THE EFFECT OF SULFATE CONCENTRATION ON COD REMOVAL AND SLUDGE GRANULATION IN UASB REACTORS

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(Received: July 29, 2001- Accepted in Revised Form: October 7, 2002)

Abstract Four identical 37.5 Liter UASB reactors R_1, R_2, R_3 and R_4 were used to study the effect of sulfate concentration on granule formation. Diluted molasses with COD range 1000–1300 mg/ l were used as feed and acclimated cow manure was used as seed. Concentration of sulfate ions in the four reactors were 100, 500, 1000 and 1500 mg/l. Granules were observed in R_2 after 33 days from startup time, while in R_1 and R_3 granules appeared after 45 days. No granules were formed in R_4. Sulfate reduction efficiencies were 84, 89, 71.5 and 59.4 % while corresponding COD removal efficiencies were 85, 91, 84 and 77% for reactorR_1 to R_4 respectively. Temperature kept at 30°C all experiments and the best pH for granulation was found to be 7.00.

Key Words Sludge Granulation, Sulfate concentration, UASB Reactor, COD/SO_4 Ratio

چکیده در این تحقیق چهار راکتور همانند ۳۷/۵ لیتری UASB (R_1، R_2، R_3 و R_4) برای مطالعه تاثیر غلظت سولفات بر دانه ای شدن مورد استفاده قرار گرفت. ملاسهای رقیق شده با گستره COD بین ۱۰۰۰ تا ۱۳۰۰ میلی گرم بر لیتر به عنوان تغذیه و کود گاوی هوادهی شده به عنوان هسته مورد استفاده قرار گرفت. غلظت یونهای سولفات در چهار راکتور برابر ۱۰۰، ۵۰۰ و ۱۵۰۰ میلی گرم بر لیتر بود. دانه ای شدن سی و سه روز بعد از شروع آزمایش در راکتور R_2 و ۴۵ روز بعد از شروع آزمایش در راکتورهای R_1 و R_3 دیده شد. هیچ دانه ای در راکتور R_4 بوجود نیامد. ضرایب احیاء سولفات برابر ۸۴، ۸۹، ۷۱/۵ و ۵۹/۴ درصد بود در حالی که ضرایب مشابه برای زدودن COD برای راکتورهای R_1 تا R_4 به ترتیب برابر ۷۶، ۸۲، ۹۳ و ۸۵ درصد بود. در تمام آزمایشها دما برابر ۲۵ درجه سانتیگراد و بهترین pH دانه ای شدن برابر ۷/۰۰ بدست آمد.

1. INTRODUCTION

Although the presence of sulfur compounds is vital for biosynthesis reactions and can 35 % wt of mineral content of granule [1,2], high sulfate concentration in feed may cause inhibitory effects on anaerobic reactors and related units[1-6]. Furthermore, the produced sulfide can cause sludge bulking in the activated sludge post-treatment unit due to the growth of sulfide oxidizing bacteria (thiothrix). Hydrogen sulfide is also highly corrosive and have obnoxious odor [5]. The inhibitory effect of sulfate ions might be different as various reactions can take place. For instance, heavy metals, which enhance bacterial activities, are easily eliminated by sulfide ions. Sulfate ions also enhance SRB to grow rapidly and become a competitor for MPB. Two species of MPB, methanosarcina and methanothrix, have significant effect on granule formation [2].

Sludge granulation is affected by increasing sulfate ions. As a consequence, for wastewaters containing high concentration of BOD and sulfate ions (such as those from distillery, paper mill and dried yeast industries), although the anaerobic treatment may be an appropriate choice, the high concentration of sulfate ions may cause problems with respect to sludge granulation. A number of researchers [3,5,6] have studied anaerobic reactor behavior with high concentration of sulfate ions, but in terms of the sulfate effect on sludge granulation, little work has been published.

TABLE 1. The Analysis of Feed for Four Reactors.

Reactor	R_1	R_2	R_3	R_4
COD(mg/l)	1000	1000	1000	1000
SO_4 (mg/l)	100	500	1000	1500
N (mg/l)	20	20	20	20
P (mg/l)	10	10	10	10
Ca (mg/l)	70	70	70	70
K (mg/l)	50	50	50	50
Na (mg/l)	420	620	870	1120
Fe (mg/l)	2	2	2	2

In anaerobic processes, sulfate is converted to sulfide by SRB. Sulfides will appear in the form of S^{2-}, HS^- and H_2S whose concentrations are pH dependent. Both MPB and SRB compete for utilizing intermediate fermented products. H_2S and CO_2 are produced by SRB reactions due to reducing of sulfate, while CH_4 and CO_2 are the end products of MPB. In other words, SRB population growth reduces MPB activities and methane production.

According to thermodynamic and kinetic studies of SRB and MPB reactions, both free energy and kinetic constant (V_m/K_m, V_m = maximum rate, K_m = michaelis constant) for SRB

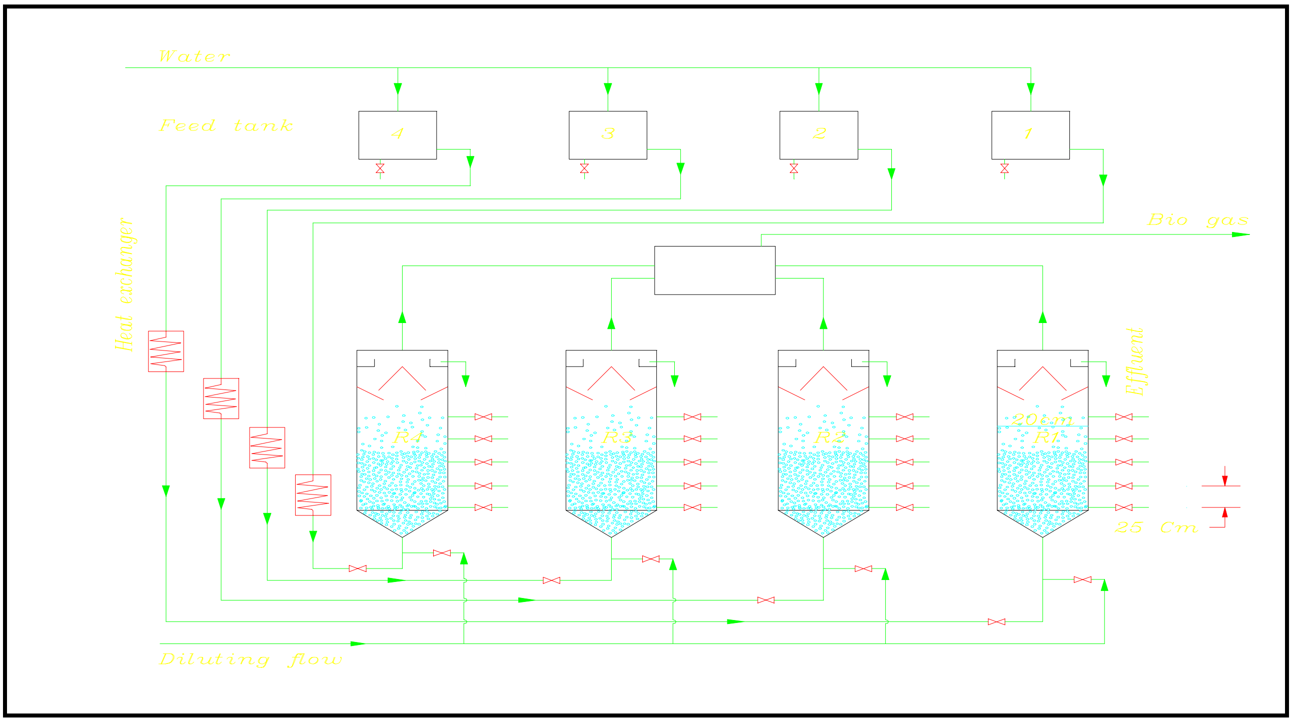

Figure 1. Schematic diagram for four pilots.

TABLE 2. The Defined Conditions for Four Reactors.

Reactor	*Upflow velocity (m/h)*	*COD (mg/l)*	*SO_4 (mg/l)*	*pH*	*T(°C)*	*COD/ SO_4*
R_1	1.0	1000	100	7	30	10
R_2	1.0	1000	500	7	30	2
R_3	1.0	1000	1000	7	30	1
R_4	1.0	1000	1500	7	30	0.67

reactions are higher than MPB reactions. In an experiment [7] three UASB reactors were fed with 600 mg/l of COD and three different sulfate concentrations of 30, 150, 600 mg/l. The Vm to Km ratio for hydrogen utilization by SRB and MPB were reported as 5.2×10^4, 0.23×10^4 respectively, and for acetate utilization by SRB and MPB were 11×10^4 and 2.2×10^4 respectively. These results indicated that the SRB affinity for acetate utilization is much higher than hydrogen. It was concluded that the conditions were more suitable and more dominant for SRB activity over MPB. In all three reactors total COD removal was approx. 90%. It was found that increasing the concentration of sulfate ion, the fraction of COD eliminated by SRB would also be increased. At 600 mg/l sulfate, 75% elimination was possible, whilst at 30 mg/l it was limited to 5%.

SRB do not effect on primary reactions and will only compete at the final stages of fermentation reactions [7]. Therefore, the rate of competition in various sludge bed layers would differ [6]. In the lower layer part of the reactor due to high concentration of acetate and hydrogen, SRB reactions have the highest rate, while in the upper zone; more MPB activity is observed [6]. The effect of wastewater characteristics and organic loading rate are also significant. It was reported that with an increase in organic loading, the MPB reaction rate was reduced especially if sulfate to COD ratio was kept high [4].

Sulfate reduction produces toxic products, which have negative effects on anaerobic bacteria. The amount of toxicity depends upon many factors such as sulfate concentration, pH, influent COD, temperature, and granule size. MPB are more sensitive than other species [5].

In another study [8] in a horizontal reactor packed with polyethylene (HAIS) with COD to sulfur ratio of 249, 66, 19.7 and 4.3, it was found that both SRB and MPB were immobilized on packing surfaces. But since SRBs are not quite adhesive, MPB were more dominate, although by increasing sulfate concentration, SRB percentage were increased in biofilm. It was found that the optimum ratio of COD to sulfate concentration was around 20.

The toxicity of H_2S on MPB becomes very important in hydrogen sulfide concentrations over 15mg/l. Above this concentration, increasing 1 mg/l of H_2S, loses almost 0.2% of MPB activity. In hydrogen sulfide concentration less than 15mg/l, MPB activity is not affected [9].

In spite of a thorough survey of the literature, there are some unanswered questions:

- To what extent the presence of sulfate ions has significant effect upon COD removal in UASB?
- How does sulfate reduction conversion factor vary?
- What is the permissible sulfate concentration for UASB reactor?
- What is the effect of sulfate on the time needed for sludge granulation?
- What is the effect of sulfate on total alkalinity?

The pilot study was carried out to answer considering the above questions.

TABLE 3. Cow Manure Variations in Three Months in 27 $^\circ C$.

Time (day)	5	10	20	30	45	60	75	90
COD (mg/l)	8100	6900	4700	4000	2800	2200	1500	1200
Sludge color	green	green	green	green	green	green	dark green	dark green
Liquid color	green	green	green	dark green	dark green	blackish	black	black

TABLE 4. The Performance of Four Reactors (All Concentration are Given In mg/l).

Time (week)	***R_1 , SO_4=100***		***R_2 , SO_4=500***		***R_3 , SO_4=1000***		***R_4 , SO_4=1500***	
	COD in	***COD out***	***COD in***	***COD out***	***COD in***	***COD out***	***COD in***	***COD out***
1	820	120	820	175	820	185	820	140
2	1100	220	1100	200	1100	220	1100	185
3	1200	170	1200	80	1200	170	1200	210
4	1050	120	1050	70	1050	140	1050	270
5	1020	110	1020	75	1020	125	1020	265
6	1000	150	1000	75	1000	150	1000	195
7	1100	180	1100	80	1100	200	1100	250
8	1050	170	1050	80	1050	200	1050	270
Mean COD	85		91		84		77	

2. MATERIAL AND METHODS

Four identical UASB reactor pilots with capacity of 37.5 *l* and diameter of 20 cm were prepared and equipped with proper control systems and recirculation flow (Figure 1). Diluted molasses was used as a synthetic wastewater and sodium sulfate and sulfate content of molasses were used as sulfate sources. Sodium carbonate was applied for pH adjustment. Batch stabilized cow manure
was used as seed sludge. Table 1 shows the feed composition for each reactor.

Methods for different a chemical analysis and also chemicals for such analysis were chosen according to the specifications mentioned in Standard Methods for the Examination of Water and Wastewater [10].

Start up Conditions The defined conditions for the four reactors at the time of start up are given in Table 2 and start up took place in two stages as follows:
At the preliminary stage, fresh cow manure was added into a 200 *l* container fed batch wise with diluted molasses until it was established and acclimated with new conditions. At the end of this stage (about three months) this sludge slurry was transferred to the reactors.

In the next stage, sludge was washed with tap water to eliminate the scum, coarse and light screen. For further cleaning and refining of sludge and eliminating fine and light materials, reactors were fed with diluted molasses (COD = 500 mg/l) and upflow velocity gradually increased from 0.1 to 2.0 m/h for about 2 weeks. After this period, reactors were ready for planned experiments.

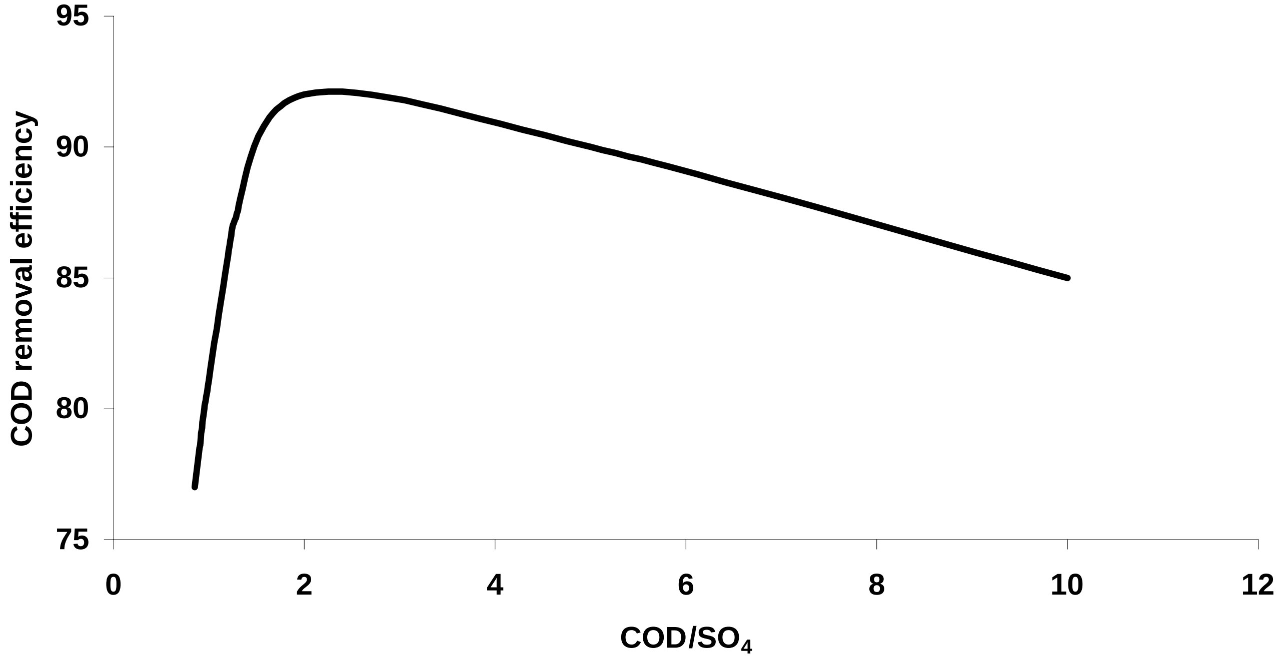

Figure 2. Effect of COD/SO_4 ratio on COD removal efficiency.

3. RESULTS AND DISCUSSION

Cow manure stabilization process, including COD reduction, liquid and sludge color change, is shown in Table 3. Also the responses of four reactors for COD removal are evaluated by measuring influents and effluents CODs. The measurements in an 8 weeks period are presented in Table 4. Influents and effluents sulfates, alkalinities, pH and mean effluent suspended solids are presented in Table 5. Table 6 shows the effluents CODs before and after contact with air. Granule formation time accompanied with sludge physical properties are given in Table 7.

Seed Sludge Preparation and Conditioning Due to lack of any proper anaerobic treatment plant and very limited number of aerobic activated sludge plants in Iran, fresh cow manure was chosen as the seed for starting up the reactors. Stabilization and adaptation of cow manure with the defined feed (Table 1) took Place in 90 days (Table 3).

Usually MPB are abundant in cow manure, but other bacteria population is not sufficient and due to undigested organic matter, COD concentration is rather high. For stabilization and conditioning of cow manure, diluted molasses was added at different time interval. Easily digestible materials did help refractory organic present in the manure to be digested gradually thus reducing the initial COD to about 1000 mg/l within three months. It is recommended that for seed sludge conditioning or animal manure digestion, a mixture of proteins, fats and carbohydrates plus necessary trace elements to be added to the digester. With this method, digestion reactions of refractory organics will be accelerated [11]. Cultivation media was also diluted every 15 days to reduce inhibiting compounds [12]. After this period, seed sludge was able to treat synthetic wastewater with COD=1000 mg/l. The COD removal efficiency was about 85% and MLVSS/MLSS was 0.8.

COD Removal According to Table 4, R_2 reactor with COD/SO_4 =2 had the highest COD removal

TABLE 5. The Amounts of COD, Alkalinity*, Suspended Solid and Ph at Various Sulfate Concentrations is 5th Week of Operation (all Concentrations are in mg/l).

Reactor	*SS out*	*Alk. in*	*Alk. out*	*SO_4 In*	*SO_4 out*	*COD in*	*COD out*	*pH*
R_1	10	650	715	100	16	1020	110	7
R_2	15	650	900	500	55	1020	75	7.1
R_3	30	650	990	1000	285	1020	125	7.2
R_4	35	650	1300	1500	609	1020	265	6.8

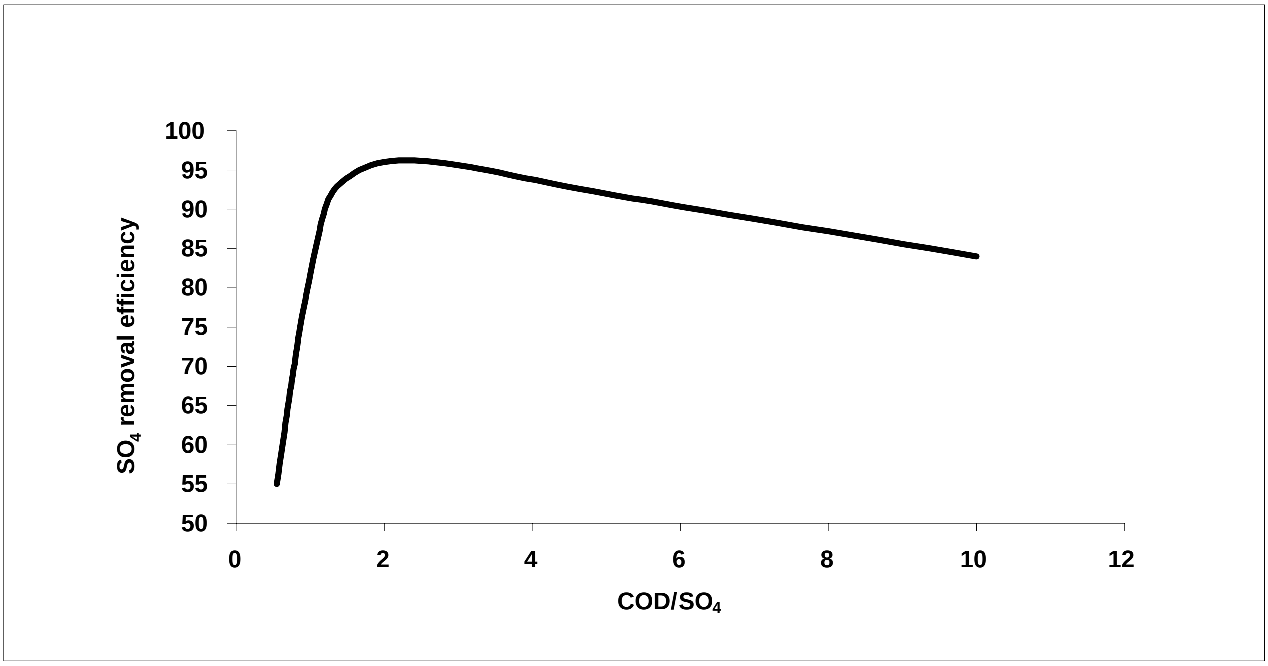

Figure 3. Effect of COD/SO_4 on SO_4 removal efficiency.

efficiency and R_4 with COD/SO_4 = 0.67 had the lowest efficiency.

For R_1 and R_3 with COD to SO_4 ratios of 10 and 1.0, respectively, the COD removal efficiency were almost the same and lower than R_2. Hence, the presence of sulfate can have both positive and negative effect on COD removal rate. It was possible to find an optimum concentration for sulfate concentration. At pH = 7 and COD = 1000 mg/l, the optimum sulfate concentration is 500 mg/l (Figure 2).

The SRB thermodynamic and kinetic tendency for utilizing the intermediate fermentation products such as acetate is more than MPB. Thus SRB will reduce the methanogenic activity and consequently decrease their growth. Moreover, the sulfide products will also act as an inhibitor for MPB. These factors are considered as sulfate negative

TABLE 6. The Reactor Effluents COD (before and after Contact with Air).

Reactor	*SO_4 (mg/l)*	*COD (mg/l) Before contact*	*COD (mg/l) After contact*	*Efficiency (%)*
R_1	100	155	150	3.2
R_2	500	85	75	12
R_3	1000	195	150	23
R_4	1500	260	195	25

TABLE 7. Sludge and Granule Specifications at The End of This Study.

Reactor	R_1	R_2	R_3	R_4
SO_4 (mg/l)	100	500	1000	1500
Granule formation time (day)	45	33	45	Not - observed
Granule size (mm)	1-3	1-4	1-3	-
Granule settling velocity (m/h)	42	50	40	-
Rate of washout (mg/l)	10	15	30	35
COD removal eff. (%)	85	91	84	77
SO_4 conversion (%)	84	89	71.5	59.4

effect on COD removal. On the other hand, the intermediate products are known as inhibitors for MPB bacteria. Then due to presence of SRB the medium products do not accumulate and hence the MPB activities do not reduce [6].

Sulfate Conversion As previously discussed, both COD/SO_4 and sulfate concentration have an important effect on COD removal and sulfate conversion efficiency. In low sulfate concentration, due to low population of SRB, the intermediate products are not removed rapidly, and as a result, both COD removal and SO_4 reduction efficiencies are low (Figure 2). At medium SO_4 concentration, the SRB population will increase and as sulfate inhibitory effect is not still high, intermediate products will be absorbed much faster and COD removal efficiency will also increase. In this case there is a synergy effect between MPB and SRB (Figure 3). At high concentration of sulfate, sulfide concentration increases and reaches to inhibitory level which has adverse effect on MPB activities and reduces both COD removal and sulfate reduction efficiencies.

Alkalinity Sulfide compounds, like carbonate compounds create buffer strength in anaerobic reactor due to H_2S production and its emission (Equation 1). This explains the main reason for increase in effluent alkalinity compound with influent alkalinity Table 5.

$$H_2O + CO_2 + HS^- \leftrightarrow H_2S + HCO_3$$

The rate of alkalinity increase depends upon many factors such as the rate of sulfide production in the reactor, pH, temperature and biogas production rate

Biogas production was approximate the same

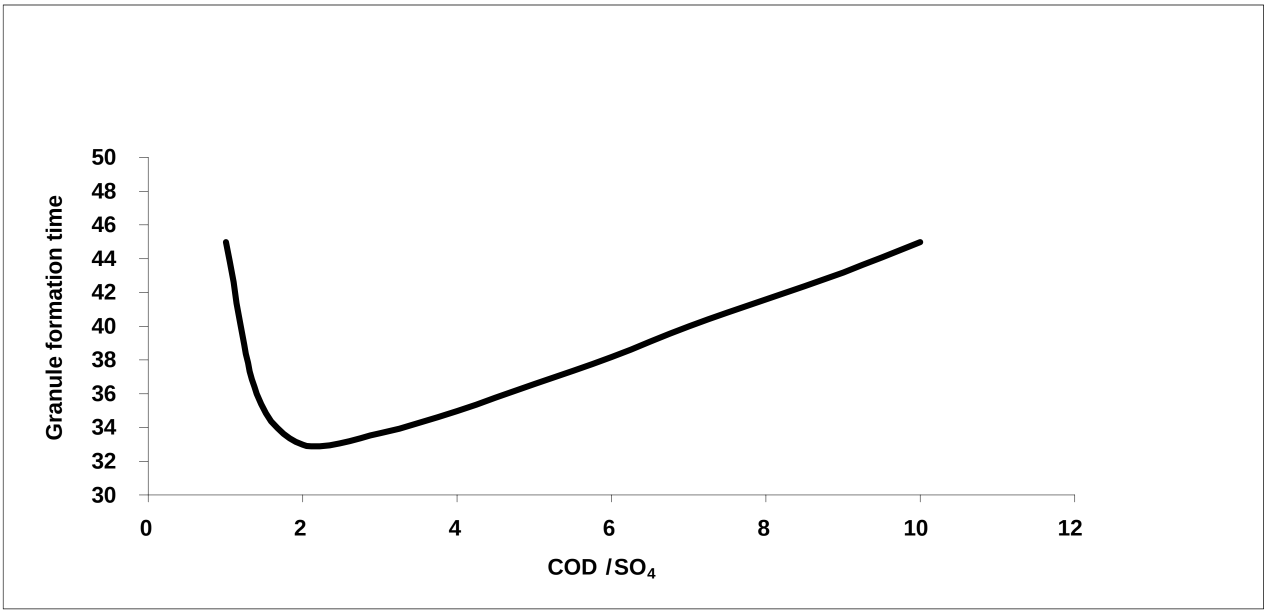

Figure 4. Effect of COD/SO_4 on granule formation time at COD=1000mg/l.

in all reactors but since pH varies in different reactors, remarkable deviation are observed from what can be the calculated alkalinity. At pH=7 and taking into account the amount of sulfate reduction the calculated alkalinity increment should be in the order of 55, 291, 486 and 583mg/l for reactors R_1 to R_4, respectively, whilst in practice these increments were 55 in R_1 at pH = 7, 250 in R_2 at pH = 7.1, 340 in R_3 at pH = 7.2 and 650 in R_4 at pH = 6.8.

Sludge Washout The effluent suspended solid contents for the reactors are shown in Table 5. Since hydraulic velocity and sludge content are approximately equal in all reactors, the operation of the settler zone should be the same. But in practice, different rates of sludge washout were observed due to different sludge quality. Results show that the washout rate is proportional to the rate of sulfate conversion within the reactor. Sludge washout is highly intensified by increasing SRB activities and the amount of toxicity of sulfide compounds, which may be the main cause of granule destruction [5].

Sulfide Oxidation In presence of air, sulfide content of effluent will diminish by stripping and oxidation actions. The sulfide oxidation may occur by three available mechanisms:

a) Conversion of sulfide to sulfate by sulfur bacteria action.
b) Conversion of sulfide to sulfur by sulfur bacteria action.
c) Conversion to sulfur and sulfate by air oxidation.

In order to measure the amount of sulfide oxidation, effluents COD were measured before and after the effluents were exposed to air and the results were presented in Table 6 COD difference were also shown in Table 6. It can be seen that by increasing sulfide in the reactor, COD difference will also increase. It is also interesting to note that the time interval between two COD measurements was less than one minute. As the total time needed for total sulfide oxidation is reported to be 13 minutes [13], the obtained results were not unexpected.

Granulation According to Table 7, it can be concluded that at COD/SO_4 = 2(COD = 1000 mg/l), granulation occurs much faster and granules become larger compared with other conditions, consequently granule settling velocity is also higher than other conditions.

It is worth mentioning that in R_2 reactor, both COD and sulfate removal efficiencies were greater than other reactors, which is an indication of more active bacteria growth inR_2. This is in accordance with the discussion in sulfate reduction section. In R_4 with SO_4 = 1500 mg/l., the inhibitory effect of sulfide and H_2S concentration is such that no granules appeared after 60 days [5,6] and the added granules were also disintegrated after 15 days.

4. CONCLUSION

1. In the absence of suitable granular sludge, fresh cow manure can be stabilized within 3 months and be utilized as seed sludge UASB reactor.
2. Due to conversion of sulfate to sulfide, alkalinity will increase in anaerobic reactor and the rate depends upon pH, biogas production rate and the amount of sulfide concentration in the effluent.
3. Sludge washout will increase by increasing sulfate concentration in the feed due to increase in SRB population and destruction of MPB cellwall due to inhibitory effect of hydrogen sulfide.
4. Effluent sulfide will oxidize very rapidly as soon as it exposes to air.
5. At COD/SO_4 about 2,
   a- Maximum COD removal and sulfate reduction occur.
   b- Granulation occurs faster than any other condition that examined in this work.
   c- The settling velocity and granule size are better than any other ratios of COD to SO_4.
6. For SO_4 concentration of equal or greater than 1500 mg/l, granulation does not take place within reasonable time.

5. ABBRIVIATIONS

BOD :	Biological Oxygen Demand
COD :	Chemical Oxygen Demand
SRB :	Sulfate Reducing Bacteria
MPB :	Methane Producing Bacteria
UASB :	Upflow Anaerobic Sludge Blanket
MLSS :	Mixed Liquor Suspended Solid
MLVSS :	Mixed Liquor Volatile Suspended Solid

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