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Tamila PETROVSKAYA and Guido RAJALO**

ELECTROCHEMICAL OXIDATION OF SULPHIDES IN TANNERY WASTE WATER

The method of soft chemical oxidation was applied for the treatment of the waste water coming from a chromium tannery. Investigations were carried out in a non-diaphragm electrolytic cell using insoluble platinum, oxide-cobalt-titanium (OCTA), and titanium-manganese dioxide (TMDA) anodes. Sulphide conversion and the decrease of chemical oxygen demand (COD) depending on time as well as current efficiency were investigated. The influence of chromium ions on the selectivity of oxidation process was established.

Introduction

Chromium tannery waste water is one of the most concentrated industrial waste waters. It contains large quantities of organic and inorganic compounds, including toxic substances such as sulphides and chromium salts. The concentration of these compounds varies within large limits. For example, the total waste water stream that comes from a chromium tannery works and is preliminarily treated by hydromechanical and flotation methods is characterized by the following properties: pH$=$$=$9—10, alkalinity 10—20 g/m^3, COD$=$1.5—5.5 kg O_2/m^3, biochemical oxygen demand (BOD)$=$1.5—2.3 kg O_2/m^3, concentrations of $Cl^-$$=$$=$1.5—3.1 kg/m^3, $Cr^{3+}$$=$25—66 g/m^3, $S^{2-}$$=$65—300 g/m^3, phosphorus$=$$=$4—20 g/m^3, ammonia nitrogen$=$100—150 g/m^3, suspended matter$=$$=$2.2—4.5 kg/m^3, surface active fats$=$81—120 g/m^3, petrochemicals$=$$=$60—230 g/m^3.

The purification of such multicomponent waste waters requires the use of a complicated set of physical and chemical methods. They may bring about some undesired side effects. In the aeration tanks and the flotation cell the sulphides decompose partially and toxic hydrogen sulphide is emitted into the atmosphere. The sulphide ions are toxic also for aerobic bacteria in the biopurification process. Therefore it is necessary to decrease the sulphide concentration of waste water before it is directed to aeration and flotation.

Several methods may be used to decrease the sulphide concentration, but often they are not selective enough. For example, by the oxidation of sulphides in waste water with an oxidizer, such as hydrogen peroxide, the bulk of the reagent is consumed in the oxidation of organic matter. This makes the oxidation process very expensive as compared with biochemical oxidation.

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* Eesti Teaduste Akadeemia Keemia Instituut (Institute of Chemistry, Estonian Academy of Sciences), Akadeemia tee 15, EE0026 Tallinn, Estonia

We have investigated a more selective sulphide oxidation process using the electrochemical method. Generally publications dealing with electrochemical oxidation at a relatively high current density (2—500 A/dm^2) report an almost complete conversion of organic substances and sulphides. For example, by the oxidation of sulphides and mercaptanes using diaphragm [1,2] and non-diaphragm [3] cells in highly concentrated solutions (7—150 kg/m^3), sulphite and sulphate ions, sometimes partially even elementary chlorine and hypochlorite ions are formed on the anode. We have tried to carry out the process differently, under soft conditions (at low current density). The aim was to achieve a low degree of oxidation only, and to transfer the sulphide ion mainly to elementary sulphur and thereby remove it from the solution

$$S^{2-} - 2e \longrightarrow S^0.$$

This makes the process possible in a non-diaphragm cell. The above-mentioned anode reaction is accompanied by partial oxidation of organic matter and the formation of hydrogen on the cathode.

We also tried to use insoluble platinum anodes, OCTA, and TMDA for sulphide oxidation. These anodes have been successfully applied for electrochemical destruction of organic compounds in waste water [4,5].

Experimental

The investigations were carried out in a laboratory rectangular non-diaphragm electrolytic cell 155×110×18 mm, made from organic glass (Fig. 1). The cell has two cathodes, between them an anode. OCTA, TMDA, and platinum anodes with titanium cathodes were used. The surface area of the anode was 300 cm^2, liquid volume 240 cm^3. The anode potential was measured using a supplementary calomel electrode. The experiments were carried out by both periodic and continuous modes of operation. In the case of the continuous regime the electrolyte flew around the anode. The current density ranged from 0.3 to 1.0 A/dm^2. The average temperature was 22±1 °C. In part of the experiments the total waste water with the average values of the above-described characteristics was used. In the other part of the experiments waste water coming from liming (unhairing) process and containing the maximum

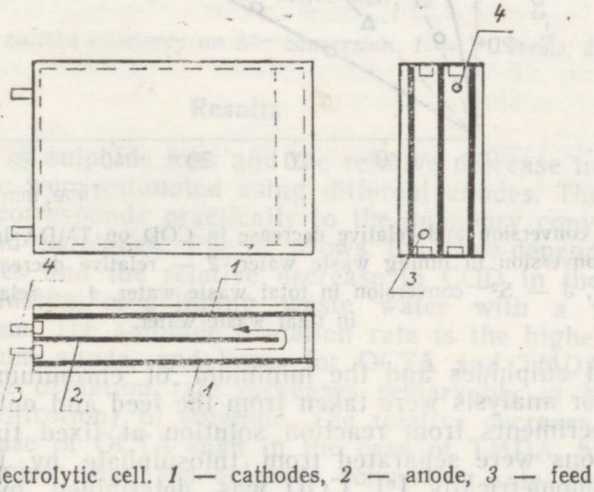

Fig. 1. Laboratory electrolytic cell. *1* — cathodes, *2* — anode, *3* — feed inlet, *4* — electrolyte outlet.

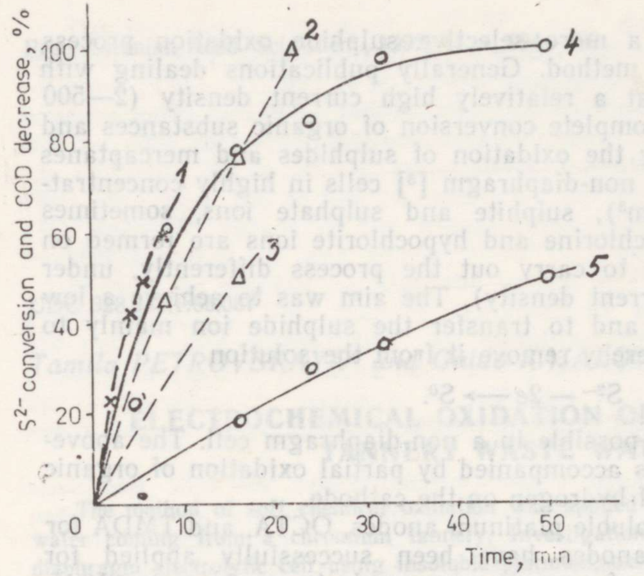

Fig. 2. Dependence of S^{2-} conversion and relative decrease in COD on time. *1* — conversion of S^{2-} on Pt anode, *2* — conversion of S^{2-} on OCTA, *3* — relative decrease in COD on OCTA, *4* — conversion of S^{2-} on TMDA, *5* — relative decrease in COD on TMDA.

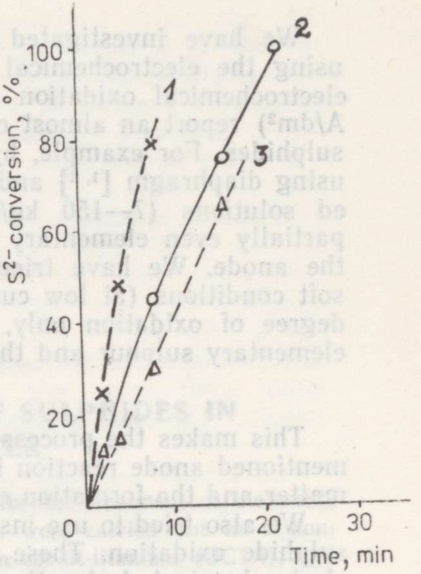

Fig. 3. S^{2-} conversion on OCTA vs. time. *1* — pure Na_2S, *2* — liming waste water, *3* — total waste water.

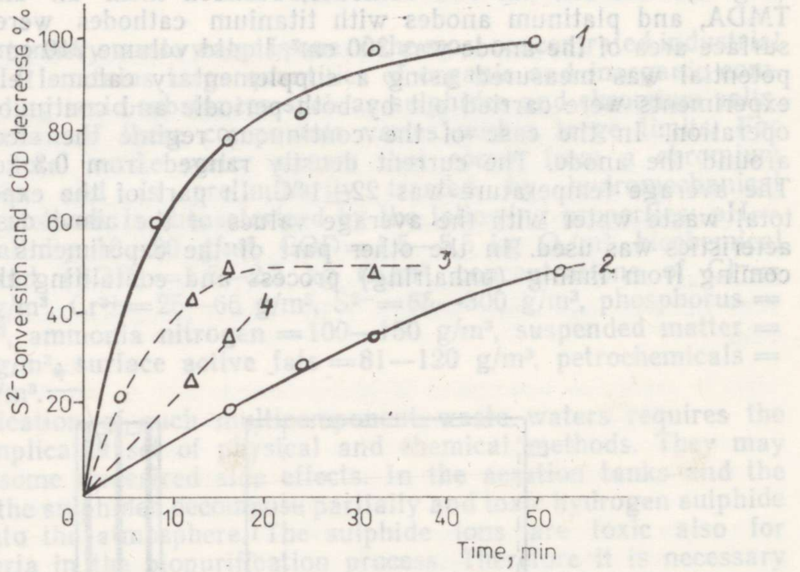

Fig. 4. S^{2-} conversion and relative decrease in COD on TMDA in dependence of time. *1* — S^{2-} conversion in liming waste water, *2* — relative decrease in COD in liming waste water, *3* — S^{2-} conversion in total waste water, *4* — relative decrease in COD in total waste water.

amount of sulphides and the minimum of chromium was used. The samples for analysis were taken from the feed and outgoing solution, in batch experiments from reaction solution at fixed time intervals. The sulphite ions were separated from thiosulphate by formaldehyde and titrated iodometrically [6]. COD was determined by the dichromate method [6].

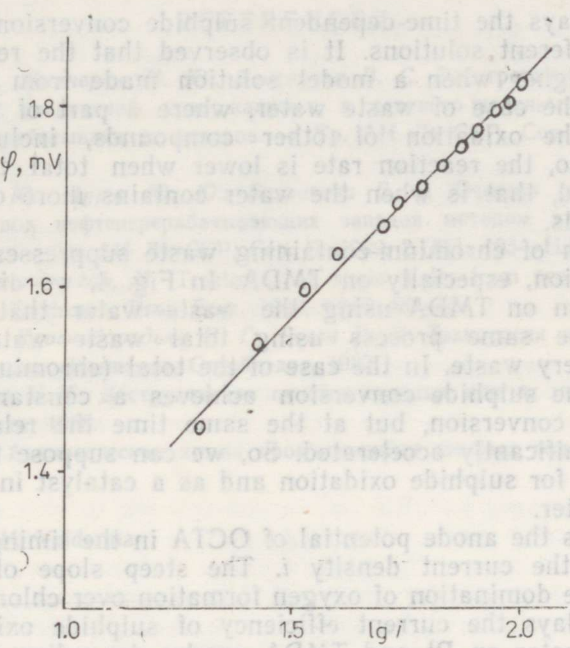

Fig. 5. Dependence of anode potential of OCTA on current density.

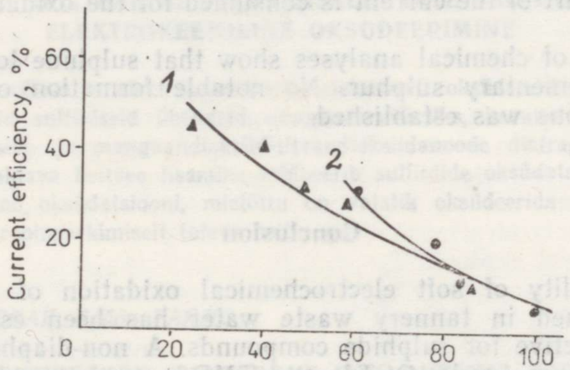

Fig. 6. Dependence of current efficiency on S^{2-} conversion. *1* — Pt anode, *2* — TMDA.

Results

The conversion of sulphide ions and the relative decrease in COD in dependence of time were estimated using different anodes. The relative decrease in COD corresponds practically to the summary conversion of organic matter and sulphides. Fig. 2 shows the time-dependent conversion of sulphides and the relative decrease in COD in the case of electrochemical oxidation of a liming waste water with a minimum amount of chromium. The sulphide oxidation rate is the highest in the case of the platinum anode, and lower for OCTA and TMDA. In the case of TMDA, the oxidation rate decreases remarkably at high conversion (low concentration) of sulphide. The relative decrease of COD is higher in the case of OCTA than in the case of TMDA, but in all cases it remains lower than the sulphide conversion rate. So, it can be concluded that the soft electrochemical oxidation process is selective with regard to sulphides.

Fig. 3 displays the time-dependent sulphide conversion on OCTA in the case of different solutions. It is observed that the reaction rate is considerably higher when a model solution made from pure Na_2S is used than in the case of waste water, where a part of the current is consumed in the oxidation of other compounds, including organic substances. Also, the reaction rate is lower when total tannery waste water is treated, that is when the water contains more chromium and other compounds.

The addition of chromium-containing waste suppresses considerably sulphide oxidation, especially on TMDA. In Fig. 4, we display the sulphide conversion on TMDA using the waste water that comes from liming and the same process using total waste water containing chromium tannery waste. In the case of the total (chromium-containing) waste water, the sulphide conversion achieves a constant equilibrium value on 50% conversion, but at the same time the relative decrease in COD is significantly accelerated. So, we can suppose that Cr^{3+} acts as an inhibitor for sulphide oxidation and as a catalyst in the oxidation of organic matter.

Fig. 5 shows the anode potential of OCTA in the liming waste water depending on the current density *i*. The steep slope of this plot is indicative of the domination of oxygen formation over chlorine formation.

Fig. 6 displays the current efficiency of sulphide oxidation in the liming waste water on Pt and TMDA anodes depending upon sulphide conversion. As can be seen, the current efficiency decreases with increasing sulphide conversion, but remains quite high considering that the essential part of the current is consumed for the oxidation of organic matter.

The results of chemical analyses show that sulphide ions are mainly oxidized to elementary sulphur. No notable formation of thiosulphate and sulphate ions was established.

Conclusion

The possibility of soft electrochemical oxidation of sulphide compounds contained in tannery waste water has been established. The process is selective for sulphide compounds. A non-diaphragm cell and insoluble platinum anode, OCTA, and TMDA can be used. The addition of total (chromium-containing) waste inhibits the sulphide oxidation and catalyzes the oxidation of organic matter, so it is necessary to carry out sulphide oxidation of liming waste water before mixing it with other chromium-containing wastes.

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Tamila PETROVSKAJA, Guido RAJALO

NAHATÖÖSTUSE HEITVEES SISALDUVATE SULFIIDIDE ELEKTROKEEMILINE OKSÜDEERIMINE

On selgitatud võimalus elektrokeemiliselt selektiivselt oksüdeerida kroomnahatehase heitvees sisalduvaid sulfiidseid ühendeid elementaarvääavliks, kasutades plaatina-, koobaltoksiid-titaanoksiid- ja mangaandioksiid-titaandioksiidanoode diafragmata elektrolüüseris. Kroomi sisaldava heitvee lisamine inhibeerib sulfiidide oksüdatsiooni ja katalüüsib orgaanilise aine oksüdatsiooni, mistõttu on vajalik oksüdeerida sulfiidset heitvett enne segunemist kroomparkimiselt tuleva heitveega.

Тамила ПЕТРОВСКАЯ, Гуйдо РАЯЛО

ЭЛЕКТРОХИМИЧЕСКОЕ ОКИСЛЕНИЕ СУЛЬФИДНЫХ СОЕДИНЕНИЙ В СТОКАХ КОЖЕВЕННОГО ПРОИЗВОДСТВА

Выяснена возможность селективного электрохимического окисления сульфидных соединений, содержащихся в сточных водах заводов хромовых кож, до элементарной серы в бездиафрагмовом электролизере с применением платинового, оксиднокобальтового и титандиоксидномарганцевого анодов. Установлено, что с добавлением хромсодержащих сточных вод к суммарному стоку окисление сульфидов ингибируется, а окисление органических веществ катализируется. Поэтому сульфидсодержащий сток зольника целесообразно окислять до его смешения с хромсодержащим стоком.