The Use of Molasses in the Process of Desulfurication

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Abstract

This paper reports results of a study on the effect of the concentration of sulphates and molasses (used as the only source of carbon) on the effectiveness of desulfurication conducted at 37°C.

Because of a high value of COD the process of oxidation of organic compounds from molasses was run after dilution to 0.2-5% vol., and the medium was supplemented with K2HPO4 and sulphates in the amount from 0.3 to 2.5 g/dm^3 [S-SO4^{2-}].

It was found that at 0.6 and 1% vol. of molasses, the reduction of sulphates occurred at the level of 0.7 g [S-SO_4^{2-}], while at its concentration 2 and 5% vol., the maximum amount of the reduced sulphates increased to 0.826 and 1.256 g [S-SO4^{2-}], respectively, which corresponds to 60 and 92% of sulphate conversion. A decrease in COD varied from 32 to 40%, and was the greatest for the medium with 5% vol. of molasses.

The results indicate that molasses, likewise some municipal waste, can be used as an alternative source of carbon acting as electron donor in reduction of sulphates to sulphides.

Keywords: *Desulfotomaculum ruminis* bacteria, desulfurication, molasses, COD

Introduction

Degradation of the natural environment and exhaustion of natural resources have become a serious global problem, especially in the last decade. Much attention has been paid to recycle products or utilization of industrial side products. The use of these substances requires the solution of many technological problems, therefore much effort is made to devise new and effective methods of pure technology leading to minimization of the waste products and pollution of the environment.

Molasses, which is a side product in sugar production, contains chlorides, sulphates, potassium and about 50% of organic compounds, some of them difficult for utilization [1]. So far it has been mainly used for production of yeast, ethanol, citric acid, protein substances and in agriculture or building industry [2, 3]. In spite of these applications large amounts of molasses are not-utilized and make a difficult charge for the environment.

Recently an attempt was made to utilize wastes from the fermentation industry and molasses in the processes of denitrification and desulfurication. In these processes the conversion of nitrates to nitrogen and sulphates to sulphides is carried out in a medium containing the organic compounds from waste products acting as electron donors [4, 5]. In this way the poorly degradable organic substances have been utilized in the processes of nitrates neutralization and biological utilization of sulphate wastes, coming from fermentation [6, 7, 8], paper [9, 10], leather [11-13], galvanic [14] and mine [15, 16] industries. The process of desulfurication can also be used for biotransformation of wastes from production of phosphoric acid from apatite and phosphorite concentrations **[17],** when different organic substances are added. In natural conditions the process of desulfurication is used for detoxication of the natural environment as it leads to neutralization of heavy metal ions through their precipitation as hardly soluble sulphides [15,18,19]. The studies on the possibility of implementation of desulfurication in utilisation of sulphate wastes (phosphogypsum, apatites etc.) and simultaneous biodegradation of organic compounds have brought promising results [20, 21].

Results of preliminary studies in molasses containing media [22] have indicated an effect of the concentration of organic substrates in the wastes and the concentration of electron acceptors on the course of the process. So the aim of this study was to establish the influence of the concentration of sulphates and molasses on the course of the process of desulfurication and the degree of biodegradation of organic compounds present in molasses. The media used contained sulphate reducing bacteria (SRB) *Desulfotomaculum ruminis.*

Materials and Methods

Microorganisms

Desulfotomaculum ruminis bacteria were isolated from the soil at a site near Poznan and grown in anaerobic conditions (helium) in Starkey medium [23] at 37°C, at pH 7.0 and C/S = 3.7.

Molasses

The molasses used was obtained from an alcohol distillery in Kolaczkowo and its physical and chemical parameters are displayed in Table 1 [24].

Table 1. Physical and chemical parameters of the molasses from Kotaczkowo distillery (Analyzed based on Polish Standards PN-76/R-64772 [20])

Parameter	Result
Fermentation evidence	undetected
Apparent dry mass [%]	81.3
Apparent saccharose [%]	47.78
Purity coefficient [%]	58.76
pH	7.21
Nitrates [g $N\text{-}NO_3^-/dm^3$]	2.2
Potassium [g/dm^3]	10.0
Iron [g/dm^3]	0.016
Magnesium [g/dm^3]	0.118
Calcium [g/dm^3]	0.200
Sodium [g/dm^3]	0.231
COD [g O_2/dm^3]	1034
Density of molasses [g/cm^3]	1.4
Sulphates [$S\text{-}SO_4^{2-}$ g/dm^3]	2.08

Desulfurication

The process of desulfurication was conducted in the media containing 5 g/dm^3 KH_2PO_4, sulphates at concentrations 0.355, 0.710 or 2.500 g/dm^3 [$S\text{-}SO_4^{2-}$] and molasses in concentrations from 0.2 to 5% vol. The samples of 60 ml were placed in reactors, their pH was corrected to 7.0. To remove oxygen the media were purged with helium and then inoculated with 4% vol. of the bacteria inoculum and incubated at 37°C. The sulphates acting as electron acceptors were reduced to hydrogen sulphide, which was removed by blowing helium every 24 hours, and then the amount of cadmium sulphide was determined [25]. The sulphides originating from the inoculum were determined by the iodometric method at the beginning of the process [26]. On the basis of the concentrations of sulphates and sulphides the degree of sulphate reduction was found. The content of organic pollutants was assessed by measuring COD.

Analytical Methods

The current concentration of CdS was determined by the gravimetric method after absorption of H_2S in cadmium acetate [25].

COD was measured according to the method described in Standard Methods [27].

The concentration of nitrates was measured by the nitrate electrode "Detector".

The concentrations of iron, potassium, sodium, calcium and magnesium were determined by the ASA method.

The concentration of phosphates was measured by the spectrophotomeric method (Beckmann DU 640, λ = 700 nm).

Results and Discussions

In the processes of sulphate biotransformation carried out with the use of sulphate reducing bacteria, an important role is played by organic compounds assimilable by the bacteria. The bacteria cells get the energy needed to sustain their physiological functions by oxidation of these substrates and reduction of sulphates [28]. The hydrogen sulphide formed can be biologically or chemically converted to elemental sulphur or metal sulphides, e.g. pigments. This study was performed to find a way of utilization of molasses, which is a side product of the sugar industry, and could be an economically effective and easily accessible source of carbon in processes of utilization of sulphate wastes. The results were expected to be of importance in designing processes of degradation of wastes from phosphoric acid production or those in fumes from power plants.

The influence of the concentration of molasses and sulphates in the medium on the process of desulfurication (biological reduction of sulphates) is illustrated by the data collected in Table 2, and Figs. 1-4.

After completing the 4-day process, the concentration of sulphides obtained in the process of desulfurication at the initial [$S\text{-}SO_4^{2-}$] concentration of 0.355 g/dm^3 and various molasses concentration (0.2 to 5% vol.) is approximately 0.3 g/dm^3. The degree of reduction of sulphates in the medium containing from 0.2 to 0.6% vol. molasses varied from 87 to 94% (Table 2). An increase of the molasses concentration up to 5% vol., did not affect the process as the degree of reduction of [SO_4^{2-}] was maintained at the level 85% (Fig. 1, Table 2). Upon desulfurication the value of pH changed from the initial 7.0 to 4.51 for the medium with 5% vol. molas-

Table 2. The influence of the concentration of molasses on the process of microbiological reduction of sulphates and on COD (temp. 37ºC, pH = 7, *Desulfotomaculum ruminis)*

Molasses concentration [% vol.]	Duration of the process [day]	pH after the process	Changes in concentration of $[S^{2-}]$ [g/dm³]	Degree of reduction $[SO_4^{2-}]$ [%]	COD initial value [g O₂/dm³]	COD After value process [g O₂/dm³]	Decrease in COD [g O₂/dm³]	Decrease in COD [%]
A. $[S\text{-}SO_4^{2-}]_o$ = 0.355 g/dm³								
0.2	4	7.17	0.308	87	2.3	2.00	0.30	13
0.4	4	6.86	0.316	89	3.9	2.8	1.1	28
0.6	4	6.38	0.334	94	7.1	4.7	2.4	34
1	4	5.50	0.300	85	10.0	6.7	3.3	33
2	4	4.56	0.301	85	19.1	13.9	5.2	27
5	4	4.51	0.305	86	44	37	7	16
B. $[S\text{-}SO_4^{2-}]_o$ = 0.710 g/dm³								
0.2	3	6.93	0.341	48	2.24	1.89	0.35	15
0.4	3	6.91	0.514	72	3.9	2.9	1.0	26
0.6	4	6.77	0.710	100	7.0	4.7	2.3	33
1	4	6.15	0.672	95	10.0	6.8	3.2	32
2	4	4.85	0.652	92	18.4	14	4.4	23
5	4	4.75	0.597	84	44	39	5	11
C. $[S\text{-}SO_4^{2-}]_o$ = 2.500 g/dm³								
0.2	7	6.91	0.318	13	2.29	1.94	0.35	15
0.4	7	6.79	0.487	19	3.7	2.8	0.9	24
0.6	7	6.48	0.667	27	6.8	4.9	1.9	28
1	7	5.97	0.866	35	9.9	7.7	2.2	22
2	7	4.93	0.776	31	18.7	16.4	2.3	12
5	7	4.81	1.001	40	44	40	4	9

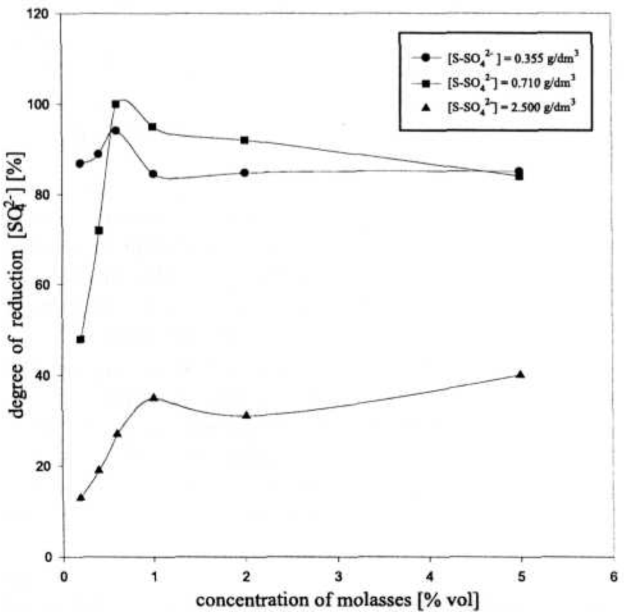

Fig. 1. The degree of SO_4^{2-} reduction to S^{2-} versus the concentration of molasses and sulphates in the medium (temp. 37°C, pH = 7, *Desulfotomaculum ruminis* bacteria)

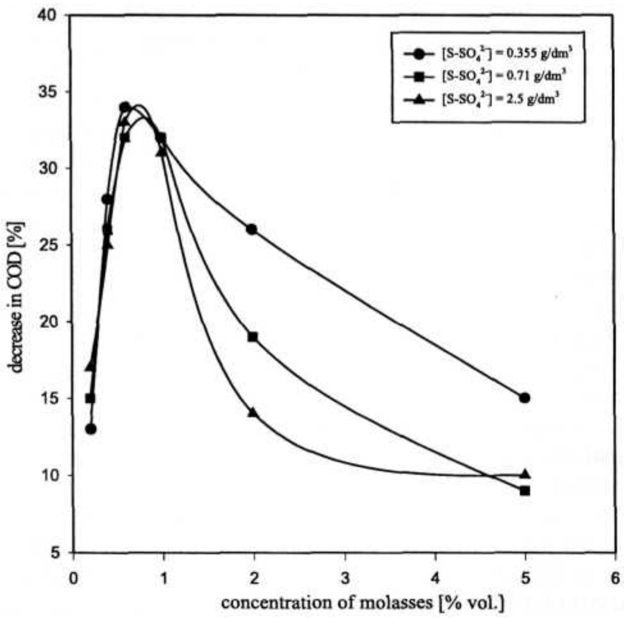

Fig. 2. A decrease in COD in percent, in the media with different concentrations of SO_4^{2-} and molasses (temp. 37°C, pH = 7, *Desulfotomaculum rum'mis* bacteria)

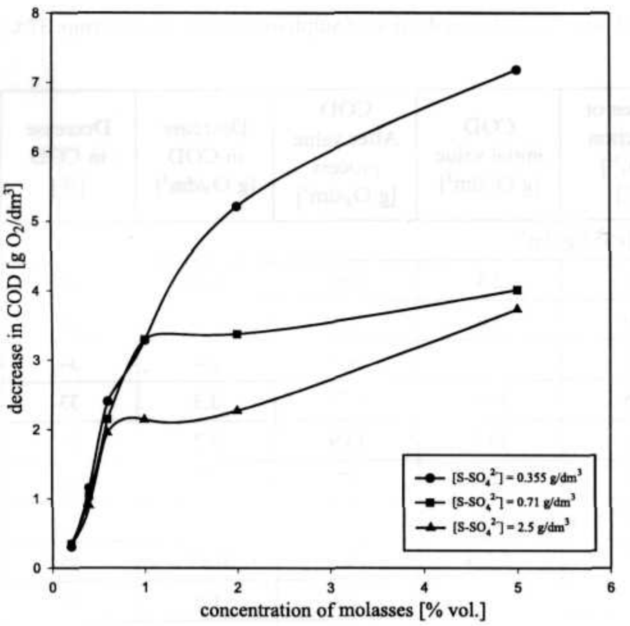

Fig. 3. Decrease in COD versus the concentration of molasses and sulphates in the medium upon desulfurication (temp. 37°C, pH = 7, *Desulfoiomaculum* ***ruminis*** bacteria).

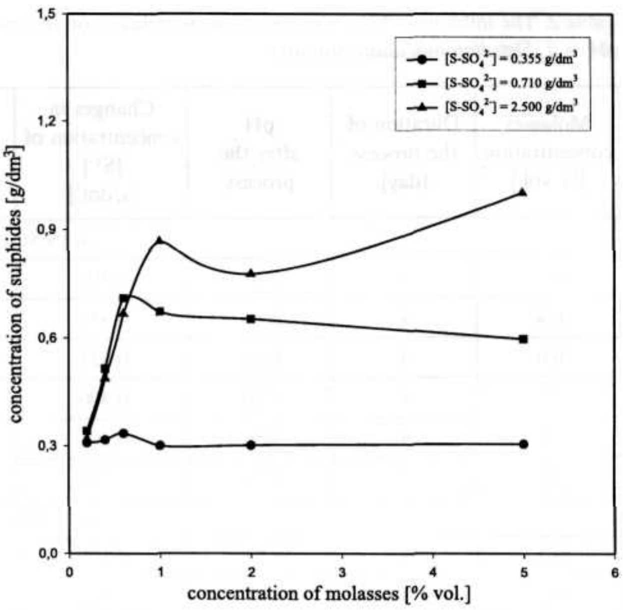

Fig. 4. The influence of concentration of molasses and sulphates on the concentration of sulphides formed upon desulfurication (temp. 37°C, pH = 7, *Desulfoiomaculum ruminis* bacteria)

ses. The final pH was a result of simultaneous formation of basic products of the bacteria metabolism and acid products of fermentation of organic substrates contained in the molasses.

The process of desulfurication was accompanied by changes in COD. The relevant data are given in Table 2 and in Figs. 2 and 3. The degree of reduction of COD [%] in the media studied containing sulphates (0.355 g/dm^3 [S-SO_4^{2-}]) and different concentrations of molasses was the highest (34%) for the medium with 0.6% vol. of molasses. The decrease of COD expressed as g 0_2/dm^3 increases with molasses concentration from 0.3 g 0_2/dm^3 (for 0.2% vol. of molasses) to 7.0 g 0_2/dm^3 (for 5% vol. of molasses). The differences in COD reduction are probably related to molasses fermentation in which an additional amount of organic carbon is used up. The contribution of the fermentation rises the higher the molasses concentration in the medium. For the medium with sulphates at 0.355 g/dm^3 [S-SO_4^{2-}] and molasses in 5% vol., the decrease of COD is the greatest (7.0 g O_2/dm^3) and the degree of sulphates conversion is very high (86%); nevertheless, after the process the value of COD remains very high (37 g 0_2/dm^3).

A high degree of sulphate conversion and biotransformation of molasses was also obtained for the medium containing 0.71 g/dm^3 [S-SO_4^{2-}] (100% conversion at the molasses concentration of 0.6% vol.). As follows from Table 2, the value of COD decrease upon the process varied from 0.35 to 5.0 g O_2/dm^3 in the media with molasses concentration increasing from 0.2 to 5% volume. In the media with 1% vol. of molasses the value of COD decreased by about 32%. The decrease in the conversion degree in the media containing 2 and 5% vol. of molasses was a consequence of acidification of the medium as its pH decreased to 4.7. In the media containing molasses at concentrations of 0.2 and 0.4% vol., the lower degree of sulphate conversion was attributed to insufficient concentration of the available organic carbon needed to reduce the sulphates.

In the media with 2.5 g/dm^3 [S-SO_4^{2-}] and molasses at concentrations from 0.2 to 5% vol. apart from the decrease of pH from 6.91 to 4.8, a relatively low degree of sulphate reduction was observed. The yield of the process varied from 13 to 40% and was accompanied by a reduction of COD from 0.35 to 4 g /dm^3 O2 depending on the concentration of molasses. The waste left after the process contained unreacted sulphates in the amount from 2.182 to 1.499 g/dm^3 [S-SO_4^{2-}]

As follows from the results (Table 2), in the media containing 0.71 g/dm^3 [S-SO_4^{2-}] and 0.2 or 0.4% vol. of molasses the time of the process is 25% shorter than in the medium with 0.355 g/dm^3 [S-SO_4^{2-}]. In the media with molasses at higher concentrations (to 5% vol.), the time of the process is approximately the same for both [S-SO_4^{2-}] concentrations. When the concentration of sulphates is increased to 2.5 g/dm^3 [S-SO_4^{2-}] the reaction time increases to 7 days for all molasses concentrations. Moreover, it has been shown that the changes in pH (acidification) depend only on the concentration of molasses. The relation between the molasses concentration and pH of the medium after the process is shown in Fig. 5.

It has been also shown that with increasing concentration of sulphates in the medium from 0.355 to 2.5 g/dm^3 [S-SO_4^{2-}] (except for the medium with 0.2% vol. of molasses) the value of reduction of COD decreases. In the medium containing 5% vol. of molasses the reduction of

COD decreases from 7.0 to 4 g Oj/dm' (Table 2). According to the data from Table 2 and in Fig. 4, in the media containing 0.4 or 0.6% vol. of molasses and 0.71 or 2.5 g /dm^3 [S-SO_4^{2-}] the content of hydrogen sulphide and sulphides has increased to about 0.5 and 0.7 g/dm^3, respectively. When the concentrations of molasses are higher an increase in the content of sulphides has only been observed in the medium with 2.5 g/dm^3 [S-SO_4^{2-}]. Analysis of COD after the process and the degree of desulfurica-tion (Table 2) shows that the process is the most effective in the medium with 0.6% vol. of molasses and the concentration of sulphates up to 0.71 g/dm^3 [S-SO_4^{2-}]. The mean rate of reduction of sulphates is 178 mg [S-SO_4^{2-}]/day dm^3. In order to increase the effectiveness of the process at the next stage of the study after one day the medium was inoculated once again. As a result the time of the reaction shortened by half a day and the degree of conversion in the media with 2 or 5% vol. of molasses slightly increased (Tables 2 and 3).

In order to establish the maximum degree of sulphate reduction the medium after one course of the process was used again. The medium used in the first stage, containing initially 0.71 g/dm^3 [S-SO_4^{2-}] and molasses in a concentration from 0.6 to 5% vol. was subjected to a correction of pH to 7.0 its concentration of sulphates was increased by adding 0.67 g/dm^3 [S-SO_4^{2-}], the oxygen was removed and the sample was inoculated.

After 2.5 days of desulfurication the content of sulphides in the samples denoted by numbers from 3 to 6 (Tab. 3) increased from 0.051 to 0.232 g/dm^3 [SO_4^{2-}], which was accompanied by a reduction in COD from 0.20 to 4 g OVdm^3, respectively. The pH of the medium varied from 7.6 to 8.3, and only in sample 6 did it decrease to 4.87, so this medium was used for the third time having corrected its pH and inoculated it (III stage). The results are given in Table 3 (II and III stages).

As follows from these data, in the media containing 0.6 and 1% vol. of molasses 0.7 g [S-SO_4^{2-}] was reduced to

Table 3. Results of the study on microbiological reduction of sulphates (desulfurcation) conducted in the medium containing molasses as the only source of carbon.
After completion of the process of desulfurication the medium was supplemented with [SO_4^{2-}] and inoculated once again with a fresh culture of the bacteria (temp.= 37°C, pH = 7.0, *Desulfotomaculum ruminis* bacteria)

Sample no.	Concentration of molasses [% vol.]	Duration of the process [day]	pH after the process	Changes in concentration of [S^{2-}] [g/dm^3]	Degree of reduction [SO_4^{2-}] [%]	COD initial value [g O_2/dm^3]	COD after the process [g O_2/dm^3]	Decrease in COD [g O_2/dm^3]	Decrease in COD [%]
I stage – the medium additionally inoculated after one day [S-SO_4^{2-}]$_o$ = 0.710 g/dm^3									
1	0.2	3	7.64	0.334	47	2.2	1.90	0.30	14
2	0.4	3	7.58	0.488	69	3.9	2.8	1.1	28
3	0.6	3	7.43	0.657	93	6.9	4.9	2.0	29
4	1	3.5	7.36	0.662	93	9.9	7.5	2.4	24
5	2	3.5	5.53	0.661	93	18.1	14.1	4.0	22
6	5	3.5	5.07	0.669	94	45	40	5	11
II stage – the medium from stage I after completion of the process with sulphates added, after correction pH and repeated inoculation [S-SO_4^{2-}]$_o$ = ~ 0.670 g/dm^3									
3	–	2.5	7.63	0.051	7	4.9	4.7	0.2	4
4	–	2.5	7.85	0.053	8	7.5	6.5	1.0	13
5	–	2.5	8.36	0.165	25	14.1	11.2	2.9	21
6	–	2.5	4.87	0.232	34	40	36	4	10
III stage – the medium from stage II after correction pH and repeated inoculation									
6	–	2	6.92	0.355	53	36	27	9	25
Total effect of the two stage – process on recycled wastes [S-SO_4^{2-}]$_o$ = 1.377 g/dm^3									
3	–	5.5	7.63	0.708	52	6.9	4.7	2.2	32
4	–	6	7.85	0.715	52	9.9	6.5	3.4	35
5	–	6	8.36	0.826	60	18.1	11.2	6.9	38
6	–	8	6.92	1.256	92	45	27	18	40

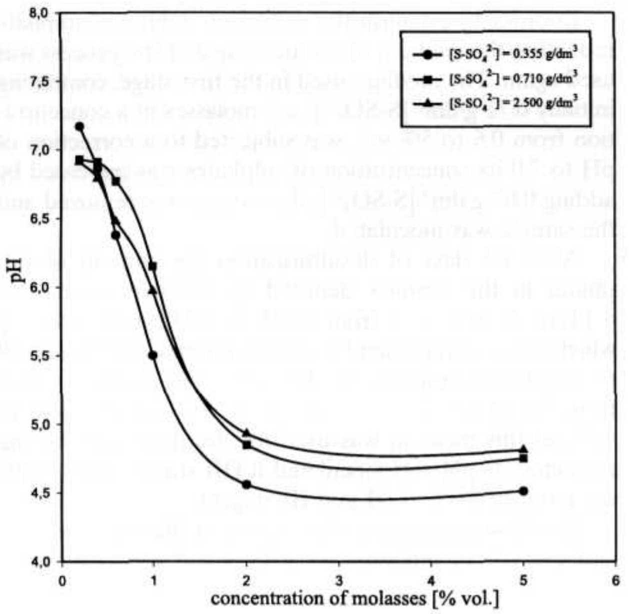

Fig. 5. The pH of the medium after desulfurication versus the concentrations of molasses and SO_4^{2-} (temp. 37°C, pH = 7, *Desulfotomaculum ruminis* bacteria)

sulphides, while for molasses concentrations of 2 and 5% vol., the maximum amount of the reduced sulphates increased to 0.826 g and 1.256 g [S-SO_4^{2-}], respectively, which makes 60 and 92% conversion of sulphates. The decrease in COD varied from 32 to 40%, and the maximum values were obtained for the medium with 5% vol. of molasses. Data in Table 2 and 3 show that the optimum medium for sulphate reduction is the one containing 0.71 g/dm^3 [S-SO_4^{2-}] and 0.6% vol. of molasses. In this case complete reduction is observed after 4 days and a 33% decrease of COD takes place.

To the waste containing 0.71 g/dm^3 [S-SO_4^{2-}] 0.67 g/dm^3 [S-SO_4^{2-}] was introduced, pH was adjusted to 7.0. Samples were inoculated again and flushed with helium. In these conditions maximum decrease (total) in sulphates concentration is obtained (1.256 g/dm^3) in the samples containing 5% vol. of molasses. However, the high final COD value excludes the possibility of application of this variant.

In conclusion, molasses similarly as some other municipal wastes can be used as an alternative source of carbon, acting as electron donor in reduction of waste sulphates. In certain conditions of utilization of the waste sulphates this source of carbon may be more advantageous than others.

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