

Oxidation of Sulphides in Tannery Wastewater by Use of Manganese (IV) Oxide

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Abstract

One of the methods of detoxification of sulphides in wastewater (WW) of tanneries could be their oxidation by use of MnO_2 . This material, as well as the product of the chemical reaction between sulphides and this material is not left in WW and does not pollute it.

The amount of sulphides and the pH of solution have an influence on oxidation process duration; it is longer when the sulphide amount and pH in the WW is higher. Optimal temperature of the treatment is 30°C. Oxidation goes faster if the size of MnO_2 particles does not exceed 0.1 mm.

The possibilities of repeated use of MnO_2 were investigated. The stable efficiency of the MnO_2 could be obtained by putting at first 0.5% of MnO_2 and additionally 0.05% of MnO_2 of the solution mass for every following cycle of the treatment.

Keywords: leather, liming, sulphides, oxidation, manganese oxide.

Introduction

Nowadays almost every tannery uses sulphides in the process of transforming animal hide into leather. Mostly it is sodium sulphide and (or) sodium hydrosulphide. The sulphides are not dangerous when they are in strongly alkaline medium. However, production of very poisonous H_2S begins, polluting the atmosphere, after dilution or mixing solutions containing sulphides with acid WW. It is known that pollutants, which are formed during liming, make up to 60-80% of all polluting materials of tanneries.

A treatment of liming process WW, which is polluted by products of degradation of hair, noncollagenous and collagen proteins, lime and sulphide, is a complicated and expensive process. The main problem when cleaning WW is detoxification of sulphides.

It can be said that the methods mentioned below are based on two principles only: when oxidation degree of sulphur does not change and when it changes. But these

two principles let various methods of sulphide removal from WW develop. The analysis of references has shown that all proposals on how to decrease the pollution by sulphides or detoxify them can be classified in this way:

1. filtration of WW after liming and recycling [1-7]
2. neutralization of WW, recuperation of sulphides and reuse [8]
3. precipitation of sulphides by iron salts [9]
4. oxidation by oxidizers [10-14]
5. oxidation by air oxygen [15]
6. oxidation by air oxygen using catalyst [12, 16-19]
7. biological detoxification of sulphides [20-22]

It can be seen that there is plenty of various methods of different investigators how to remove sulphides from WW. However, at the current time plenty of tanneries still do not use any of the mentioned methods for detoxification of sulphides. The part of them does not carry out actions which would be targeted to remove sulphides from WW. In our opinion, there are three main reasons for this. First, in some countries there are insufficiently strict requirements about pollution with sulphides. Second, some methods of

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sulphide removal are too expensive and third, some of them are much too complicated.

Taking into account the main advantages and drawbacks of the methods mentioned above it should be said that the most attractive are the first two methods. Theoretically, their use allows avoiding pollution by sulphides, because all WW and materials in them are reused. Unfortunately, the repeated use of liming solution markedly decreases the quality of the processed leather. The second method is expensive, because large (about 36% of overall WW of tanneries contain sulphides[23]) quantities of WW should be neutralized and recuperated.

A simple and inexpensive method is precipitation of sulphides, treating them by iron salts. But what to do with the obtained settlings?

The second simple and effective method is to oxidize sulphides by oxidizers. Which material is to be used depends on its cost and toxicity. The most often suggested material is H_2O_2 , but authors notice the high cost of the method. It should be said that oxidizing sulphides using H_2O_2 is the most common way to remove sulphides in practice. The same may not apply to oxidation of sulphides by air oxygen. This method is wasteful of time and demands the dissipation of energy for circulation of WW.

The detoxification of sulphides by oxidation with air oxygen using catalyst is the second case, which often is noted as a very acceptable method for use in practice. We agree that it is the most commonly used method because it lets us dispatch removal of sulphides. The suggested materials are not high-priced, but all of us should not forget that the suggested catalysts pollute WW after use.

Biological detoxification can be carried out only when the concentration of sulphides is low; it should not exceed 50 mg per litre. It means that used liming solutions should be diluted many times before treatment.

We would like to present one more simple method of sulphide detoxification that is based on using material insoluble in alkaline solution. The material used and product of chemical reaction between sulphides and this material neither falls into WW nor pollutes it. The main objective

of this research was the determination of better conditions and necessary parameters allowing us to optimize the sulphide detoxification reaction.

Materials and Methods

Materials

Pure MnO_2 (Russia, GOST 4470–70) was used for the experiments.

Operational Conditions

For determining oxidation way and rate different assays were carried out:

- investigation of the reaction between Na_2S and MnO_2 (assay A);
- evaluation of the addition of different amounts of MnO_2 (assay B);
- estimation of time reaction between Na_2S and MnO_2 for different pH (assay C);
- evaluation of the temperature on sulphide oxidation (assay D);
- influence of particle size on the time of reaction (assay E);
- recycling of the oxidizing material.

Experimental Procedures

The treatment of alkaline sulphide solution in nitrogen environment was carried out using special equipment (Fig. 1, A), which allowed removing oxygen of air from the solution and treating it to avoid contact with air.

The treatment of WW was carried out in laboratory apparatus (Fig. 1, B), which rolled vessels (the volume of the vessel was 1 litre). The rate of rolling was 20 ± 1 revolutions per minute. The amount of WW for treatment was 0.2 litres every time.

Table 1. Conditions of the experiments.

Assay	Na_2S concentration, g/l	Amount of MnO_2 , %*	Atmosphere	Temperature, °C	pH of solution	MnO_2 particle size, mm
A	5.6	0.5	air nitrogen	18-20	13.2	0.05-0.1
B	2.87 1.32	0-0.3-0.5-1	air	18-20	13.11 11.92	0.05-0.1
C	3.16	0 0.5	air	18-20	9-11-13	0.05-0.1
D	3.02	0.5	air	18-30-40-50	12.8	0.05-0.1
E	3.9	0.5	air	18-20	12.92	0.16-2.5 0.1-0.63 0.05-0.1

* amount of MnO_2 given in% of solution mass

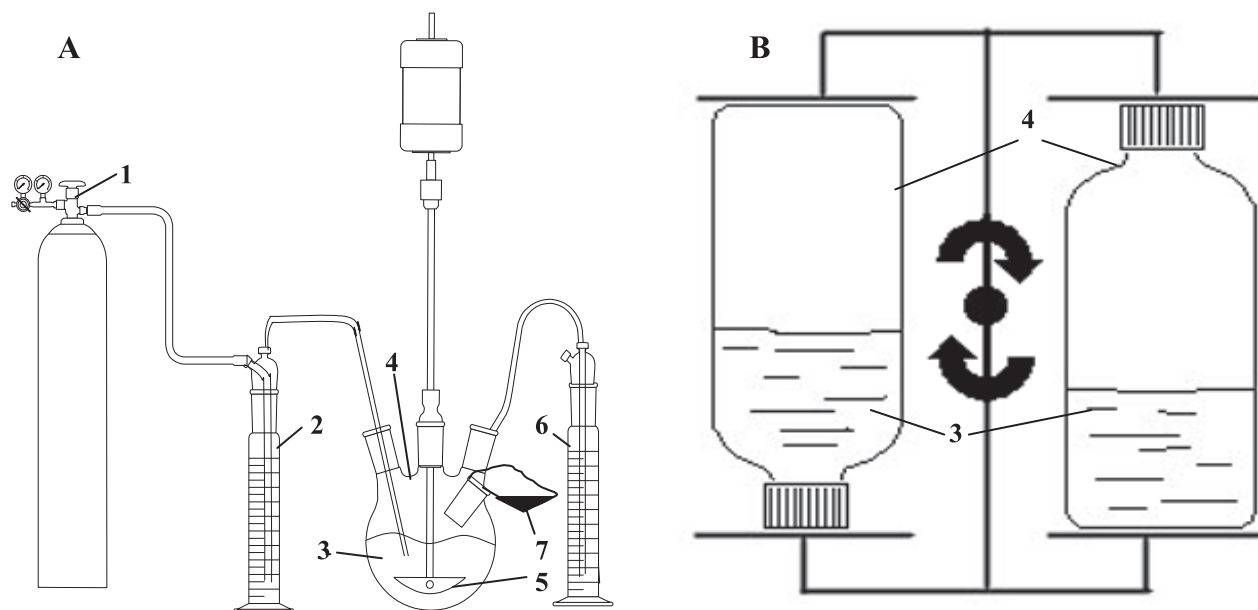


Fig. 1. Equipment for carrying out assay A (A) and assays B, C, D, E (B): 1 – nitrogen gas cylinder; 2 – Drechsel bottle with pyrogalol; 3 – sulphide solution; 4 – vessel of reaction; 5 – mixer; 6 – Drechsel bottle with water; 7 – special vessel with MnO₂.

Analytical Methods

The size of MnO₂ particles was established using *Malvern Laser Diffraction Particle Sizer* (Series 2600c, England).

The concentration of Na₂S in WW was established by complexometric method [24].

IR spectroscopic analysis was carried out using pills formed from 200 mg of KBr and 1 mg of investigated material. IR spectra were written using apparatus *PERKIN-ELMER 1330*.

DT analysis was carried out by apparatus *STA 409PC* in air environment, increasing temperature by 10°C per minute to 1000°C.

Sulphur was determined by extracting it from a solution using chloroform according to the method described in literature [25].

Sodium sulphite and thiosulphate were determined by iodometric method [26].

The sulphate was determined by the gravimetric method using precipitation of sulphites and sulphates by barium chloride. The amount of sodium sulphate was calculated as a difference between a mass of sulphite and sulphate settlings and a mass of sodium sulphite determined by iodometric method.

Results

Investigation of the Reaction Between Na₂S and MnO₂

It is known that MnO₂ is a very strong oxidiser, but it also is used in various chemical reactions as a catalyst.

MnO₂ can oxidise H₂S in this way [27]:

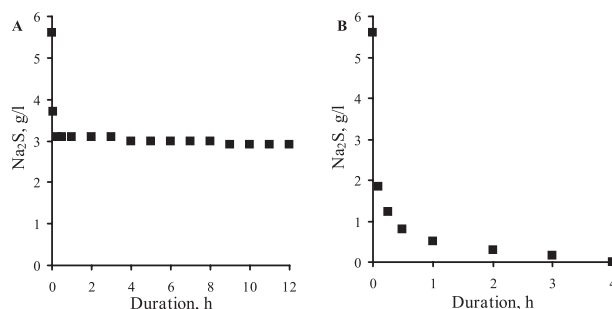
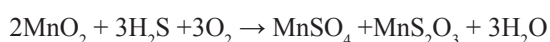
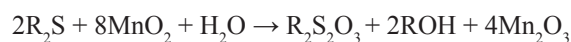


Fig. 2. Dependence of concentration of Na₂S on duration of treatment. Treatment was carried out: A – in nitrogen atmosphere; B – in air atmosphere.

Analyzing old literature uncovered one more interesting reaction which proceeds in boiling solution of sulphides [28]:



No more possible reactions were found which could go in strongly alkaline medium between sulphides and MnO₂.

Adding of 0.5% MnO₂ into the strongly alkaline (pH 13.2) solution of Na₂S (solution contained 10 g/l NaOH and 5.6 g/l Na₂S) and treating it in air or nitrogen atmosphere has shown the interest course of the process (Fig.2).

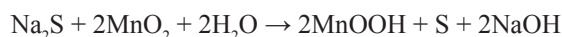
It can be seen that the Na₂S concentration quickly decreases in the first 15 minutes and practically does not change after that, when treating a solution in nitrogen atmosphere. When treating in conventional atmosphere, the rapid decreasing of Na₂S concentration is also observed, but the process does not stop after that and goes

further until no Na_2S is left in the solution. This character of reaction proceeding let us suppose that the process of oxidizing Na_2S using MnO_2 goes by two stages. In the first stage the chemical reaction between MnO_2 and Na_2S predominates. In the second stage only the catalysis reaction between Na_2S and air oxygen takes part. (By the way, in this stage the catalyst is not MnO_2 but the product of chemical reaction between MnO_2 and Na_2S .)

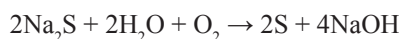
The further investigation (IR spectroscopy and DT analysis) has shown that during the first stage MnO_2 turns insoluble in alkaline solution MnOOH (this means that no manganese of any kind gets into the solution), which acts as a catalyst in the second stage. After the investigation of products of oxidation of Na_2S after treatment of solution the suggestion was made that in the first stage the following reactions are possible:

- 1) $\text{Na}_2\text{S} + 2\text{MnO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{MnOOH} + \text{S} + 2\text{NaOH}$
- 2) $2\text{Na}_2\text{S} + 8\text{MnO}_2 + 5\text{H}_2\text{O} \rightarrow 8\text{MnOOH} + \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH}$
- 3) $\text{Na}_2\text{S} + 6\text{MnO}_2 + 3\text{H}_2\text{O} \rightarrow 6\text{MnOOH} + \text{Na}_2\text{SO}_3$
- 4) $\text{Na}_2\text{S} + 8\text{MnO}_2 + 4\text{H}_2\text{O} \rightarrow 8\text{MnOOH} + \text{Na}_2\text{SO}_4$

The analysis of the decreasing Na_2S concentration in air atmosphere as shown in Fig. 1 has confirmed that in the first stage this reaction prevails:



We suppose that in the second stage the reaction takes part, where MnOOH acts as catalyst:



In parallel, the reactions of further sulphur oxidation went on, because not only free sulphur was found in the solution after finish of oxidation, but also tiosulphates, sulphites and sulphates.

Evaluation of the Addition of Different Amounts of MnO_2

It is known that sulphides get into WW after liming, pelt washing and deliming-bating processes. There are not only alkalis and sulphides in these solutions, but products of hair and collagen degradation, as well. The main aim of this investigation was to establish how the oxidation of sulphides in WW proceeds using MnO_2 , and what factors in which way influence this process.

At first, the influence of MnO_2 amount on duration of sulphides' oxidation in WW was investigated. Two assays using two different WW of taneries there were carried out:

- WW after liming (I), which contained 24.8 g/l $\text{Ca}(\text{OH})_2$, 2.87 g/l Na_2S , its pH was 13.11;
- mixture of solutions after liming, washing of pelt and

deliming (II): 8.9 g/l $\text{Ca}(\text{OH})_2$, 1.32 g/l Na_2S , its pH was 11.92.

For each WW the effect of the addition of different amounts of MnO_2 on the velocity of the reaction was evaluated.

The amount of MnO_2 added for treatment was - 0.3, 0.5 and 1% (control treatment - without MnO_2). Treatment was carried out at 18-20°C. The results obtained are presented in Fig. 3.

As one can see in Fig. 3, the duration of sulphide oxidation without MnO_2 was 26-28 h, using MnO_2 it was remarkably shorter: 0.6-1 h in WW I and 1.5-2.5 h in WW II. The duration of this process depended on the amount of MnO_2 . We suppose that depending on the concentration of sulphide in solution, optimum amount of MnO_2 for treatment is 0.3-0.5% from the solution mass. It has more meaning to have a little longer duration of oxidation than to add 2-3 times more (1%) of MnO_2 .

Estimation of Time Reaction between Na_2S and MnO_2 for Different pH

WW used in this assay contained 21.7 g/l $\text{Ca}(\text{OH})_2$, 3.16 g/l Na_2S , its pH was 11.92. By use of solution NaOH (10%) or HCl (10%) the pH was adjusted to values 9, 11 and 13. The amount of MnO_2 added for treatment was 0.5% (control treatment proceeded without MnO_2). The treatment was carried out at 18-20°C. The results obtained are presented in Fig. 4.

One can see that sulphides are totally removed during

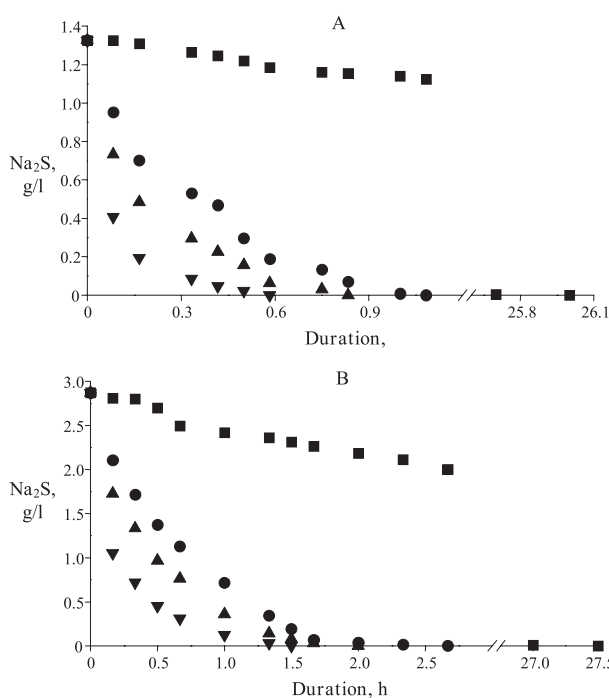


Fig. 3. Influence of amount of MnO_2 on sulphide oxidation rate. Treatment carried out using MnO_2 : ■ - without MnO_2 ; ● - 0.3%; ▲ - 0.5%; ▼ - 1.0%.

5 or 7 hours when treating without MnO_2 the WW, pH of which was 9 or 11. It is known that Na_2S is converted to H_2S when pH is 10 and lower. The smell of H_2S was slightly perceptible in the vessel with the solution having pH 11 and the strong smell was in the vessel with the solution having pH 9. This means that during the treatment of these solutions the sulphides are not only oxidized but also removed as H_2S . In summary, it should be said that sulphides are removed more rapidly when the pH of solution is lower.

The data in Fig. 4 (B) show that using MnO_2 sulphides were removed during the considerably shorter time. This time was 80 min when pH of solution was 9 and 120 min when pH was 13. Those durations differed 1.5 times. Durations treating without MnO_2 differed about 6 times. This means that the addition of MnO_2 considerably decreased the influence of pH of solution on the duration of sulphide removal.

The results obtained have shown that in the case of treatment the WW having pH 10 and lower (generally the mixture of solutions after beamhouse processes had pH about 10) a large amount of H_2S gets into atmosphere. To escape that, the sulphides should be treated in a mixture of used liming-unhairing and pelt washing solution, which has pH 11-12. This WW takes about 15-20% of all WW of tanneries and that means that distinctly less amount of solutions should be treated compared to total WW in this case.

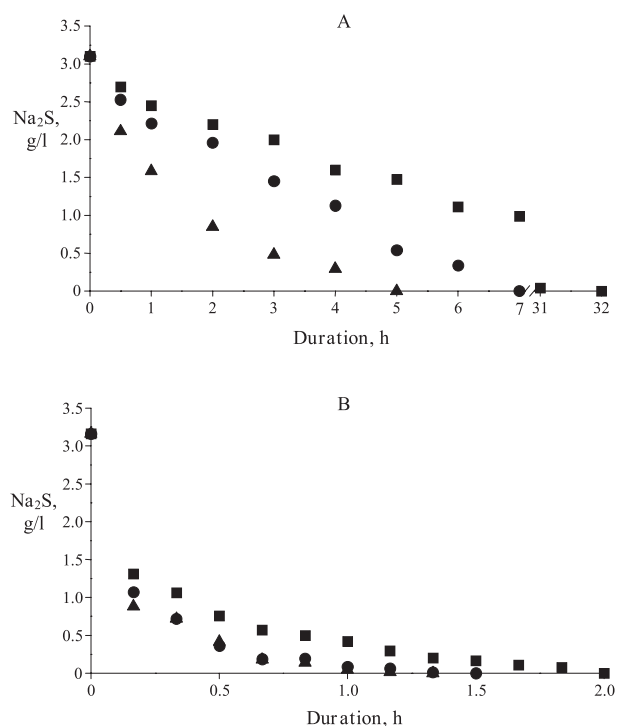


Fig. 4. Effect of pH on the time of reaction between Na_2S and MnO_2 . Treatment carried out without MnO_2 (A) or using 0.5% MnO_2 (B). pH of wastewater: ■ – 13; ● – 11; ▲ – 9.

Evaluation of Temperature on Sulphide Oxidation

The second factor, which naturally has influence on the chemical reaction, is temperature. For the investigation of this influence the used unhairing liquor containing 24.8 g/l $\text{Ca}(\text{OH})_2$, 3.02 g/l Na_2S (pH was 12.8) was treated. The amount of MnO_2 added for treatment was 0.5%. The treatment was carried out at the 18, 30, 40 and 50°C.

It was established that temperature had an influence on the duration of sulphide oxidation. This influence is ambivalent. The chemical action between Na_2S and MnO_2 proceeded more rapidly when temperature was being increased, but after that the increase of the temperature decreases the speed of the catalysis reaction between Na_2S and air oxygen. Total duration of the oxidation process became shorter when increasing the temperature from 18 to 30°C. The shortest time of process was obtained at 30°C (Fig. 5). The further increase of temperature from 30°C increased the total duration of sulphide oxidation.

We suppose that to warm up WW to 30°C is not worth trying because such warming allows shortening the process only for about 10 minutes. The liming-unhairing is usually carried out at 23-25°C and the washing of limed pelt accordingly at 20°C. If leather is processed in winter-time, the treatment is to be carried out while the solution of sulphides has not cooled down.

Since one of the components of the oxidation process is a solid material (MnO_2), the size of particles of this material also has influence on the progress of oxidation. This influence is reflected in the data presented in Fig. 6.

It can be seen that this factor plays a great role in the process of sulphide oxidation. It goes without saying, because the process of sulphide oxidation is based on a heterogeneous reaction in which the area of surface of a solid-state material influences speed of the reaction. This means that the size of particles of MnO_2 should not exceed 0.1 mm if more rapid process of sulphide oxidation is required.

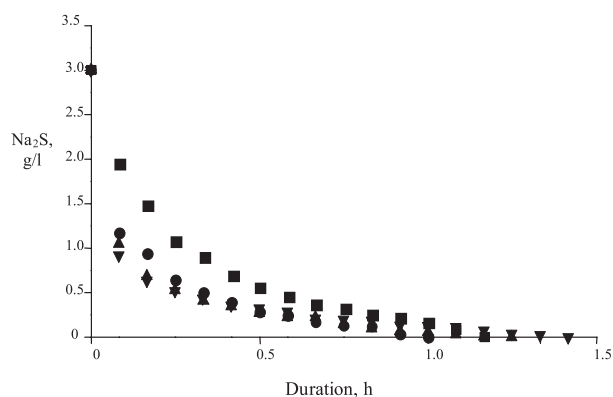


Fig. 5. Dependence of velocity of sulphide oxidation on temperature of treatment. Temperature: ■ – 18°C; ● – 30°C; ▲ – 40°C and ▼ – 50°C.

Recycling the Oxidizing Material

MnO₂ and the product of the oxidation MnOOH are not soluble in alkaline medium. This property has two advantages: it is easy to separate the MnOOH from the treated solution (therefore, this material neither gets into WW nor pollutes it); the possibility to use MnOOH repeatedly gets possible after the separation (the process becomes cheaper).

It is known that activity of a catalyst changes when it is used for a long time. To establish how the activity of MnOOH changes when it is used repeatedly, the unhairing liquor containing 23.6 g/l Ca(OH)₂, 2.51 g/l Na₂S (pH was 12.4) was treated. For first-time treatment the amount of MnO₂ added to unhairing solution was 0.2 and 0.5%. Control treatment proceeded without MnO₂. Temperature was 18-20°C.

Treatment continued until sulphides were not found in the solution. After that the treated solution was left at rest for about 15 minutes for sedimentation of the catalyst to the bottom of the vessel. The solution was carefully poured out, leaving the solid catalyst (to leave the maximum quantity of this, about 5% of the treated solution was left altogether).

After that a new portion of WW was poured on the used catalyst for treatment. The obtained results are presented in Table 2.

As one can see from this table, the efficiency of the catalyst decreases when it is used repeatedly. We used it until the duration of treatment reached 10 hours. From the technological point of view, it is a long time for treatment. This duration when adding 0.2% MnO₂ was reached the 5th time of catalyst use, and on the 10th time, when adding 0.5% MnO₂.

We suppose that the efficiency of the catalyst decreases due to the effect of organic and inorganic materials found in the liquor. But it can be said that it still is economical to use the catalyst a few times though its efficiency decreases.

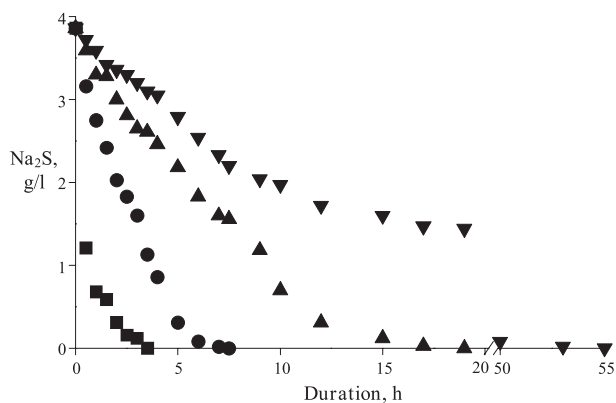
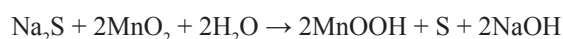


Fig. 6. Dependence of concentration of Na₂S on duration of treatment when treating without MnO₂ (▼) or using 0.5% MnO₂, whose particles' size was: ▲ – 0.16-2.5 mm; ● – 0.1-0.63 mm; ■ – 0.05-0.1 mm.

The repeated use of the catalyst with an additional amount of MnO₂ at each new cycle of treatment was investigated. WW and conditions of the treatment were the same as in the previous experiment. The considerable difference was that for the first time of treatment we added 0.5% MnO₂, and 0.05% MnO₂ additionally on the second and every subsequent time. 22 portions of WW were treated by this way. Treating the first 2 cycles the duration was 2 hours, treating next 20 times it was 2.5-3 hours. This means that stable efficiency of sulphide oxidation was achieved. It was calculated that when treated 22 times, the amount of MnO₂ required for one cycle of treatment was only 0.07%.

Discussions of Results

The sulphides in WW of tanneries can be oxidized using MnO₂. The oxidation of Na₂S proceeds in two stages. In the first stage Na₂S reacts with MnO₂ in this way:



In the second stage, the catalysis reaction between Na₂S and air O₂ is taking part. The MnOOH acts as a catalyst in this reaction. The MnO₂ and MnOOH are insoluble and neither not fall into WW nor pollute it.

The amount of sulphides and the pH of solution have an influence on oxidation process duration; it is longer when the sulphide amount and pH in WW is higher. The type of WW is of no significance. 0.2–0.5% of MnO₂ should be used for the treatment of various WW.

The optimal temperature of the treatment is 30°C; at this temperature the oxidation proceeds more rapidly. The process becomes a little longer if the temperature is lower or higher than 30°C.

Table 2. Influence of number of repeated use of catalyst on duration of sulphide oxidation.

Number of repeated use time	Duration of sulphide oxidation, h		
	0% MnO ₂ (control)	0.2% MnO ₂	0.5% MnO ₂
1	42	3	2.5
2	-	5	3.5
3	-	5	4
4	-	6	5
5	-	10	5
6	-	-	5
7	-	-	6
8	-	-	6
9	-	-	7
10	-	-	10

Not only the amount of MnO_2 , but also the size of MnO_2 particles has an influence on the duration of the sulphide oxidation process. It is faster if the size of particles does not exceed 0.1 mm.

The possibility of reuse of the catalyst was investigated. The efficiency of the catalyst decreased when it was used repeatedly for a few times. Stable efficiency of the process could be obtained by putting at first 0.5% MnO_2 and additionally 0.05% MnO_2 every following time of treatment.

Acknowledgements

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