

Oxidizing Purification of Subturpentine Waters from Sulphate Cellulose Production by Intermediates of Catalytic Decomposition of H₂O₂

N. V. CHAENKO¹, G. V. KORNIENKO¹, V. L. KORNIENKO¹, G. I. STROMSKAYA² and F. M. GIZETDINOV²

¹*Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Ul. K. Marksa 42, Krasnoyarsk 660049 (Russia)*

E-mail: kvl@icct.ru

²*SibNII TsBP Co., P.O. Box 464, Bratsk 665718 (Russia)*

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Abstract

Investigations into oxidizing purification of subturpentine waters from sulphate cellulose production that contain hydrogen sulphide, methyl mercaptans, thiomethyl sulphides, dimethyl disulphides, turpentine, and methanol have been made. Hydrogen peroxide was chosen as an oxidizer. It has been found that hydrogen sulphide, dimethyl sulphides, dimethyl disulphides are subject to easy oxidation in the presence of H₂O₂. Methyl mercaptans and alternative organic compounds can be oxidized more effectively with the classic Fenton's reagent (H₂O₂, FeSO₄, pH 2–3) and electrochemically with the use of H₂O₂.

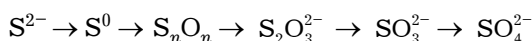
INTRODUCTION

It is known that subturpentine waters from sulphate cellulose production contain a great quantity of mineral and organic solutes. The offensive odour of the flow, which is determined by the presence of methyl mercaptan, dimethyl sulphide, dimethyl disulphide, and hydrogen sulphide, does not disappear even with thousand-fold dilution [1]. Discharge of the evil-smelling sewage without an appropriate purification causes a great ecological stress and can lead to disturbance of oxygen regime in the water bodies and thus to death of fishes, microorganisms, and vegetation.

To purify such waters, the variety of ways is suggested: aeration, chlorination, rectification, distillation, treatment with flue gases, oxidation by air oxygen under pressure, extraction, adsorption, and microbiological oxidation [1]. One of the most interesting and promising methods for decontamination from sulphides is an oxidation by air oxygen in the presence of catalysts, which enable conducting

decontamination under ordinary conditions. Hydroxide and salts of iron, copper and manganese salts, as well as absorbent carbon have been tested as the catalysts [2, 3].

From the published literature data, it follows that depending on the conditions of the process, several products can be obtained with a variable sulphur oxidation state:

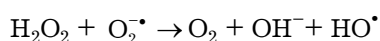
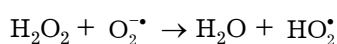
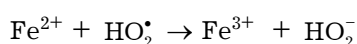
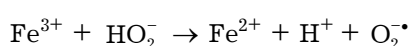
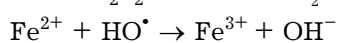
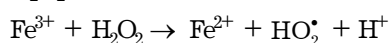
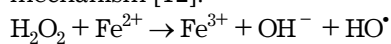


The use of hydrogen peroxide that is one among the forms of the fixed oxygen shows a number of advantages such as a high solubility in water solutions, no necessity to operate under the elevated pressure regime, together with high standard redox potential ($E^0_{H_2O_2/H_2O} = +1.776$ V in acidic media, and +0.88 V in alkaline media) [4].

It is common knowledge that H₂O₂, being a stronger oxidizer as compared to molecular oxygen in the presence of catalysts of decomposition, specifically, the metals of variable valence (ions of iron, copper, vanadium, manganese, etc.), forms highly reactive intermediates (HO[•], HO₂⁻, HO₂[•], O₂^{-•})

with a various oxidizing capacity. This leads to destruction of organic substances with the complete mineralization to form CO_2 and H_2O [5–9].

Investigations of oxidizing treatment of sewage from ash dumps of thermal processing of combustible slates, which had been performed in the work [10], have demonstrated that application of H_2O_2 in the version of Fenton's reagent drastically reduces the toxicity of sewage at the expense of selective oxidation of phenolic compounds. Discovered by Fenton [11], the classic method to produce HO^\bullet radicals consists in the catalytic disintegration of H_2O_2 in acidic medium in the presence of Fe^{2+} . It is described by the following stage-by-stage mechanism [12]:



The presence of organic compounds (methyl mercaptans, dimethyl sulphides, turpentine, and methanol) together with H_2S in subturpentine waters suggests that the use of H_2O_2 for the catalytic obtaining of highly reactive intermediates must result in an effective oxidation of both sulphur-containing and organic compounds.

The purpose of this work is to study the possibility of H_2O_2 application for the effective oxidizing purification of subturpentine waters from various sulphur-containing compounds.

EXPERIMENTAL

For oxidizing treatment, the samples of subturpentine waters from the Bratsk timber industry complex were used that had the following composition, mg/l: H_2S 2.5417, methyl mercaptan 1.2969, dimethyl sulphide 508.14, dimethyl disulphide 237.97, turpentine 0.843, methanol 3335.0. Oxidizing treatment of a sample, 50 ml in volume, was conducted in a temperature-controlled cell equipped with a magnetic stirrer at 50 °C with stirring for 2 h.

Determination of hydrogen sulphide, methyl mercaptan, dimethyl sulphide, and dimethyl disulphide was performed in the gas chromatograph "Tsvet" with the flame photometric detector according to the procedure [13], which was based on the chromatographic fractionation and selective detection of sulphur-containing compounds with the flame photometric detector. The use was made of 4-D chromatographic column from fluoroplastic material with an inner diameter of 0.3 m, 2.5 m in length; chromatographic packing constituted 15 % PEG on C-22 celite.

Turpentine and methanol determination was conducted in LKhM-80 gas chromatograph with a flame ionization detector by the procedure [14]. A column chromatographic was 4-D from fluoroplastic material with an inner diameter of 0.3 m, 2.5 m in length; chromatographic packing was 15 % squalane on Cromaton N-AW. A determination error is less than 25 %.

According to the data of preliminary determination that was performed by the atomic adsorption method for cations of metals in the subturpentine water, the presence of metals of variable valence has been found at a rate of, mg/l: nickel ions – 0.2, iron ions – 0.3, cobalt ions – 0.1.

Based on the composition of subturpentine water, we tested several schemes to carry out the oxidation process: a) oxidation with H_2O_2 at a temperature of 50 °C with no other reagents added; b) oxidation by Fenton's reagent at a temperature of 50 °C; c) oxidation in an electrochemical cell by intermediates of anodic oxidation of water and H_2O_2 .

RESULTS AND DISCUSSION

Oxidation with H_2O_2 at a temperature of 50 °C with no other reagents added

The availability of ions of variable valence in the initial water at alkalescent reaction of the medium and at a temperature of 50 °C that contribute to the kinetic instability of H_2O_2 has made it possible to conduct the process of H_2O_2 oxidation with no any additional reagents introduced. The results arrived at (Table 1) testify that H_2O_2 effectively (by 99 %) oxidizes hydrogen sulphide, dimethyl sulphide, and

TABLE 1

Efficiency of sewage oxidation with hydrogen peroxide, Fenton's reagent, and by the electrochemical way

Concentration of H ₂ O ₂ , mol/l	Efficiency of oxidation, %					
	Hydrogen sulphide	Methyl mercaptan	Dimethyl sulphide	Dimethyl disulphide	Methanol	Turpentine
<i>Hydrogen peroxide</i>						
0.11	99.15	62.95	99.99	98.98	88.16	91.72
0.20	99.59	77.22	99.99	98.84	89.17	79.53
0.41	91.42	95.13	99.99	99.91	88.42	90.47
0.65	99.94	92.45	99.99	99.95	88.69	92.88
<i>Fenton's reagent</i>						
0.02	99.00	98.55	99.91	98.95	88.41	84.57
0.11	98.72	97.84	99.99	98.74	86.87	93.16
0.20	99.40	99.36	99.99	99.71	92.42	93.52
0.40	98.08	99.86	99.99	99.99	78.29	93.34
0.65	99.93	99.82	99.99	99.99	95.85	93.86
<i>Electrochemical way</i>						
0	99.75	86.25	85.30	85.01	25.52	28.95
0.4	98.75	99.88	99.99	99.99	79.31	100.00

dimethyl disulphide. The efficiency of methyl mercaptan oxidation increases from 62.5 to 95.1 % with an increase in H₂O₂ concentration. The content of methanol in the sewage was reduced from 3335.0 to 370 mg/l (88 %).

Chromatographic analysis has shown an unidentified substance present in the sample, the content of which can be as high as 0.020–0.035 mg/l.

Oxidation by Fenton's reagent at a temperature of 50 °C

The analysis of results of subturpentine water treatment using the classic Fenton's reagent (H₂O₂, FeSO₄ in acidic medium) demonstrates (see Table 1) that effective oxidation of hydrogen sulphide, dimethyl sulphide, and dimethyl disulphide (99 %) is achieved with lower H₂O₂ content, specifically, 0.74 g/l. The concentration of methyl mercaptan in the process also drops (98.6 %).

Methanol is oxidized only by 88.4 %. To enhance the efficiency of methanol oxidation up to 92.4 %, it is necessary to increase the consumption of H₂O₂ 10 times (to 7.4 g/l). The residual content of turpentine is less than 0.06 g/l (~7 %).

The chromatographic analysis performed has demonstrated that only the residual quantities of the oxidizable substances are present. Turbidity of a solution of calcium chloride while passing the evolving gas products bears witness to mineralization of organic matter to form CO₂. An increase of the mass of BaSO₄ deposit confirms that the oxidation of sulphides runs with formation of sulphate ions.

Oxidation by intermediates from anodic oxidation of water and H₂O₂ in an electrochemical cell

An electrochemical scheme of the oxidizing purification involved the use of an oxide-lead anode and graphite cathode in acidic medium (pH 2.3). A sample was acidified with H₂SO₄. Oxidation was conducted in a diaphragmless electrolytic cell in the water volume that was equal to 50 ml, without H₂O₂ and with its addition (0.4 mol/l) into the solution. The current intensity was 200 mA. The results of the analysis of electrolyte after electrolysis are presented in Table 1.

The results are indicative of an increased efficiency of sewage oxidation when the

additional H_2O_2 is introduced. Meanwhile, the introduction of H_2O_2 did not manifest itself in changing the concentration of hydrogen sulphide, which is effectively (99.75 %) oxidized on the oxide-lead anode. It is worth noting also that when the solution was free from H_2O_2 , the anode passivation happened with time and the voltage on the electrolytic cell drastically increased, while the current intensity sharply decreased. With H_2O_2 added in the electrolyte, the like phenomena were not observed. Analysis of the electrolyte after electrolysis has shown only residual concentrations of the starting substances in the solution.

Turpentine has been completely oxidized under these conditions: the analysis has shown its complete absence in the sample.

CONCLUSIONS

Comparison of the results of the oxidation procedures applied demonstrates that all of the three schemes make it possible to conduct rather deep purification of the subturpentine water. However, when choosing the most effective procedure for an oxidizing decontamination, it is necessary to take into consideration the composition of the subturpentine sewage and

economic computations. Hydrogen sulphide, dimethyl sulphides, and dimethyl disulphides can be easily oxidized in the presence of H_2O_2 irrespective of the oxidation scheme. Methyl mercaptans and the other organic compounds are oxidized more effectively with the classic Fenton's reagent and electrochemically with the use of H_2O_2 .

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