



## Sulfate concentration effects on organic load and major effective parameters in stabilization ponds: a case study

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### ABSTRACT

Many of cations and anions existing in water can have different effects on wastewater treatment process. Sulfate is one of these anions. This study was conducted to determine the effect of sulfate anion on the reduction of organic load removal and other effective parameters in stabilization ponds. Birjand pilot treatment plant consists of anaerobic, facultative and maturation ponds, which were designed and built at the same place and were also exploited in similar conditions as the original ponds. 200, 300 and 400 mg/L of sulfate were injected into the pilot pond afterward. Then, organic load, pH, organic nitrogen, ammonia nitrogen, nitrate, biological oxygen demand (BOD<sub>5</sub>) and chemical oxygen demand (COD) were measured after passing the hydraulic retention time. The results showed that removal efficiency of COD, BOD<sub>5</sub>, total Kjeldahl nitrogen, organic nitrogen and pH decreased 15%, 14%, 44.7%, 20% and 24.2%, respectively, by increasing the sulfate concentration from 200 to 400 mg/L. Increasing the sulfate concentration from 200 mg/L had a significant impact on biological processes. It was concluded that the nitrification process was constant and gradually declined by increasing the sulfate concentration up to 300 mg/L, and when it increased to 400 mg/L, the algae growth reduced significantly.

*Keywords:* Sulfate; Organic load; Stabilization pond; Birjand

### 1. Introduction

Using the treated sewage effluent has been noticed more than ever by managers of water industry as a source of sustainable water. The usage of this wastewater in agriculture and industry has various benefits such as providing a cheap and permanent source of water, reducing the cost of treatment and saving part of good quality water resources for other purposes [1].

The stabilization ponds are used in most parts of the world due to their need to limited equipment, operation practices and maintenance, simple design and operation, the effective removal of pathogens and their capability of withstanding organic and hydraulic loading shock [2–4]. Stabilization ponds are applied broadly in most urban and rural areas to treat the urban wastewater [5,6]. The first stabilization pond system for wastewater treatment was put into operation in the city of San Antonio in Texas, America. Then, California, North Dakota and other states of America used stabilization ponds for wastewater treatment. Since 1980, about 7,000

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waste stabilization ponds (WSPs) have been used in America. A large number of WSPs are being used in countries such as America, France, Germany, Portugal, India, Pakistan, Jordan and Thailand [7]. Due to the benefits of stabilization ponds, a number of these units are being used in some cities of Iran such as Arak, Gilan-e Gharb, Folang-shahr (Isfahan), Sabzevar and Birjand [8]. Stabilization ponds are generally created and used in the form of a series of anaerobic, facultative and maturation ponds [9]. This system removes pollutants from wastewater flow by deposition or conversion through biological and chemical processes [10]. pH, sulfate, nitrate, Kjeldahl nitrogen, organic nitrogen and input organic loading can be mentioned as effective parameters on the efficiency of stabilization ponds [11]. Wastewater treatment in ponds can be done through symbiosis of algae and bacteria that follow a different ecological pattern compared with the growth conditions of microorganisms in a clean environment. Oxidation of organic matter is carried out by bacteria and happens due to the dissolved oxygen, which is provided by algae for bacteria [12–14]. Anaerobic stabilization ponds (ASPs) are used to reduce the influent organic load, especially wastewater containing high concentrations of organic matter. The performance of this type of ponds is similar to septic tanks and anaerobic digesters without equipment [11].

Sulfate-reducing bacteria (SRB) in anaerobic systems act as disturbing organisms. When sulfate concentration in the wastewater is high, problems may be created by the reduction of sulfate to sulfide. High concentrations of sulfate are toxic for methane-producing bacteria and use sulfate as an electron acceptor [15]. Sulfur bacteria in wastewater stabilization ponds have a negative impact on the quality of effluent due to color changes, the possibility of reducing the percentage of organic matter removal and high concentrations of suspended solids and odor [16].

Peng et al. [17] in 2007 in China carried out a study on phosphorus removal using stabilization ponds and showed that the highest phosphorus removal occurs in pH between 7 and 8.

Mazhab et al. in 2009 in Iran (Yazd) studied the impact of organic load, pH, Electroconductivity (EC) of input wastewater and weather conditions on the efficiency of wastewater stabilization ponds and concluded that changes in the organic load, pH and EC have no effects on the removal of BOD<sub>5</sub> and chemical oxygen demand (COD) [13].

Ghanizadeh and Yazdanbakhsh [18] in 2000 in Iran assessed the impact of environmental factors and wastewater quality on nitrification process. They found that nitrate-producing bacteria are very active when BOD to total Kjeldahl nitrogen (TKN) ratio is 1:3. Badalians-Gholikandi et al. [14] in 2012 in Iran studied the effects of dramatic growth of purple sulfur bacteria on WSP under competitive conditions and their influence on efficiency of wastewater treatment. They concluded that purple sulfur bacteria have an enzymatic capability to decompose organic matter in stabilization ponds.

Almasi et al. [7] in 2012 in Iran investigated the efficiency of ASPs in the removal of phenol from Kermanshah refinery wastewater. They concluded that a high efficiency in organic compounds removal with different concentrations of phenol can be achieved under proper management [7]. Malakootian et al. conducted research on treatment of industrial wastewater and municipal sewage [19–25].

Due to the lack of adequate research in this field, in the present study, the effect of different concentrations of sulfate on removal efficiency of organic load, organic nitrogen, ammonia nitrogen, COD, BOD<sub>5</sub> and ammonium nitrate is studied.

## 2. Materials and methods

This study adopted an experimental method and was conducted from October 2014 to April 2015 (7 months) on the pilot stabilization ponds of Birjand wastewater treatment plant. Birjand pilot treatment plant was designed on a scale of 250:1 (Fig. 1). It was built using concrete as the basic construction material and was operated. The dimensions of the pilot stabilization pond are presented in Table 1 in normal conditions. It consists of anaerobic, facultative and maturation ponds with dimensions as shown in Table 1. Ambient air temperature was 5°C–25°C during the study, and the average temperature in the pond was 18°C ± 2°C. The input flow into the pilot ponds was adjusted to 23.4 L/d using a Jesco dosing pump.

After 2 months of installation, the conditions in the ponds are stabilized; 200, 300 and 400 mg/L of sulfate concentrations were injected into the input of pilot ponds. Then, pH, organic nitrogen, nitrate, ammonia nitrogen, BOD<sub>5</sub> and COD in influent and effluent of stabilization pond systems were measured separately. To study each of the mentioned variables, a total of 495 samples were tested in triplicate. Sampling and tests were done according to the standard procedures mentioned in the Examination of Water and Wastewater [26]. Analysis of variance statistical analysis was performed by SPSS software version 16 to investigate the effects of different concentrations of sulfate on organic load and effective parameters removal.



Fig. 1. View of the pilot stabilization ponds.

Table 1  
Design criteria of pilot Stabilization pond

	Anaerobic pond	Facultative pond	Maturation pond
Useful volume of pond (m <sup>3</sup> )	0.16	0.336	0.032
Useful depth (m) on scale of 1:5	1	0.4	0.2
Number of pond	1	1	1
Retention time (d)	7.5	20.5	3.5
Dimensions (m) in scale of 1:250	0.4 × 0.4	2.1 × 0.4	0.4 × 0.4
Free height (m)	0.10	0.10	0.10

3. Results and discussion

The results showed that average BOD in influent anaerobic, facultative and maturation ponds are 513, 280, 180, 170 mg/L, respectively. Increase of sulfate concentration from 200 to 400 mg/L in pilot decreased BOD removal 12%, 28% and 28% in anaerobic, facultative and maturation ponds respectively (Fig. 2).

The characteristics of influent and effluent wastewater from Birjand treatment plant before the project are given in Table 2.

The removal efficiency of BOD<sub>5</sub>, COD, organic nitrogen, TKN, nitrate and sulfate in Birjand treatment plant decreased to 66.7%, 61.6%, 50%, 49, 9% and 40%, respectively, and ammonia nitrogen and pH increased to 25% and 1.9 units, respectively.

The results of the influent and effluent quality of pilot stabilization ponds at sulfate concentration of 200 mg/L are shown in Table 3.

The removal efficiency of BOD<sub>5</sub>, COD, organic nitrogen, TKN, nitrate and sulfate in Birjand pilot stabilization ponds

decreased to 67%, 62%, 60%, 59.7%, 7.5% and 42.5%, respectively, and ammonia nitrogen and pH increased to 19% and 1.7 units, respectively.

As it is evident from the results in Tables 2 and 3, the pilot plant has the same conditions as the real treatment plant.

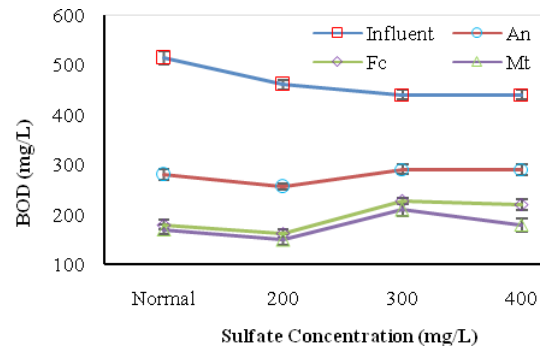


Fig. 2. Effect of sulfate concentration on BOD load.

Table 2 Characteristics of Birjand wastewater treatment plant

Parameter	Average of influent, mg/L	Effluent wastewater						Total removal (%)
		Anaerobic pond		Facultative pond		Maturation pond		
		Average, mg/L	Removal %	Average, mg/L	Removal %	Average, mg/L	Removal %	
BOD <sub>5</sub>	513 ± 21	280 ± 10	45	180 ± 10	36	170 ± 10	4	66.7
COD	860 ± 10	522 ± 11	38	377 ± 15	28	330 ± 10	13	61.6
Organic nitrogen	44 ± 1	30 ± 2	32	23 ± 1	23	22 ± 7.6	13	50
Ammonia nitrogen	3 ± 1	3 ± 1	33	3.8 ± 0.3	–	4 ± 1	–	–
TKN	47 ± 1	32 ± 1.5	32	26 ± 1.3	17.2	24 ± 1	35	49
Nitrate	6.5 ± 0.5	4.5 ± 0.9	34	7 ± 0.3	–	5.9 ± 0.3	15.9	9
Sulfate	233 ± 4	192 ± 7.6	18	150 ± 10	21	140 ± 10	6.6	40
pH	7.9	8.4		9.1		9.8		

Table 3 The characteristics of influent and effluent wastewater of pilot stabilization ponds at sulfate concentration 200 mg/L

Parameter	Average of influent, mg/L	Effluent wastewater						Total removal %
		Anaerobic pond		Facultative pond		Maturation pond		
		Average, mg/L	Removal %	Average, mg/L	Removal %	Average, mg/L	Removal %	
BOD <sub>5</sub>	460 ± 10	256 ± 5.7	44	162 ± 7.6	38	150 ± 10	7.4	67
COD	770 ± 10	476 ± 5.7	38	370 ± 10	22	291 ± 10	21	62
Organic nitrogen	39 ± 1	25 ± 0.2	35	18 ± 1	29	15 ± 0.2	15	60
Ammonia nitrogen	0.81 ± 0.12	0.56 ± 0.2	24	0.9 ± 0.07	–	1 ± 0.06	–	–
TKN	39.8 ± 1.1	25.7 ± 0.2	35	19 ± 1	26	16 ± 0.2	14	59.7
Nitrate	1.3 ± 0.15	0.9 ± 0.2	31	1.5 ± 0.4	–	1.2 ± 0.15	20	7.5
Sulfate	200 ± 10	170 ± 11	15	120 ± 9	29	115 ± 10	4.1	42.5
pH	7.8	8.25		8.9		9.5		

Table 3 shows the effluent quality of pilot stabilization ponds at sulfate concentration of 200 mg/L. The results displayed in Table 3 demonstrate that sulfate concentration of 200 mg/L had no significant impact on the algae growth process and final pH.

The results of the influent and effluent quality of pilot stabilization ponds at sulfate concentration of 300 mg/L are shown in Table 4.

The removal efficiency of BOD<sub>5</sub>, COD, organic nitrogen, TKN, nitrate and sulfate in pilot stabilization ponds decreased to 59%, 57.4%, 53%, 48%, 10% and 35%, respectively, and ammonia nitrogen and pH increased to 31% and 1.5 units, respectively. As indicated in Table 4, the removal of BOD<sub>5</sub>, COD, organic nitrogen, ammonia nitrogen, TKN and sulfate decreased. These results demonstrated that sulfate increase causes algae death in facultative and maturation ponds and then reduced the percentage removal of parameters.

The results of the influent and effluent of wastewater quality of pilot stabilization ponds at sulfate increasing to 400 mg/L are shown in Table 5.

The removal efficiency of BOD<sub>5</sub>, COD, organic nitrogen, TKN, nitrate and sulfate in pilot stabilization ponds decreased to 52%, 48%, 40%, 15%, 11% and 20%, respectively. pH decreased to 0.8 units, and ammonia nitrogen increased 5 times (400%). As shown in Table 5, pH decreased at anaerobic, facultative and maturation ponds by increasing sulfate to 400 mg/L.

Changes in COD and BOD organic load in pilot effluent with the increased concentrations of sulfate are presented in Fig. 3.

BOD removal efficiency of organic load in stabilization ponds at sulfate concentrations of 200, 300 and 400 mg/L decreased to 67.4%, 59% and 52%, respectively. COD organic load decreased to 62.2%, 57.4% and 48%, respectively.

Changes of BOD to TKN ratio with increased concentrations of sulfate in pilot stabilization ponds are shown in Fig. 4.

The ratio of BOD to TKN increased from 9.4 to 16.2 by the increase of sulfate concentration from 200 to 400 mg/L. Thus, acidity condition increased by the increase of sulfate

Table 4

The characteristics of influent and effluent wastewater of pilot stabilization ponds at sulfate concentration of 300 mg/L

Parameter	Average of influent mg/L	Effluent wastewater						Total removal (%)
		Anaerobic pond		Facultative pond		Maturation pond		
		Average mg/L	Removal %	Average mg/L	Removal %	Average mg/L	Removal %	
BOD <sub>5</sub>	440 ± 10	290 ± 10	34	210 ± 10	27	180 ± 15	14	59
COD	720 ± 10	463 ± 7.6	36	363 ± 21	17	307 ± 12	15	57.4
Organic nitrogen	27 ± 3.2	19 ± 0.5	30	14.5 ± 0.5	21	12.0 ± 0.8	10	53
Ammonia nitrogen	0.8 ± 0.1	0.6 ± 0.1	13	1.2 ± 0.3	–	1.2 ± 0.05	–	–
TKN	27 ± 3	19 ± 0.5	29	16 ± 0.5	17	13 ± 0.7	15	48
Nitrate	2 ± 0.1	1.4 ± 0.1	27	2 ± 0.25	–	1.8 ± 0.2	4	10
Sulfate	300 ± 10	270 ± 14	10	200 ± 22	25.9	195 ± 10	2.5	35
pH	8	8.45		9.3		9.5		

Table 5

The characteristics of influent and effluent wastewater of pilot stabilization ponds at sulfate concentration of 400 mg/L

Parameter	Average of influent, mg/L	Effluent wastewater						Total removal (%)
		Anaerobic pond		Facultative pond		Maturation pond		
		Average mg/L	Removal %	Average mg/L	Removal %	Average mg/L	Removal %	
BOD <sub>5</sub>	440 ± 10	292 ± 10	33.6	227 ± 5.8	22	210 ± 12	7.4	52
COD	590 ± 10	407 ± 15	30	353 ± 5.6	13	308 ± 8	13	48
Organic nitrogen	13 ± 1.2	10 ± 1.5	23	9 ± 0.5	18	8 ± 0.5	9	40
Ammonia nitrogen	1 ± 0.15	2.5 ± 0.1	–	4.5 ± 0.2	–	5 ± 0.5	–	–
TKN	14 ± 1.2	13 ± 1.5	9	7 ± 0.3	44	13 ± 1	3	15
Nitrate	1.8 ± 0.4	1.35 ± 0.2	26	1.5 ± 0.15	–	1.5 ± 0.13	20	11
Sulfate	400 ± 20	380 ± 10	5	327 ± 24	14	320 ± 10	2.14	20
pH	8	7.5		6.9		7.2		

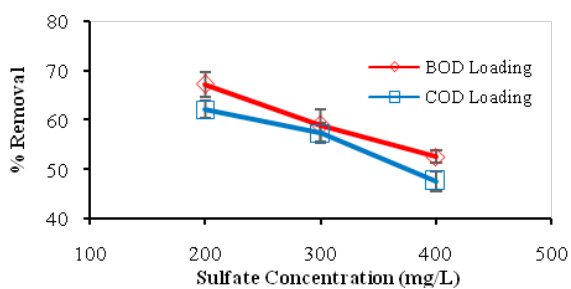


Fig. 3. Effect of sulfate concentration on BOD and COD load removal.

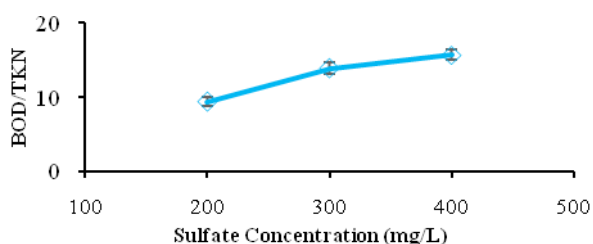


Fig. 4. Effect of sulfate concentration on BOD to TKN ratio.

concentration up to 400 mg/L. This decrease in pH presented a decrease in algal growth. Sulfate as an electron acceptor consumes 0.667 g of oxygen per gram. Therefore, the environment changes to an anaerobic condition by sulfate increased. Therefore, organic nitrogen (protein, amino acids, etc.) is hydrolyzed and converted to ammonia. It is also confirmed by the increase of sulfate up to 400 mg/L and ammonia from 1 to 5 mg/L. Furthermore, by increasing sulfate, the amount of nitrate does not show significant changes. The amount of nitrates changed from 2 to 1.8 mg/L and from 1.8 to 1.5 mg/L at the sulfate concentration of 300 and 400 mg/L, respectively. As a result, nitrate concentrations do not have any significant decrease as an electron acceptor. Therefore, sulfate reduction and its high concentration in the environment begins and thereby causes odor. The methane-producing bacteria and SRB may compete for acetate and  $H_2$  (electron donors). The synthetic study of growth of these two groups of bacteria shows that SRB compared with methane-producing bacteria have a higher affinity for acetate. This means that SRB at low concentrations of acetate can defeat methane-producing bacteria. This competitive inhibition leads to the redirection of electrons from methane production to sulfate reduction. When COD to sulfate ratio is 1.7:2.7, the sulfate-reducing and methane-producing bacteria intensely compete with each other. Increase in this ratio is favorable for methane production while its reduction is desirable for SRB [27]. According to the obtained results, the removal percentage of COD decreased by the increase of sulfate concentration. Furthermore, the COD/SO<sub>4</sub> ratio decreased by increasing the sulfate concentration (in the present research, COD/SO<sub>4</sub> ratio decreased from 2.5 to 1). As a result, the unpleasant odor of hydrogen sulfide could be transpired. Choi and Rim [28] in 1991 in Korea assessed the competition between SRB and methane-producing bacteria in anaerobic treatment. Pazouki et al. [29] in 2006 in Iran showed that at sulfate concentration of 500 mg/L, the SO<sub>4</sub>/COD ratio is more than 2 [29]. The result of this research is consistent with the mentioned studies.

The description and explanation of Fig. 2 showed that when the sulfate which enters the facultative pond (FP) in anaerobic conditions converts sulfate to hydrogen sulfide ( $H_2S$ ) which acts as an inhibitor. Due to the limited solubility of gases in liquids, the presence of hydrogen sulfide will cause the exclusion of dissolved oxygen from the environment, and the growth of SRB (increasing the hydrogen sulfide concentration) dominates the activity of the algae (depletion of dissolved oxygen); thus, the methane production processes get more intense in FPs and change them to anaerobic pond. On the other hand, reducing the amount of algae and photosynthetic bacteria has an inverse relation with organic loading rate. Increasing the sulfate concentration from 200 to 400 mg/L leads to a reduction in the removal efficiency of biochemical oxygen demand (from 67% to 52%), which arises as a result of the hydrogen sulfide production. Ammonia nitrogen and acidity increase, and the algae die off. The wastewater color gets dark gray due to lack of oxygen. Badalians-Gholikadi et al. [14] in a research conducted in 2014 in Iran found that increasing the concentration of hydrogen sulfide leads to the increase of the chemical and biochemical oxygen demand. The study of Badalians-Gholikadi et al., in Iran showed as a result that increasing organic loading in FP, the amount of algae reduced but sulfur bacteria increased [14]. Sirianuntapiboon and Srikul [16] in 2006 in Thailand found that the concentration of hydrogen sulfide ( $H_2S$ ) and the growth of sulfur bacteria were increased by death of algae. Rastakhiz et al. [30] in 2008 in Iran showed that by increasing the amount of biodegradable organic load, COD removal rate decreases. The present study showed that increasing the sulfate and organic load to FP resulted in BOD and COD removal reduction, which is consistent with the mentioned studies. Furthermore, Fig. 3 showed that increasing the BOD to TKN ratio leads to the reduction of the activity of nitrate production organisms. With the increase of sulfate concentration, the ratio of BOD/TKN is increased. Nitrate redox potential reduction and increasing sulfate at the same time not only produce an acidic environment but also lower algal activity and increase odor production. Ghanizadeh and Yazdanbakhsh [18] in 2000 in Iran found that at a 1:3 BOD to TKN ratio, nitrate-producing bacteria are more active. Their findings are consistent with the present results.

#### 4. Conclusion

The increase of sulfate concentration to 400 mg/L has a significant impact on biological processes. Nitrification rate was constant up to 300 mg/L and then gradually declined at higher concentrations of sulfate. At concentrations higher than 400 mg/L, algae growth significantly reduced too. The Besides sulfate concentration from 200 to 400 mg/L leads to increasing BOD/TKN ratio above 42% so odor increasing and reduction of the nitrate-producing bacteria were observed.

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