figure 3. Sulfate profile in all compartments during step organic shocks.

first compartment increased as well, because more COD were available for SRB to convert sulfate to sulfide and about 4.8 h was sufficient for 72% - 84% of sulfate removal in acidogenic phase.

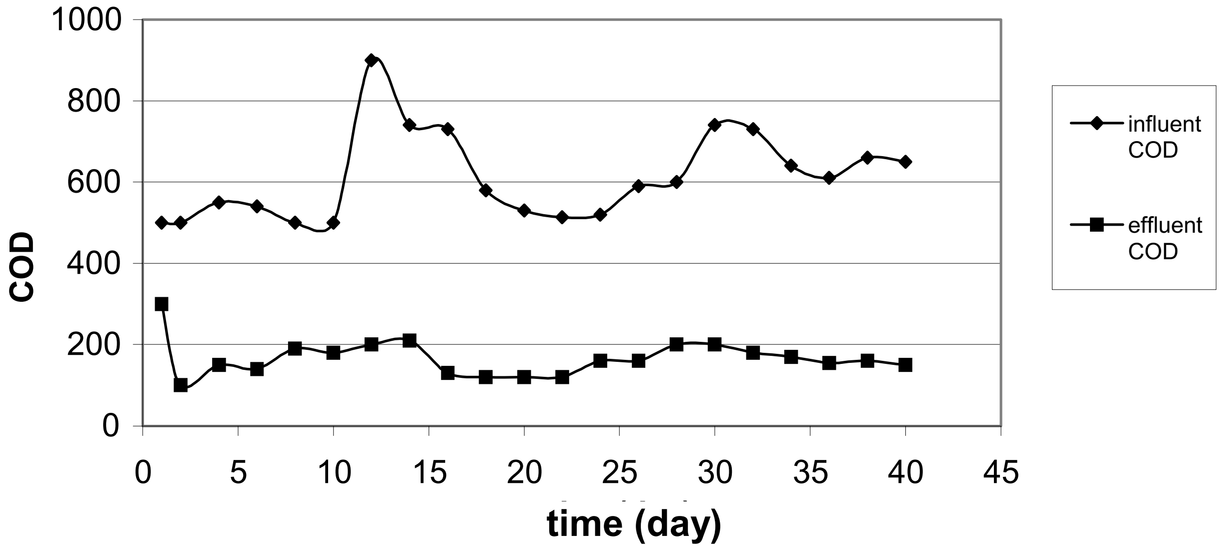

Figure 4. Variation of COD in the activated sludge in first phase.

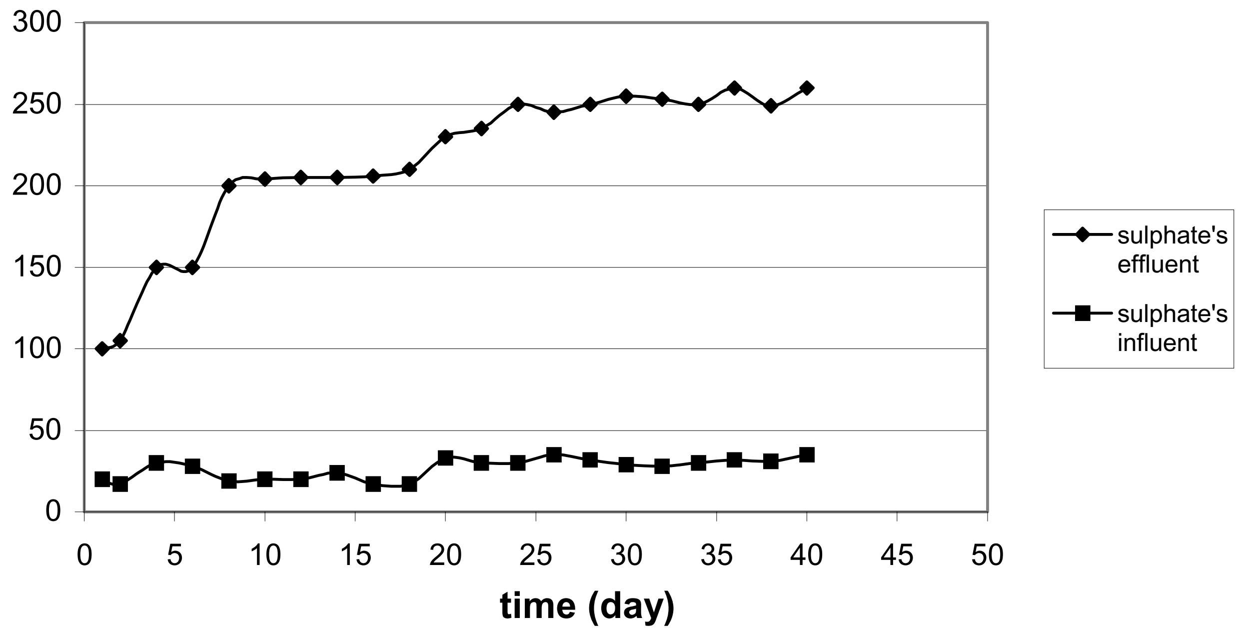

Figure 5. Variation of sulfate in activated sludge during first phase.

Sulfate reduction occurred in the acidogenic phase even at HRTs as short as 2 h [12]. Also in the ABR system after 15th day, pH difference between the first and the fifth compartments was about 1 unit. This phenomenon is an important parameter of ABR because systems with two phases cause

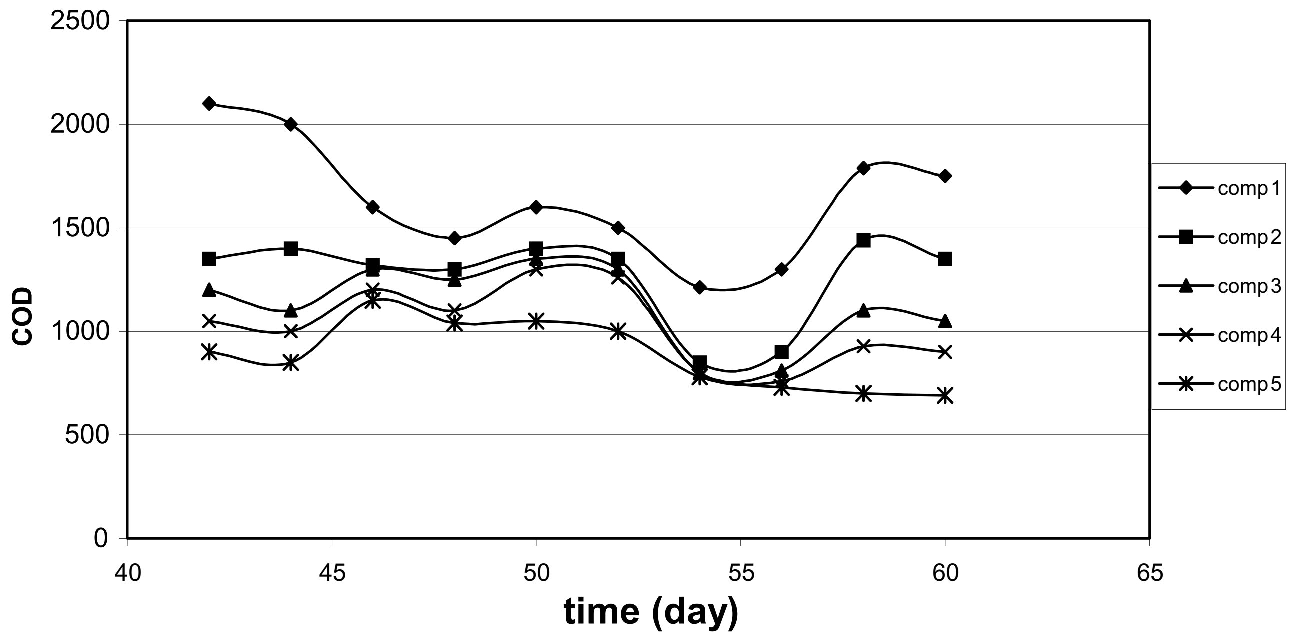

Figure 6. COD profile in all compartment during step sulfate shocks.

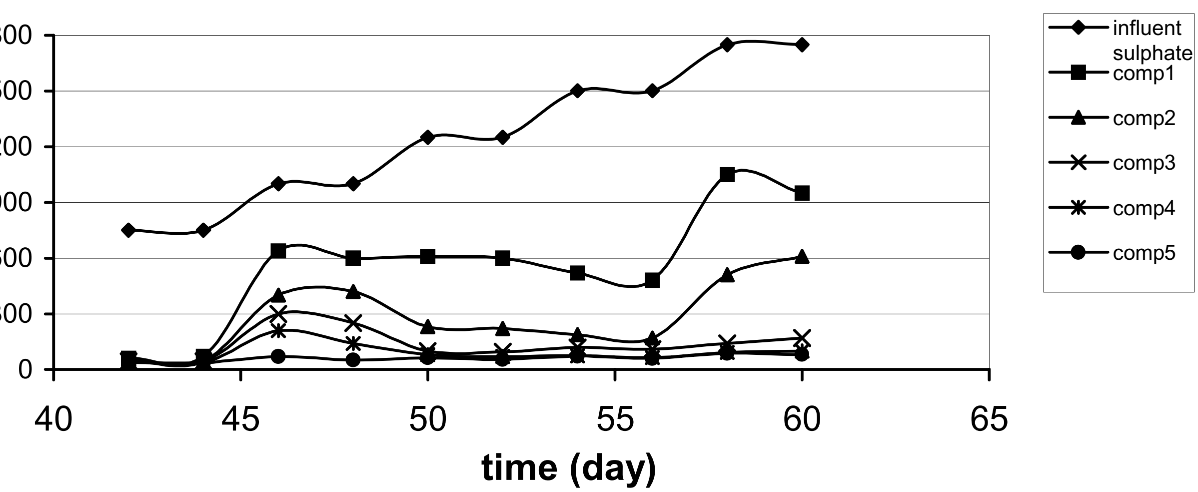

Figure 7. SO_4 profile in all compartments during sulfate step shocks.

more COD to be converted.

Figure 4 shows the effect of activated sludge on ABR effluent. It is shown that in the first days when COD levels in

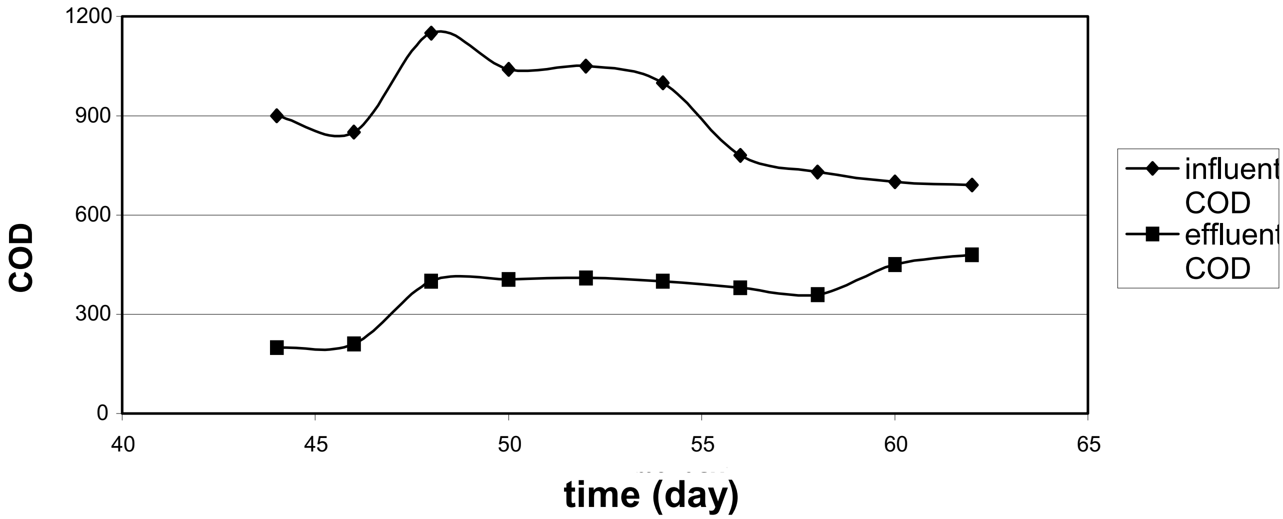

Figure 8. COD variation in the activated sludge during second phase.

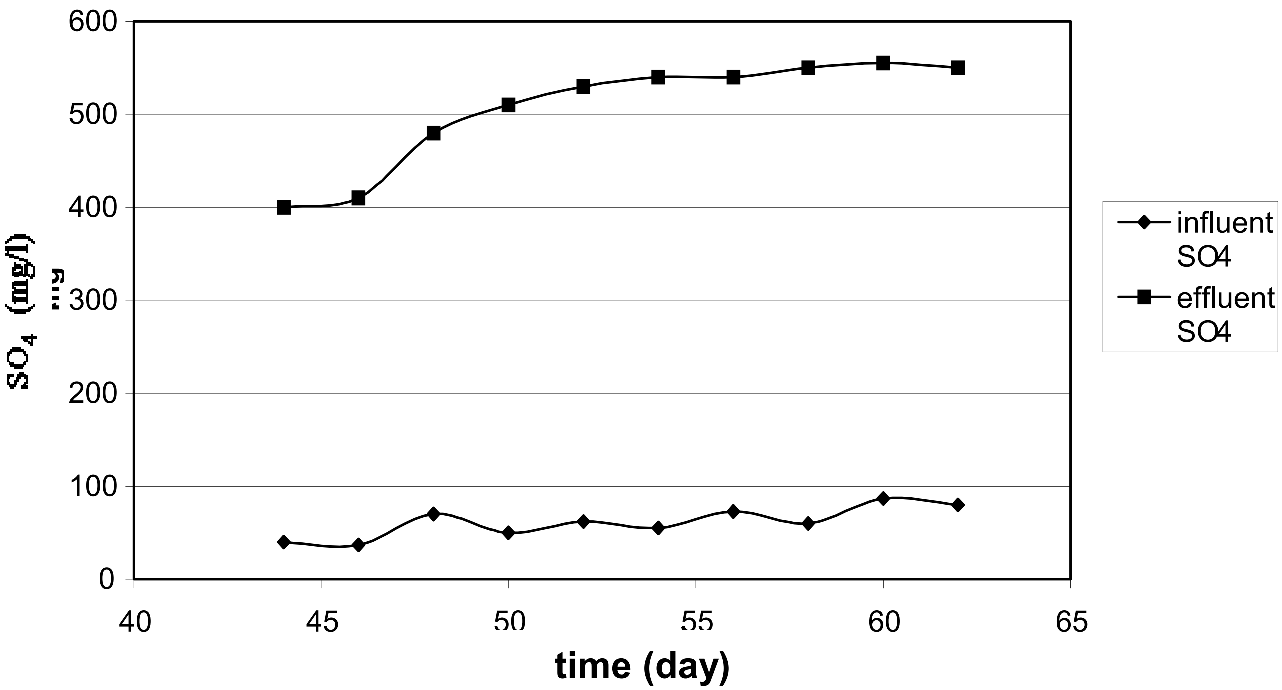

Figure 9. Variation of sulfate in activated sludge system during second phase.

effluent are shorter than 500 mg/l, with increase in effluent of ABR, COD removal in activated sludge is almost bigger than primary value. Because activated sludge was more adaptive with effluent's ABR. Figure 5 shows when influent of ABR entered to activated sludge, the SO_4 concentration was increased, because most of sulfide in effluent was converted to SO_4. This phenomenon causes some of energy dissipation, because conversion of 1 mole of sulfide to sulfate, needs 2 moles of oxygen. But conversion of sulfide to sulfate has the advantage of avoiding odor problem by inhibiting H_2S. From pretreated wastewater, it was obvious that an activated sludge post-treatment was necessary to be installed.

Figure 6 shows that in second phase, when SO_4 concentration increased from 500 to 1750mg/l with step increase shocks of sulfate, COD levels in effluent did not significantly change, and with any step shocks in sulfate increase, almost COD levels in the first compartment was increased, but another compartment caused COD conversion. Therefore 1 to 2 days after shocks, the effect of shocks was removed. The percentage of the COD removal in the first compartment was about 65%-75%, and shorter than 17% of COD removal occurred in another compartment except for the first compartment. This phenomena show that it is possible to treat strength wastewater by using more than one compartment. When sulfate concentration reached more than 1500 mg/l, COD level in effluent decreased, but in the first compartment COD level increased because conversion of sulfate in another compartment causes the level of COD in compartments to decrease. The reduction of one gram sulfate consumes 1.2 ml molasses and requires 6 h for completion [13]. As shown in Figure 7, at the first step change (500 to 750mg/l), variation was not observed in sulfate concentration in compartments. But in another step shock when SO_4 concentration was greater than 750 mg/l, sulfate concentration increased in the first compartment, and sulfate efficiency removal in the first compartment decreased to shorter than 55%, but sulfate efficiency removal in effluent did not change. This efficiency removal was about 95%.

When sulfate concentration increased from 500 mg/l to 1750 mg/l, inhibition by produced sulfide was not observed. Because some of this sulfide converted to elemental sulfur by photosynthetic bacteria and participated in the PVC packing as granules white, a thin layers of sulfur was formed on the PVC packing. Sulfide can be oxidized to elemental sulfur by the photosynthetic green sulfur bacterium, chlorobium that is capable of growing at very low light intensities [7]. In this case the following reaction applies:

$$17\,H_2S + 8\,CO_2 \rightarrow 2\,(C_4H_3O_3) + 17\,S + 10\,H_2O$$

Sulfide converting to elemental sulfur and participating in the packing is a possible way for disappearing from sulfide inhibition.

Therefore, with converting sulfide to elemental sulfur, we could reach a high COD removal in high concentration of sulfate. The variation of COD in activated sludge is shown in Figure 8. With increasing of sulfide effluent from ABR, the COD level in effluent of activated sludge system increased because some of the oxygen in activated sludge system was consumed by sulfide. Also sulfide causes bulking in this system.

Sulfate analyzed in activated sludge reactor, shown in Figure 9, shows that SO_4 concentration in this system increased, because sulfide and elemental sulfur entered to activated sludge could be converted to sulfate.

5. SUMMARIES AND CONCLUSION

Based on the findings of this study, the following conclusions can be made:

1) Coupled anaerobic baffled reactor/activated sludge system was a good alternative for treatment of a synthetic wastewater with high concentration of sulfate and COD.

2) Some of the sulfide in anaerobic reactor can be converted to sulfur. Therefore, sulfide inhibition cab be alleviated.

3) Some of the sulfides in activated sludge was converted to sulfate, therefore, activated sludge system is the process most favorable for alleviating the bad odor of hydrogen sulfide, but converting sulfide to sulfate caused some oxygen consumption.

4) The ABR is extremely stable at constant HRTs to step changes in feed COD and sulfate.

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