



Occasions and Possible Mechanisms of Mutual Acceleration and Inhibition of Joint Oxidation Reactions of Sulfide Anion and Cysteine

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Authors' contributions

All authors participated in the formulation of the goal and objectives of the study. Authors SA and ZM synthesized the catalyst and obtained kinetic curves of the investigated processes. Authors SA and YS investigated the surface of the catalyst. Author LM managed the literature search. All authors read and approved the final manuscript.

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ABSTRACT

The model system simulating oxidation of sulfuric-alkaline drains is investigated. The mutual influence of processes of joint oxidation of sulfide-anion and cysteine, revealed strong alkaline environments both at the presence, and in the absence of the catalyst, causes occurrent synergism (non-additivity effects) in the system. The reasons of occurrence of non-additivity effects can be due to a consecutive course of sulfide-anion and cysteine oxidation in a mix and the modification of the catalyst which is shown to have a negative effect. The positive effect is caused by the influence of cystine (a product of cysteine oxidation) on the sodium sulfide oxidation.

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ABBREVIATIONS

PAAH : Polyacrylamidichydrogel,
 Cys : Cysteine,
 (Cys)₂ : Cystine,
 AA : Acrylamide,
 B : N,N'-methylene-bis-acrylamide,
 P : Ammonium persulphate,
 TMED : N,N,N',N'-tetramethylethylenediamine

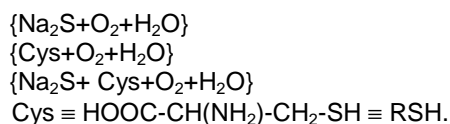
1. INTRODUCTION

The development of modern technologies require - understanding the patterns of behavior of complex systems, which is necessary for the effective conversion of substrates in polycomponent catalytic systems. Complex catalysts are successfully used in industry and widely distributed in nature.

The numerous reports in the literature and the practical effects of nonadditive enhancement (synergism) of activity, selectivity and other characteristics may occur when the component composition of the catalyst becomes more complex [1-8]. For example, Cu-Co synergism in Cu_{1-x}Co_xFe₂O₄ – catalysis [7].

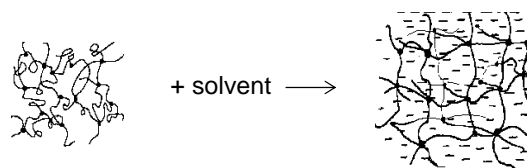
However, the component composition of the catalyst system can also be complicated by the addition of additional substrates, carrying out two or more reactions in the presence of one catalyst.

As a synergistic pair to study the effects of non-additivity in the model catalytic system, the oxidation reactions of sodium sulfide and cysteine (as an analog of mercaptans) by molecular oxygen were chosen. The choice of these reactions can be useful for optimizing the conditions during oxidizing processes in mixtures of sulfur-containing compounds, which are one of the main environmental problems in the oil refining and petrochemical industry (utilization of contaminated sulfur compounds of spent alkaline solutions and aqueous process condensates forming sulfur-alkaline drains) [9-12].

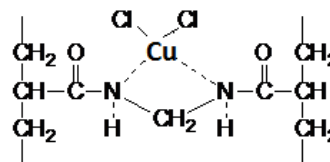


Now as the most perspective for clearing of sulfur-alkaline waste water, the experts count heterogeneous catalysts, in which an active basis are organometallic complexes of variable valencies, and the polymer as a carrier.

Copper (II) -containing polyacrylamide hydrogel was used as a catalyst in this work. According to [13], the gel is a structural grid of a polymer dispersed in a liquid and has a number of specific properties.



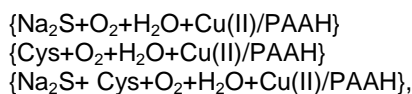
The specific properties of gels include their ability to retain a mass of liquid that is many times greater than its own mass, and which has high conformational mobility of the mesh structures. A consequence of this mobility of the three-dimensional polymer network with functional groups may be the possibility of a unique "tuning" of the catalyst onto the substrate.



The purpose of this work was to investigate the reasons and conditions of appearance of the various non-additive effects, different in sign and size, arising from the oxidation by molecular oxygen of mixes of the data substrates.

2. MATERIALS AND METHODS

Requirements – Catalytic and non catalytic systems of separate and joint oxidation of sodium sulfide and cysteine by molecular oxygen in an aqueous solution:



Conditions of experiment: $T = 313 \text{ K}$; volume of reaction-mix = 5 ml; $m_{\text{cat}} = 0.2087 \text{ g}$; $[\text{Cu(II)}]_{\text{PAAH}} = 0.903 \cdot 10^{-6} \text{ mol/g}_{\text{cat}}$; $[\text{substrate}] = 0.02 \div 0.1 \text{ M}$; $[\text{Na}_2\text{S} + \text{Cys}] = 0.1 \text{ M}$; $[\text{Na}_2\text{S}] / [\text{Cys}] = 20/80 \div 80/20$, $\text{pH} = 12.5$.

Account of the size of non-additivity effect (Ξ) for any moment of time of experience carried out under the following formula:

$$\Xi = (V_{\text{mix}} - V_{\text{add}}) / V_{\text{add}} = V_{\text{mix}} / V_{\text{add}} - 1 = V_{\text{mix}} / (V_{\text{Cys}} + V_{\text{Na}_2\text{S}}) - 1, \quad (1)$$

V_{mix} – volume of the oxygen, absorbed to the given moment of time by a substrate mix of the respective structure; V_{add} – the sum of volumes of oxygen absorbed besides the moment of time to every substrate at their separate oxidation.

The PAAH was prepared by the radical polymerization of acrylamide (AA) and N, N'-methylene-bis-acrylamide (B), pre-recrystallized from ethanol. The initiator of the reaction was ammonium persulphate (P), initiator promoter - N,N,N',N'-tetramethylethylenediamine (TMED). The reagents were mixed in the following order: 4 ml of solution B containing 0.02 g of B added to 12 ml of an aqueous AA solution containing 0.98 g of AA. After stirring, 1.4 ml of 0.043 M solutions of P were added successively to the resulting mixture TMED, and the total volume of the reaction mixture was adjusted to 20 ml with water and left to stand for 18-20 hours at room temperature. The resulting gels (degree of crosslinking of 2%) were granulated by punching them into distilled water through a sieve with holes $d = 1 \text{ mm}$, washed several times with water and dried with water-acetone mixtures, gradually increasing the acetone content in them from 50 to 100%.

The swelling capacity of PAAH in water – q (g H_2O / g polymer) was determined by the weight method and calculated by the formula:

$$q = (m_{\text{H}} - m_0) / m_0,$$

where m_0 is the mass of the dry polymer; m_{H} is the mass of the equilibrium swollen gel. To achieve equilibrium, the samples were kept at room temperature in water for at least 48 hours, filtered and weighed in a calibrated sealed container. The swelling of the resulting PAAH was $20 \pm 2 \text{ g H}_2\text{O} / \text{g polymer}$ (the average of 20 determinations).

The catalysts were prepared by impregnation. To this, 0.2 ml of a 0.01 M solution of CuCl_2 was

added to a 0.0087 g of dry sample. As a result, when the solution was completely absorbed, samples with $[\text{Cu(II)}]_{\text{PAAH}} = 0.903 \cdot 10^{-6} \text{ mol/g}_{\text{cat}}$ were obtained. The volume of the CuCl_2 solution was calculated taking into account the concentration of CuCl_2 and the swelling capacity of the polymer. Thus, all Cu (II) ions passed quantitatively into the gel phase, and its state after impregnation was close to the maximum swollen state. This method made it possible to reproducibly prepare catalysts Cu (II)/PAAH with a specified content of the active phase.

In some cases, the copper-containing gels were modified with sodium sulfide, treating each sample of Cu(II)/PAAH with 5 ml of 0.1 M Na_2S solution at room temperature with stirring on a magnetic stirrer. After 20 minutes, each gel portion was filtered, washed from the modifying solution, and $\text{Cu}_x\text{S}_y/\text{PAAH}$ catalysts were immediately used to oxidize the cysteine solutions.

Photographs of the catalyst at 1000x magnification were obtained on a multi-purpose scanning electron microscope (SEM) JSM-6490LV by JEOL, Japan, the leading engineer of Institute of Geology of Diamond and Noble Metals of the Siberian Branch of the RAS Khristoforova N.N. in the presence of authors AS and SY. The catalytic samples were pre-coated with graphite to improve conductivity.

3. RESULTS AND DISCUSSION

Substrate oxidation in the absence of the catalyst in separate and joint oxidation of sodium sulfide and cysteine at the first stage of work investigated.

3.1 Oxidation of Substrates without the Catalyst

The processing and comparison of the primary kinetic data has shown, that at non catalytic oxidation of sodium sulfide and cysteine from their mix, out of any content, the absorbance of oxygen gave less appropriate additive meanings. Therefore formal account of the size of non-additivity effect under the formula (1), results in its negative meanings (Fig. 1).

The received negative effects can have two explanations:

- 1) One or both substrates in a mix oxidate is slower, than at individual oxidation;
- 2) Their oxidation in a mix passes consistently.

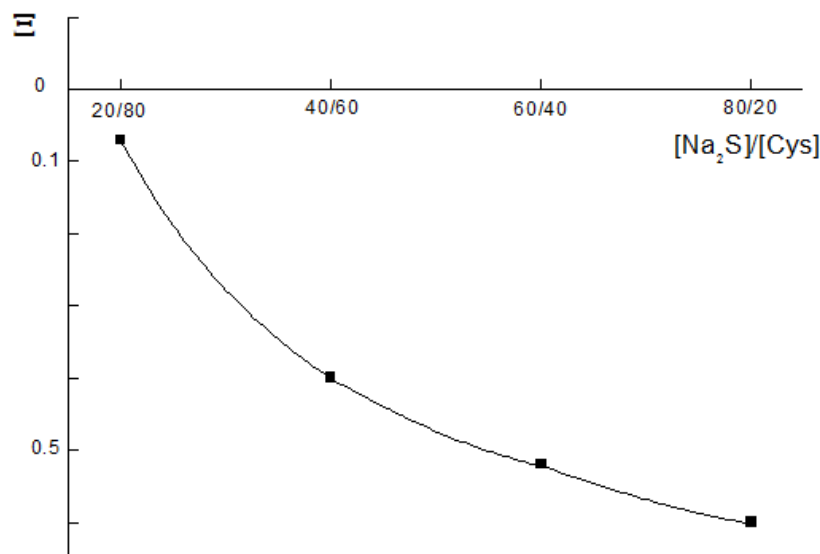


Fig. 1. Dependence of non-additivity effect Ξ contains a mixture of 0.1 M of solutions Na_2S and Cys, without the catalyst

The comparison of the rates of oxidation of mixes and individual substrates show, that substrate mixes oxidate with rates close to rates of oxidation of individual cysteine. It is possible to assume, that in a mix the cysteine is oxidated completely and only then is the sodium sulfide oxidation carried out. As the formula (1) accounts for the size of non-additivity effect which takes into account the sum of the contributions of oxygen absorbed by every substrate at individual oxidation, in a denominator the overestimated meaning V_{add} is pawned. It is also connected by negative values of non-additivity effect.

Due to the fact that oxidation products of each substrate can influence the rate of individual and combined conversion of sodium sulfide and cysteine, each of the substrates is oxidized in the presence of reaction products (P1, P2). P1 are products of the oxidation of sodium sulfide (Na_2SO_3 ; $\text{Na}_2\text{S}_2\text{O}_3$; Na_2SO_4), P2 is product of the oxidation of cysteine ($(\text{Cys})_2 \equiv \text{HOOC}-\text{CH}(\text{NH}_2)-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH} \equiv \text{RSSR}$, cystine). P1 practically do not influence the oxidation rate

of sodium sulfide. In the presence of cystine (Cys)₂ the oxidation rate of sodium sulfide is significantly accelerated. Similar experiments with cysteine solutions showed that P1 and P2 do not practically change of its oxidation rate.

The following stage of the research work involved the separate and joint oxidation of sodium sulfide and cysteine in the presence of the catalyst.

3.2 Catalytic Oxidation of Substrates

The data submitted in Table 1 shows the influence of the catalyst on the maximal rate of absorption of oxygen at separate oxidation of sodium sulfide and cysteine.

The transition from non catalytic systems to catalytic systems not only leads to an increase in the rates of oxidation of each substrate separately, but also changes the ratio of these rates: if in the absence of a catalyst sodium sulphide is oxidized at a higher rate than

Table 1. A role of the catalyst during separate oxidation Na_2S and Cys

[Substrate], M		$W_{\text{max}}, 10^{-8} \text{ moles O}_2 / \text{c}$		Rate-up, $\frac{W_{\text{cat}}}{W_{\text{without cat}}}$
		Without catalyst	With catalyst	
Na_2S	0.02	1.5	14.1	9.5
	0.10	8.2	35.7	4.4
Cys	0.02	0.7	50.6	68.4
	0.10	1.5	72.9	49.0

cysteine, then in the presence of the catalyst the situation changes to the opposite and the rate of oxidation of cysteine more than twice the rate of oxidation of Na_2S . That is, there is an inversion of the ratio of the rates of separate oxidation of substrates.

The study of a condition of the catalyst at substrate influence is shown in Fig. 2, a-d. Addition of a cysteine solution to the catalyst results in the formation of copper-cysteine complexes of yellow colour (Fig. 2, c). When the solution of sodium sulfide is added to the catalyst, finely dispersed dark copper sulphides are formed inside the polymer (Fig. 2, b). After processing the initial catalyst with a mixture of substrates, it acquires a dark color, characteristic of copper sulfides (Fig. 2, d). This is due to the

fact that the sulfide anion is a stronger complexing agent than the cysteine anion. In this case, it is hardly worth expecting identical rates of oxidation of cysteine at centers of different nature.

Therefore, a catalyst is specially prepared with copper sulfide centers in the gel phase. For this, the copper(II)-containing polyacrylamide hydrogel is treated with a solution of sodium sulfide. The resulting catalyst is separated from the modifying solution and washed off from excess sodium sulphide. Oxidation of cysteine is accomplished in the presence of the modified catalyst. Fig. 3, b illustrates the data on the oxidation of cysteine in a mixture of cysteine and sodium sulphide in the presence of the starting catalyst.



Fig. 2. Change in the state of the catalyst Cu(II)/PAAH in the presence of substrates: a) the starting sample, b) after treatment with 0.1 M sodium sulfide solution, c) after treatment with a 0.1 M cysteine solution, alkaline to pH 12.5, d) after treatment with a mixture of sodium sulfide and cysteine

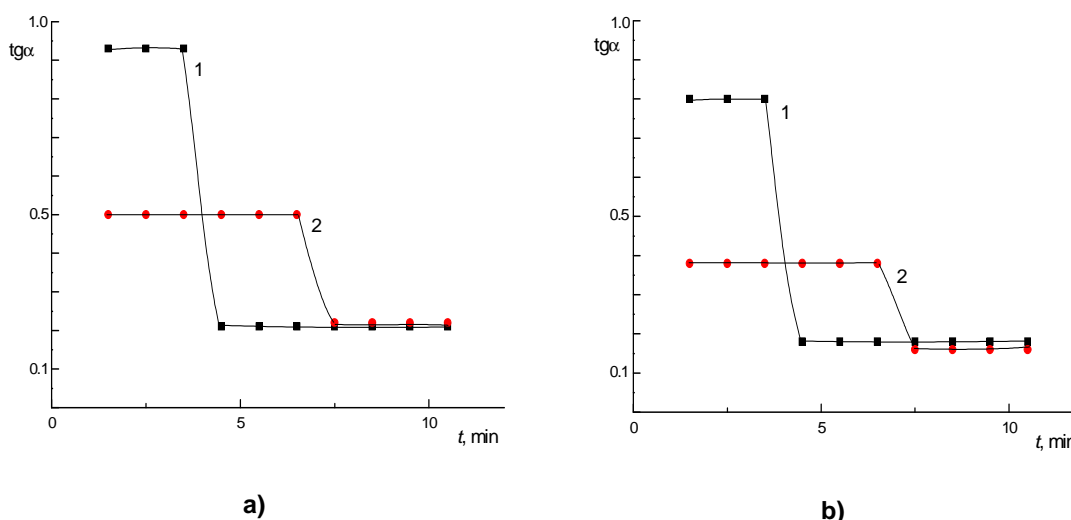


Fig. 3. Kinetics of cysteine oxidation at centres of different nature.
a – 0.1 M cysteine in the presence of Cu(II)/PAAH (1), in the presence of Cu(II)/PAAH, pre-treated with Na_2S (2)
b – 0.08 M cysteine in the presence of Cu(II)/PAAH (1) and mix of $[\text{Na}_2\text{S}]/[\text{Cys}] = 20/80$ in the presence of Cu(II)/PAAH (2)

Fig. 3 presents a comparison of the results of the model experiment with the data obtained during the oxidation of a mixture of Na_2S and Cys in the presence of Cu(II) / PAAH . The maximum rate of oxidation of a mixture of substrates (curve 2 in Fig. 3, b), as in the case of individual oxidation of cysteine at the presence of the model catalyst $\text{Cu}_x\text{S}_y / \text{PAAH}$ (curve 2, Fig. 3, a), is 2 times lower than in the case of individual oxidation of cysteine, carried out on copper-cysteine centers (curve 1, Fig. 3, a and b). And the data as a whole repeats the result obtained during the oxidation of the mixture, which indicates their conversion to copper sulfide centers.

Nevertheless, the presence of cysteine in the reaction solution affects the surface structure of the copper sulfide catalyst (Fig. 4, c, d).

Obviously, the oxidation of sodium sulphide can proceed in different way in the presence of a catalyst modified by this method (Fig. 4, d). Therefore, an individual sodium sulfide is oxidized in the presence of Cu(II)/PAAH , treated with a 0.1 M cysteine solution [14]. Indeed, the oxidation rates of sodium sulfide in the presence of cysteine-treated catalysts are about 2 or more times lower than in the initial ones. In this case, a period of development of the catalyst appears, especially clearly visible with a greater concentration of the substrate.

Thus, the modification of the catalyst in the oxidation of substrates causes the development of negative effects of non-additivity in catalytic systems is also.

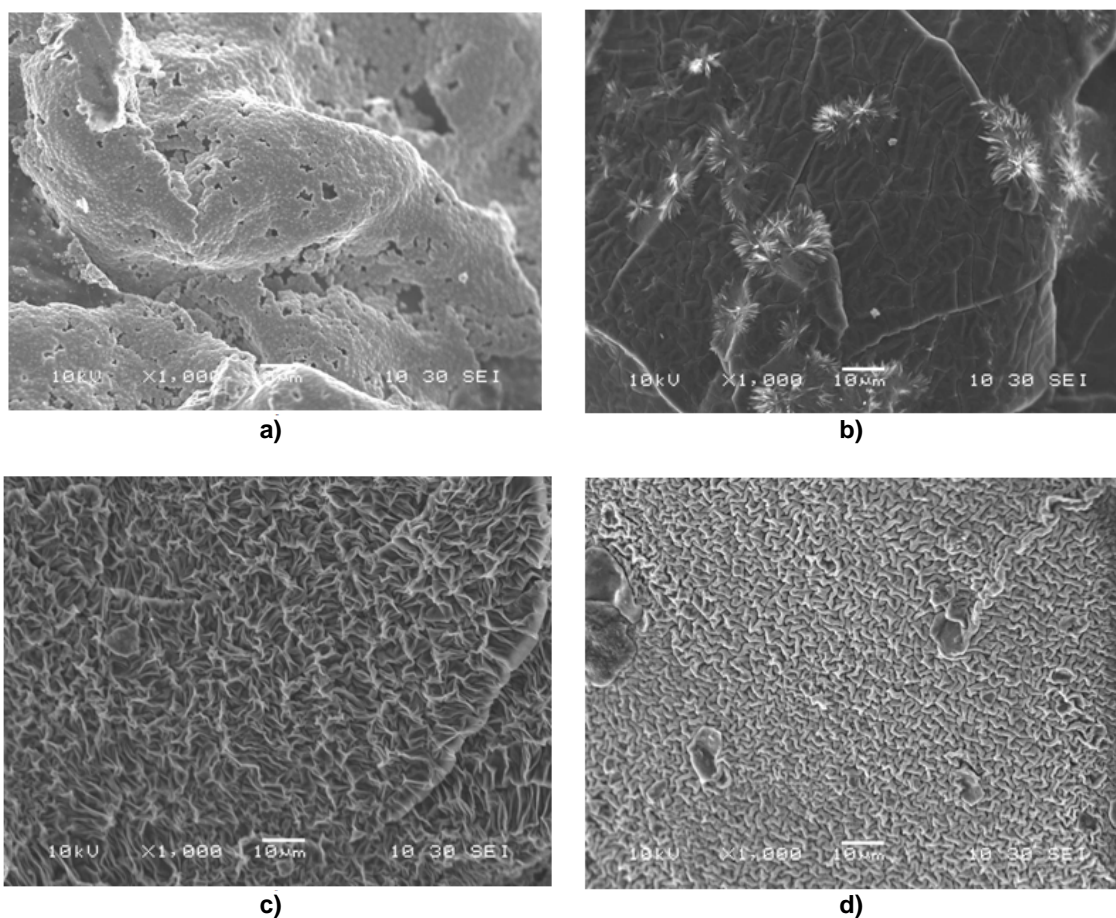
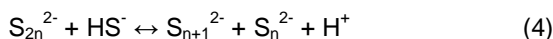
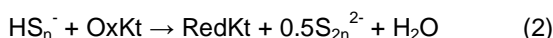


Fig. 4. Surface structure of the catalyst:
**a) Initial catalyst, Cu(II)/PAAH , b) Cu(II)/PAAH , treated with 0.1 M cysteine, c) Cu(II)/PAAH , treated with 0.1 M sodium sulfide solution, d) Cu(II)/PAAH , treated with a mixture of substrates $[\text{Na}_2\text{S}] / [\text{Cys}] = 80/20$.
 Increase x 1000**

3.3 Probable Mechanisms of Substrate Transformation

According to the literature [15], the catalytic oxidation of sodium sulfide in both weakly and strongly alkaline media can be carried out by the polysulfide mechanism. Schematically, the polysulfide mechanism can be represented in the following form:

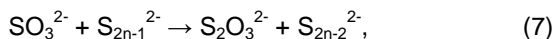
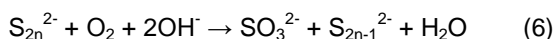
Growth of a polysulfide chain –



Sulfur formation –



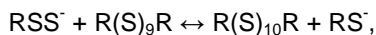
The formation of oxygen compounds of sulfur –



OxKt - is oxidized, RedKt is the reduced form of the catalyst.

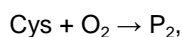
When the sulfide anion oxidation reaction proceeds through the polysulfide mechanism, the length of the polysulfide chain can grow according to (4) or decrease (6, 7), and according to the published data, the rate of the sodium sulfide oxidation process is higher the longer the polysulfide chain.

The growth of the polysulfide chain is facilitated by the presence in the mixture of cystine, which triggers the following chain of transformations associated with the interaction of the hydrosulfide anion with cystine:



This explains the mutual influence of reactions on each other through the participation of the product of one reaction in the course of the other. Although this scheme is simplified, it allows us to explain the observed phenomena.

Thus, as a result of analysis and comparison of the literature data obtained in the present work, it is possible to state the possible causes of negative and positive effects of nonadditivity observed in the joint oxidation of sodium sulfide and cysteine: the negative effect of nonadditivity is associated with the oxidation of substrates in the mixture:



as well as the modification of the catalyst during the oxidation process, and the positive effect - with the change in the mechanism of oxidation of individual sodium sulfide compared with its oxidation in the mixture.

4. CONCLUSION

The mutual influence of the processes of oxidation of sodium sulfide and cysteine on each other in alkaline media has been revealed both in the presence and absence of the catalyst, which causes the appearance of non-additivity effects.

Conditions are established under which the effects of non-additivity of different signs appear:

- Only a negative effect is observed at all proportions of sodium sulfide and cysteine from 20/80 to 80/20 in the absence of a catalyst.
- Negative effect in catalytic systems is developed mainly in strongly alkaline media (pH = 12.5) with substrate ratios $[\text{Na}_2\text{S}] / [\text{Cys}] = 20/80, 40/60, 60/40$.
- The non-additivity effect is actually equal to zero when $[\text{Na}_2\text{S}] / [\text{Cys}] = 80/20$, at pH = 12.5, in the presence of a catalyst.

The causes of non-additivity effects can be:

- The sequential oxidation of sodium sulfide and cysteine in the mixture leads to a negative effect.
- The development of a negative effect in catalytic systems is enhanced by the modification of the catalyst by substrates during the oxidation processes.

- The positive effect is due to the effect of the oxidation product cysteine-cystine on the oxidation of sodium sulphide.

Thus, in the oxidation of sulphurous alkaline wastewaters with molecular oxygen in the presence of copper (II) -containing polyacrylamide hydrogel as a catalyst, at pH = 12.5, the ratio of substrates at $[Na_2S] / [Cys] = 80/20$ can be advised.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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