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Sulfate Reduction in an Upflow Anaerobic Sludge Blanket Bioreactor and Optimization of Operational Conditions: pH, Hydraulic Retention Time, Sulfate Loading Rate, COD/SO$_4^{2-}$ Ratio

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Abstract

This paper introduces an application of biological treatment for industrial wastewater (IWW) contaminated with sulfate ions. Lab-scale up-flow anaerobic sludge blanket (UASB) bioreactor was fabricated for detecting the optimal operational conditions of sulfate ions removal with other impurities from IWW. Sulfate reducing bacteria (SRB) was effectively reduced sulfate into sulfide and let H$_2$S gas liberated. The experiment has been carried out along 345 days of operational time. Results showed that, at pH 6.2, hydraulic retention time (HRT) between 24-18 h on increasing sulfate loading rate (SLR) up to 1.3 g SO$_4^{2-}$ L^{-1} d^{-1}, the sulfate reduction efficiency (SRE) was increased from (53±11) up to (87±7) %, in addition to 99% heavy elements removal, respectively. However, on decreasing HRT to 12.0 h with increasing SLR up to 3.6 g SO$_4^{2-}$ L^{-1}d^{-1}, the sulfate reduction (SR) rate decreased to 66±3 %. On increasing the temperature from 25 to 35°C, the SRE was increased from 68 to 83%. When COD/SO$_4^{2-}$ ratio was increased from 2.0 to 5.0, the SRE was slightly decreased from 74±10 to 68±6%, respectively. Moreover, when COD/SO$_4^{2-}$ ratio was increased from 5.0 to 10.0, (SRE) decreased from 68±6 to 66±3%. Consequently, the optimal operational conditions of the UASB reactor for maximum SRB at temperature, HRT, SLR, and COD/SO$_4^{2-}$ ratio of 35°C, 18h, 1.3g SO$_4^{2-}$L^{-1}d^{-1}, and 2.0, respectively, while Fe^{2+} is essential.

Key Words: Sulfate removal, Biological treatment, Anaerobic treatment, Industrial wastewater, Sulfate reducing bacteria, Up-flow anaerobic sludge blanket.

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1. Introduction

Sulfate (SO$_4^{2-}$) is mainly originating from the processes of chemical weathering of sulphur containing minerals and the oxidation of sulfide and sulphur. Its ions are leached from rocks and soil containing SO$_4^{2-}$ ions that dissolved in natural water. The oxidation of sulfur compounds like pyrite Fe$_2$S, with oxygen in presence of water, produced a high concentrated wastewater with sulfate. This changes it to polluted and unusable water for some purposes [1]. In addition, SO$_4^{2-}$ are discharging with high concentrations from IWW such as mining effluents, metallurgical, electronics, electroplating, paint/ pigment manufacturing, stainless steel production, leather tanning, textile, wood preservation, and acid-mine drainage. Drinking water containing SO$_4^{2-}$ exceeded 500 mg/L could affect its taste and cause diarrhea [2-3]. In accordance, the world health organization recommended that health authorities

were being notified if sulfate exceed 500 mg SO$_4^{2-}$/L in drinking water. High concentrations of SO$_4^{2-}$ in IWW can cause environmental problems, corrosion of cooling tower, pipes, and concrete buildings. Therefore, environmental agencies in many countries applying trigger level between 250 and 500 mg/L in mine drainages and industrial effluents, respectively [4]. Hence, in order to protect the environment, it is necessary to reduce the sulfate ions in the IWW to meet the regulatory standards for safe discharging. Several technologies, or a combination of one or more of these technologies have been developed to reduce sulfate ions in WW, such as: chemical adsorption, bio-electrochemical cell, electrodialysis, electro-coagulation, crystallization, microalgal, membrane filtration, and chemical precipitation [5-12]. However, those methods were not suitable for the treatment of highly concentrated SO$_4^{2-}$ in WW, that fulfilled limited removal efficiency or need high cost. In addition, ion

exchange and membrane separation technologies involved the generation of a liquid waste stream that might require proper management. The chemical precipitation method (CPM) mainly included barium chloride precipitated as barium sulfate. Although, CPM could reach high SRE, but chloride and barium ions were corrosive and toxic. It also had high cost because barium chloride salt was expensive than lime, so CPM was rarely used in IWWT. Although lime is being widely used in the field of WWT; but SRE was still limited due to the relatively high solubility of 2000 mg/L gypsum. The biological sulfate reduction (BSR) offered the most versatile and widely applicable approach to sulfate removal and had the benefits of being able to couple sulfate and metal removal. The advantages of BSR had also metal recovery, with low maintenance. Highly organic loaded Agro-IWW was perfectly treated using UASB reactor sequenced with rotating biological contactor (RBC). This combined system (UASB-RBC) achieved remarkable pollutants reduction to comply with the discharging limits onto the water bodies or to be reused as investigated by El-Awady et al [13]. Biological treatment of industrial wastewater using UASB has been investigated for application and implementation in the industrial sector [14]. Physico-chemical, dissolved air flotation (DAF), chemical coagulation and biological treatment of highly polluted food IWW were chosen. Results revealed that DAF exhibited remarkable removal of floated and suspended matters, while chemical treatment revealed noticeable efficiency. Consequently, the biologically treated effluent fulfilled compliance limits for discharging WW onto the sewerage network [15]. So, the aims of this study are: (i) to reduce sulfate ions via biological technique, (ii) to optimize the operational conditions for a UASB bioreactor for treating IWW based on the effect of HRT, SLR, temperature, and COD/SO_4^{2-} ratio. Residual SO_4^{2-} and H_2S generation were main parameters to evaluate the reduction of sulfate in the UASB.

2. Materials and Methods
2.1. Design and setup of UASB bioreactor for biological reduction of sulfate

The IWW was continuously passed into the treatment unit via a peristaltic pump with a calculated flow from bottom to pass through the UASB. To accomplish the objectives of this study, a biological treatment UASB reactor that manufactured with total volume of 3.20 L from poly-vinyl chloride (PVC), was used with synthetic IWW and calculated anaerobic sludge. The treatment unit was located at National Research Centre pilot area. It was fed continuously with sugarcane industrial end-of pipe wastewater impregnated with known dose of sulphate. The treatment system was operated during summer and winter seasons, hence different organic loading rates (OLR) and different temperatures were investigated.

The inoculum source was anaerobic sludge from a UASB reactor treating sugarcane-vinas' wastewater. Figure.1 shows a schematic diagram and photo of the used UASB reactor, in which points (1-2) represents the influent feeding inlet, and point 4 is representing treatment plant outlet. The numbers 5–7 representing the samples locations where aliquots could be collected for analysis, while Point 8 represents biogas outlet. The unit was setup by adjusting sludge blanket and continuously fed by IWW for a week to be adapted with SRB media growth [16].

2.2. Analytical methods

The physico-chemical analysis of raw and treated wastewater has been carried out to evaluate and monitor the qualities and quantities of samples. All analyses have been carried out according to the American standard methods for examination the water and wastewater, APHA, 23rd Eden, 2017 [16]. The experimental tests were carried out according to the following methods: 5220-D (COD); 4500-SO_4^{2-}; 4500-S^{2-}; and 3500 Fe. COD, SO_4^{2-}, S^{2-}, pH, and Fe analyses were performed for both influent and effluent using 100 ml each. The inlet IWW and treated outlet have been collected to identify the treatment performance. Sulfate concentration was measured using Carry-100 UV-Vis spectrophotometer; Agilent technologies. The pH-values were measured using ADWA-8000 multi-parameter. The concentration of heavy metal's ions, such as chromium, iron, manganese, nickel, cadmium, lead and zinc were measured using Inductively coupled plasma emission; ICP-AES 5000, Agilent Technologies Spectrometer.
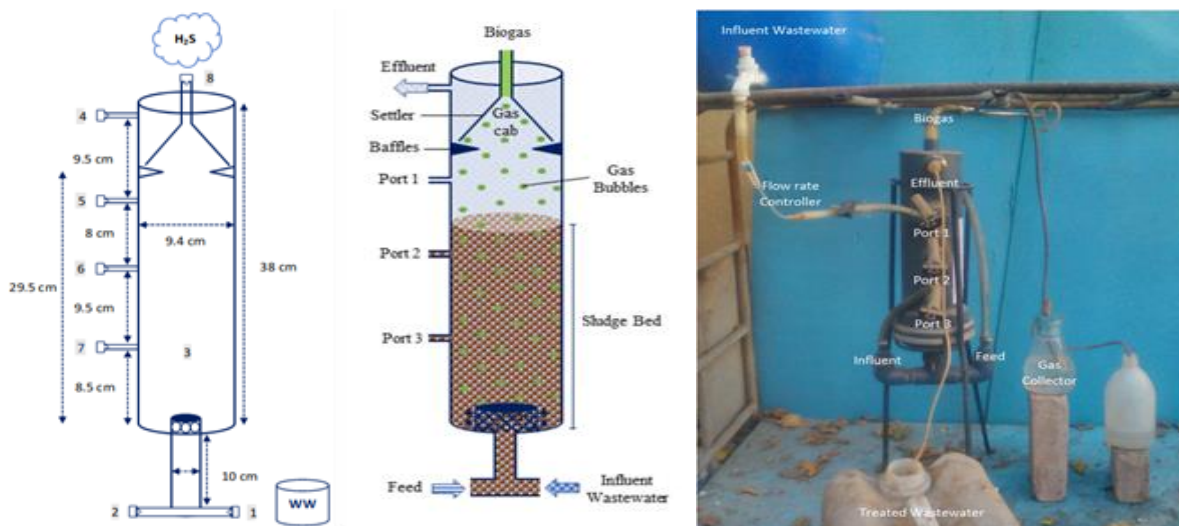
Figure 1: Schematic diagram and a photo of the used UASB

2.3. Identification of sulfate reducing bacteria.

A synthetic medium was prepared from 3.5 g L^{-1} sodium lactate, 1.0 g L^{-1} beef extract, 2.0 g L^{-1} peptone, 2.0 g L^{-1} $MgSO_4.7H_2O$ magnesium sulfate, 1.5 g L^{-1} Na_2SO_4 sodium sulfate, 0.5 K_2HPO_4 di-potassium hydrogen phosphate, 0.392 g L^{-1} Fe $(NH_4)_2(SO_4)_2.6H_2O$ ferrous ammonium sulfate, 0.10 g L^{-1} $CaCl_2$ calcium chloride, sodium ascorbate, excluding ferrous ammonium sulfate, sodium ascorbate. Medium dispensed in screw-capped test tubes, and sterilize via autoclaving (121°C, 15 min). Final pH should be 7.5 ± 0.3. Use completely filled tubes. Separately sterilize extra medium to be added to tubes for filling. On day of use, prepare separate solutions of 3.92 g/100 mL ferrous ammonium sulfate, 1.0 g/100 mL sodium ascorbate, filter through a 0.45-m membrane filter, and aseptically add 0.1 mL each solution/10 mL basal medium [16]. Yellow color indicates no SRB growth, the black color indicates sulfate reducing bacteria growth (Figure 2).
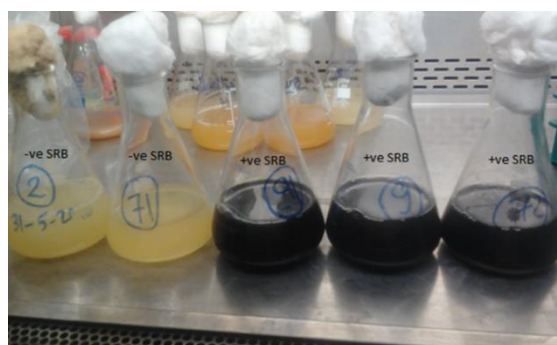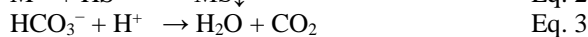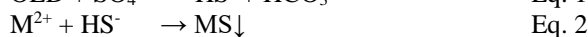

Figure 2: Identification of SRB

2.4. Treatment methodology:

In this technique, SRB can utilize sugar as electron donor, and to use sulfate as electron acceptors, to produce end products such as H_2S, CO_2, while most of metals can precipitate as metal sulfide represented in Eq's (1-3), organic electron donor (OED)

$$OED + SO_4^{2-} \rightarrow HS^- + HCO_3^- \qquad \text{Eq. 1}$$
$$M^{2+} + HS^- \rightarrow MS\downarrow \qquad \text{Eq. 2}$$
$$HCO_3^- + H^+ \rightarrow H_2O + CO_2 \qquad \text{Eq. 3}$$

2.5. SRB metabolism mechanism:

The fundamental way to increase the growth and reproduction of SRB from the metabolic mechanism. It utilizes sugars, alcohols, acetic acid, higher fatty acids, hydrogen, aromatic compounds, partial amino acids, and various benzene ring substituents as electron donors. SRB uses also sulfates, sulfonate, dimethyl sulfoxide, fumaric acid as electron acceptors, to produce H_2S, CO_2, CH_3COOH as end products [17]. The reduction route of sulfate is shown in scheme.1 [18], where SO_4^{2-}/SO_3^{2-} self-oxidation/ reduction potential is too low. SO_4^{2-} must be activated as a strong oxidizer, then it reverts to S^{2-}. The adenine triphosphate (ATP) and high-energy electrons were produced when the organic carbon source in the wastewater degraded and benefited in this way. Some SRBs can also utilize nitrite as the sole source of nitrogen for assimilation.
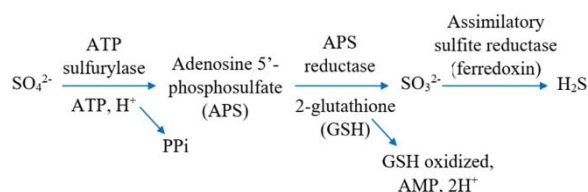
Scheme.1: Pathway: assimilatory of sulfate-reduction

Reaction of sulfate-reduction reaction /Sulfidogenic Pathways:
$$2C(H_2O) + SO_4^{2-} \rightarrow HS^- + 2HCO_3^- \quad \Delta G^o = -47.6 \text{ KJ.mol}^{-1}$$

Where: $C(H_2O)$; represents organic electron donor's substrate. Anaerobic methanogenic population archaeon (MPA) was capable for acetic acid, H_2/CO_2 and methyl compounds synthesis for methane production [19].

Table 1 Operational conditions applied to the UASB reactor

Parameter	Unit	I	II	III	IV	V	VI	VII	VIII
Temp.	^oC	25±10	25±10	25±10	25±10	25±10	25±10	25±10	25±10
HRT	hour	24	18	18	18	18	12	12	12
Time	day	88	54	40	30	28	42	44	19
COD	gL^{-1}	1.0	1.0	1.0	2.0	3.6	3.6	9.0	18
OLR	$gL^{-1}d^{-1}$	1.0	1.3	1.3	2.6	4.8	7.2	18	36
SO_4^{2-}	gL^{-1}	0.5	0.5	0.5	1.0	1.8	1.8	1.8	1.8
SLR	$gL^{-1}d^{-1}$	0.5	0.67	0.67	1.3	2.4	3.6	3.6	3.6
COD/ SO_4^{2-}	= =	2.0	2.0	2.0	2.0	2.0	2.0	5.0	10.0
Fe^{+2}	gL^{-1}	-	-	0.1	0.1	0.1	0.1	0.1	0.1

2.6. Experimental procedure:

The performance of UASB was evaluated by studying some variables like HRT, temperature, SLR, COD/SO_4^{2-} ratios, and metal addition followed by measuring SRE, H_2S production, COD and metals removal. The HRT was studied at 24 h in stage I, 18.0 h in stages II–V, and 12 h in stages VI–VIII, while the SLR was set at 0.5 g SO_4^{2-}/L/d in stage I, 0.67 g SO_4^{2-}/L/d in stages II–III, 1.3 g SO_4^{2-}/L/d in stage IV, 2.4 g SO_4^{2-}/L/d in stage V, and 3.6 g SO_4^{2-}/L/d in stages VI–VIII, while COD/SO_4^{2-} ratio was increased from 2.0 in Stages I–VI to 5.0 in stage VII followed by 10.0 in stage VIII. Moreover, 100 mg Fe^{2+} metal/L was added at Stage III as represented in Table 1. Finally, post-treatment was performed of the UASB effluent to remove residual H_2S from the industrial wastewater.

3. Results and discussion:

The UASB reactor was continuously fed and operated for 345 days to evaluate its performance in SO_4^{2-} reduction. HRT was studied along this period, from 24h to 12h, while SLR was increased from 0.5 g $SO_4^{2-} L^{-1} d^{-1}$ to 3.6 g $SO_4^{2-} L^{-1} d^{-1}$. When COD/SO_4^{2-} ratio was increased from 2.0 to 5.0 &10.0 as shown in Table 1, the temperatures were studied at 25°C and 35°C, respectively. The performance of UASB reactor was represented in terms of SO_4^{2-} reduction, H_2S production, and COD removal during this period.

The metabolic activity and the substrates competition of SRB and MPA affected by environmental factors includes pH, HRT, SO_4^{2-}, COD concentrations and other substrates like PO_4^{3-}, TN, Fe^{2+}. the competition between SRB, MPA incline to be complicated since the reactions took place in a special micro-environment. Hence, the biological treatment process occurs through a competition between SRB, and MPA for substrates.

In addition, operational parameters such as the inoculum source, organic matters source, sulfide diffusion, HRT, SLR and COD/SO_4^{2-} ratio that enabled SRB to outcompete the microbial community. The pH of SRB and MPA growth and numeration was optimized at 7.5 ± 0.3 [20].

3.1. The Effect of Temperature on SRE:

The effect of temperature on the anaerobic SR was studied in a batch skill, at temperature increased in the range of 25-35°C, where the SRE was increased from 68 to 83%. The temperature has an effective role on the SR. On decreasing the temperature, the biological activity of microorganism was being decreased, consequently the SR decreased. On the contrary, at higher temperature the biological activity of microorganism was increased, and SR increased too [21].
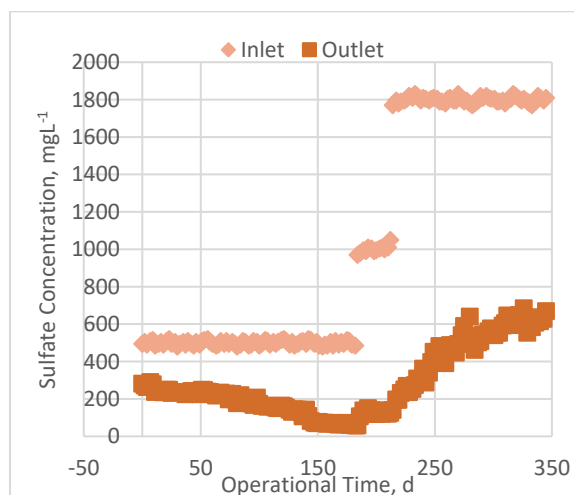

Figure 3: Sulfate concentration variation along operational time

3.2. Effect of Fe^{2+} addition on SRB activity, SRE, and its metal removal:

Iron was added at optimum HRT 18h at stage III with 0.1 g $Fe^{2+}L^{-1}$ concentration. The addition of proper Fe^{2+} decreased the sulfide inhibition and increased SRE removal from 69±10 to 86±2. This is because Fe^{2+} as a cell nutrient transported and prolonged the proliferative peak period help to enhance the metabolic activity of both SRB and MBA [19]. Addition of Fe^{2+} during treatment was very effective for sulfides removal and microbial community inhibition. Fe^{2+} improved sulfate reduction metabolism, and promoted metals precipitation. It helped dissolved sulfides consumption, and chemically reduce sulfate to sulfides via thermodynamically reduction, where total sulfides decreased from (34±9) to (17±8) mg/L (Stage III), and sulphates removal reached (99±0.5) % after Fe^{2+}, respectively [22].

3.3. Effect of HRT and SLR on sulfate reduction:

In the UASB bioreactor, on decreasing the hydraulic retention time, (HRT) from 24.0 to 18.0 h (stages I, II), the SRE increased from (53 ± 11) to (69 ± 10) %, because the up-flow rate, Q increases eq. 2, and SRB metabolism was favorable compared to methanogens archaea metabolism as previously stated [23]. HRT was an important treatment parameter because the high HRT required a large area for treatment and higher cost for operation energy. However, when HRT was decreased from 18h to 12.0 h (stages V, VI) and SLR increased from 2.4 to 3.6 g $SO_4^{2-}L^{-1}d^{-1}$, the reduction efficiency of sulfate decreased from (86 ± 6) to (74 ± 10) %.

- Calculation of up-flow rate (Q):

Q = V / HRT   **(1)**

Where:

Q = Flow rate (m^3day^{-1}); V= Reactor volume (m^3);
HRT = Hydraulic Retention Time (day).

- Calculation of Sulfate Loading Rate (SLR):

SLR = S / HRT   **(2)**

Where:

SLR = sulfate loading rate (g $SO_4^{2-} L^{-1} d^{-1}$);
S   = sulfate concentration (g $SO_4^{2-} L^{-1}$);
HRT = hydraulic retention time (day).

The effect of SLR increasing on the SR as in Eq. 2 was observed in stages I, II, IV, V, & VI; while SLR increased from 0.5 to 0.67, 1.3, 2.4, and 3.6 g $SO_4^{2-}L^{-1}d^{-1}$, respectively. Table 2 indicates that when SLR increases from 0.5 to 0.67 g $SO_4^{2-}L^{-1}d^{-1}$, the SRE increased to (69 ± 10) %, and (87 ± 7) %. Also, when SLR increased to 1.3 g $SO_4^{2-} L^{-1}d^{-1}$, and SRE fixed at SLR of 2.4 g $SO_4^{2-} L^{-1}d^{-1}$, it decreased to (74 ± 10) % at 3.6 g $SO_4^{2-}L^{-1}d^{-1}$ SLR. Moreover, Sulphate Reducing rate depended on SLR from 0.5 to 2.4 g $SO_4^{2-}L^{-1}d^{-1}$, then up to 3.6 g $SO_4^{2-}L^{-1}d^{-1}$ depended on sulfate reduction as seen in Figure 3. Results attributed to inhibition of SRB from sulfide production was observed in a linear increase of SRE between 64 and 85 %, when sulfate concentration was increased from 1000–10000 mgL^{-1}, the SLR from 0.26 up to 2.0 g $SO_4^{2-}L^{-1}d^{-1}$ and a decrease when reached to 4.8 g $SO_4^{2-} L^{-1}d^{-1}$ [21]. Sulfate was an important parameter for evaluation of the dominance of SRB over MPA, when the SLR increased from 0.1 to 8.0 g $SO_4^{2-}L^{-1}d^{-1}$, when sulfate reduction was increased from 5 to 90% [20].

However, sulfate was also considered a problem as it caused sulfide toxicity through the reduction to sulfide.

SRB may be predominant on microbial community when SLR increased from 0.5 to 0.67, 1.3 g $SO_4^{2-}L^{-1}d^{-1}$, and SR increased to 87 ± 7% at SLR of 1.3 g $SO_4^{2-}L^{-1}d^{-1}$. The sulfate concentration may affect the reduction efficiency because it provides the electron acceptor to SRB favorable metabolism than of methanogens, while by increasing the sulfate concentration from 1.0 to 10 g L^{-1}, the SRE increased from 64 to 85 % [21].

Higher sulfate removals may be observed at 2.0 g $SO_4^{2-}L^{-1}d^{-1}$[22], while this efficiency may be decreased when SLR was continuously increased [20].
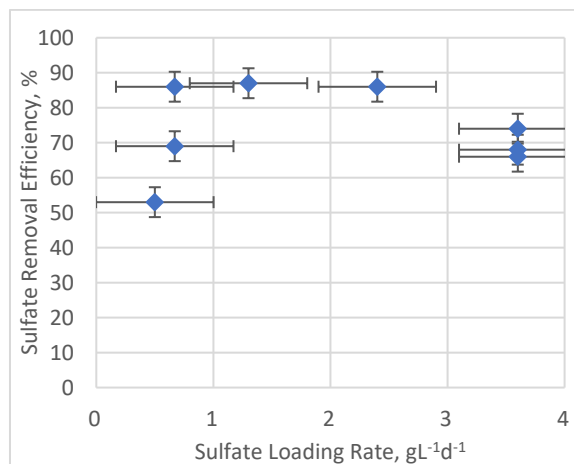

Figure 4: Effect of SLR on sulfate reduction

3.4. Effect of COD/SO_4^{2-} ratio on sulfate reduction and organic matter removal:

During the Stages VI, VII, and VIII, the COD/SO_4^{2-} ratios were evaluated at 2.0, 5.0, and 10.0 as in Table.2. When COD/SO_4^{2-} ratio was increased from 2.0 to 5.0, the sulfate reduction was slightly decreased from (74 ± 10) to (68 ± 6) %, while COD/SO_4^{2-} ratio increased from 5.0 to 10.0, the sulfate reduction decreased from (68 ± 6) to (66 ± 3) %.

Table 2 Effect of COD/SO_4^{2-} ratio on sulfate reduction

Parameter	Unit	Results		
COD/ SO_4^{2-}	= =	2.0	5.0	10.0
SO_4^{2-} removal	%	74±10	68±6	66±3

It is clear that the COD/SO_4^{2-} ratio has the greatest effect on the sulfate reduction. At a lower OLR, the organisms increase the consumption efficiency of organic matter [23]. On changing the COD/SO_4^{2-} ratios, electron donor transfer took various ways as a result of the competition between the SRB/MPA, and MPA predominate at COD/SO_4^{2-} ratios were exceeding 2.7 and at less than 1.0 COD/SO_4^{2-} ratios, SRB utilized methanogenic substrates like acetate and methanol with less efficiently than MPA [20]. In cultivated sludge, and at high COD/SO_4^{2-} ratios, the microbial community of SRB was more fragile, but when COD/SO_4^{2-} decreased with less than 1.6, the SRB populations have more sulfides tolerant [24]. The ratio of the COD/SO_4^{2-} was the most accurate parameter that affected the microbial competition [25].
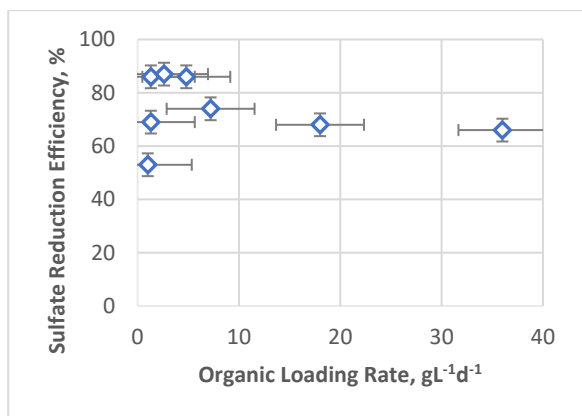
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Figure 5: Effect of OLR on sulfate reduction

Consequently, SRB was predominant when COD/SO_4^{2-} ratio was less than 1.6. It maintained that a COD/SO_4^{2-} ratio with less than 1.0 was to target a high electron flow from organic matter to sulfate [20]. Previous works showed high sulfate removals when reactors were operated at a COD/SO_4^{2-} ratio of 1.0, when the highest total sulfides concentrations were observed [19],[23],[26]. It was also showed that sulfate removal decreased as the COD/SO_4^{2-} ratios decreased to less than 1.0 as a result of sulfides inhibition [27]. On the other hand, when COD/SO_4^{2-} ratio was too low, both SRB and MA were inhibited because the sulfide produced during the sulfate reduction process could be combined with iron and iron-containing substances in the intracellular pigment, resulting in sulfide inhibition [19]. At higher COD/SO_4^{2-} ratios, the growth of SRB was limited by the substrate, so MA dominates, results showed that at a lower COD/SO_4^{2-} ratios of 2.0, an increase in sulfate reduction was observed and by increasing COD/SO_4^{2-} ratios to 5.0 and 10.0, sulfate reduction decreased because MPA became predominant organism over SRB. In conclusion, the suitable operational conditions for reduction of sulfate observed at a COD/SO_4^{2-} ratio of around 2.0, in which SRB became the predominant organism, below that range, that both organisms inhibited by sulfide inhibition, and above that range, MA predominate.

3.5. The Production of Sulfides:

The production of H_2S was evaluated in all stages from I to VIII, first, when SLR was 0.5 g $SO_4^{2-}L^{-1}d^{-1}$ in stage I, the average concentration of H_2S was 25 ± 6 mg $S^{2-}L^{-1}$. It increased to 34 ± 9 mg $S^{2-}L^{-1}$ when SLR was 0.67 g SO_4^{2-} L^{-1} d^{-1} at stages II. The average concentration of S^{2-} became 17 ± 8 mg $S^{2-}L^{-1}$, after Fe^{2+} addition in Stage III. This is because Fe^{2+} was combined with S^{2-} and yielded a black precipitate from ferrous sulfide (FeS). In addition, at SLR 1.3 g SO_4^{2-} $L^{-1}d^{-1}$ in stage IV, H_2S concentration was 67 ± 22 mg $S^{2-}L^{-1}$. In accordance, when SLR reached 3.6 g SO_4^{2-} $L^{-1}d^{-1}$ at stage VI, H_2S concentration reached 87 ± 16 mg S^{2-} L^{-1}. Consequently, the maximum H_2S

concentration reached 110 ± 23 mg S^{2-} L^{-1} when COD/SO_4^{2-} ratio was 2.0 stage V.
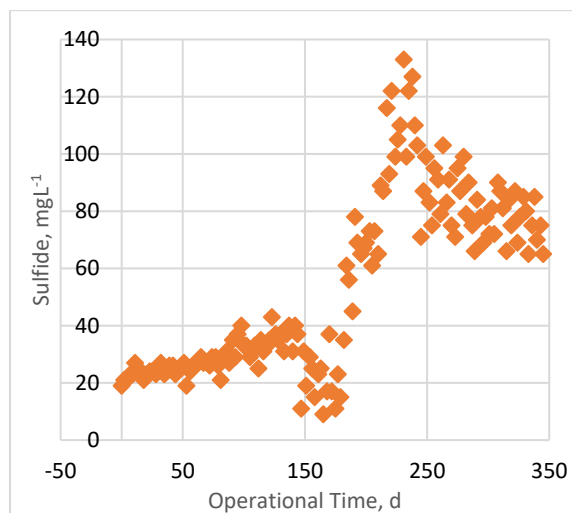

Figure 6: H_2S production through operational time

Finally; when COD/SO_4^{2-} ratio was increased to 10.0 in stage VIII, H_2S concentration decreased to 75 ± 10 mg $S^{2-}L^{-1}$, as a result of less sulfate reduction. The metabolic activities of SRB and MPA organisms were inhibited as a result of their exposure to high sulfide concentrations for a long-time, because H_2S was penetrating the cell walls and stop their normal growth with process failure [20]. The inhibition of free H_2S concentration levels ranged from 110 to 1000 mg $S^{2-}L^{-1}$ [28]; depending on the reaction conditions and organism immobilization [29]. At pH 5.0 in acidic medium, free H_2S inhibited the sulfate reduction process at 100 mg $S^{2-}L^{-1}$ [30] and sulfide was the main parameter causing toxicity to the sludge [27]. The effect of pH on presence of sulfide species $H_2S/HS^-/S^{2-}$ that altered its concentrations that made an inhibitory effect on a bioreactor microbial community. This is because it combined with Fe in cytochromes or any other metal-containing compounds. Sulfide may be used to precipitate metals as metal sulfides [26]. The optimum produced free H_2S in the experiments of this paper reached to 70 mg $S^{2-}L^{-1}$, so, it doesn't reach the inhibition limit for the bioreactor microbial community.

3.6. Applications of H_2S gas in industry and removal of the residual sulfide:

H_2S gas production was used in the preparing of sulfuric acid [31]. The dissolved sulfide in the treated water was present in the formula of HS^- and S^{2-} that converted to free H_2S by addition of HCl (1:1) to the treated water with stirring for 30 min, where the residual dissolved sulfide decreased from 45 mg $S^{2-}L^{-1}$ to 10 mg $S^{2-}L^{-1}$. Finally, the residual sulfide was removed by adding activated carbon (AC), where1 kg AC removed about 10 g S^{2-}.

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4. Conclusions

The UASB bioreactor technique was fabricated and setup to evaluate SO_4^{2-} reduction and metals removal from IWW. The UASB was running at different SLR, HRT, and COD/SO_4^{2-} ratio to detect the optimal operating conditions. Results showed that the HRT was decreased from 24.0 to 18.0 h with increasing the sulfate reduction efficiency, while at 12.0 h the process was decreased. It was noticed that the SLR has a greatest effect on the sulfate reduction efficiency. The full-scale UASB bioreactor achieved high performance for SO_4^{2-} reduction and metals removal from IWW. Sulfidogenic process was observed at HRT, SLR, and COD/SO_4^{2-} ratio at 18.0 h, 1.3 g SO_4^{2-} $L^{-1}d^{-1}$, and 2.0 respectively. Finally, the running system can fulfil very efficient sulfate and heavy metals removal using hybrid chemical/biological or UASB method depending on the initial concentration of sulfate and metals in the IWW. In addition, each unit in the hybrid system may be used separately depending on the wastewater characteristics.

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