

Comparative study of the catalytic and non-catalytic oxidation of sulfide from model solutions of sea water

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Oxidation of sulfide ions from model sea water solutions with and without a catalyst was investigated. The catalyst used is zirconium dioxide (ZrO_2) incorporated in activated carbon matrix the surface of which was characterized by adsorption to iodine. The experiments were conducted at different initial sulfide ion concentrations and temperatures and two modes of operation - continuous aeration and stirring at constant speed. The influence of the presence of light was also studied. The rate of oxidation in continuous aeration processes is twice as high as that of constant-rate stirring processes without aeration. In the presence of a catalyst and a continuous aeration process, the sulfide ions are oxidized for 1 hour at 60 °C and 2 hours at 20 °C with the reaction products being 90% sulfate ions relative to the initial sulfide. At the same temperatures and concentrations, but in the non-aeration-stirring processes, a significant amount of intermediate compounds - resistant reducers - were obtained, and therefore this option is ecologically unacceptable. The oxidation rate of the processes carried out without a catalyst was by 50-80% lower in both modes of operation.

In order to increase the active surface and to use instead of powdered catalyst a structured one appropriate for real use or as electrode in a fuel cell, the ZrO_2 was incorporated into pyrolyzed and activated carbon padding. Comparative experiments were carried out with padding with and without a catalyst, as well as with non-pyrolyzed padding. The number of cycles, at which the padding can be used, was also studied.

Keywords: oxidation, sea water, sulfide ions, ZrO_2 catalyst

INTRODUCTION

Hydrogen sulfide in solution occurs naturally in some thermal springs and closed deep water basins. Black Sea waters under a certain depth contain a significant amount of hydrogen sulfide [1,2]. This is the reason for the lack of aquatic life in the deep sea. The latest data show that the level of the "dead zone" is constantly rising. Some industries such as leather, textile paper, petroleum, etc. also release sulfides in high quantity.

Different methods are used for decomposition of hydrogen sulfide to harmless products [3-6]. In many of them the end product is elemental sulfur [3]. According to the literature [2, 7] metal cations Me^{2+} ($Me=Mn, Co, Ni, Fe, Cu$) catalyze the process. However, the elemental sulfur is undesirable because it inhibits the catalytic oxidation by blocking the active sites of the catalyst. Moreover, sulfur is not of particular interest as a commercial product and its return back into the Black Sea water is inappropriate from an environmental point of view. Although Zr is not reported to be a catalyst, experiments with ZrO_2 incorporated into an activated carbon matrix are also carried out. On the other hand, it is not environmentally acceptable to use large quantities of catalyst and dumping it into the water. Therefore it was decided to synthesize spinel-type metal oxides incorporated in the matrix of activated

carbon. An additional advantage in this case is that the activated carbon is also a catalyst [8]. The principle of obtaining such catalysts includes impregnation of the initial organic material with a salt of the given metal and subsequent pyrolysis with simultaneous activation [9].

The aim of the present research is to determine the kinetic parameters of the catalytic and non catalytic oxidation of sulfide ions in a model solution of sea water. Different hydrodynamic regimes were also studied, as well as the influence of light. As the investigated catalyst is obtained in powdered form, structured activated padding with the incorporated catalyst was prepared and studied.

EXPERIMENTAL

Materials and methods

Experimental conditions. The kinetics of the oxidation process of sulfide ions was investigated. Two types of experiments were carried out for determination of the kinetic parameters: 1) at continuous aeration and 2) by stirring at constant rate (200 rpm) but without aeration. The air flow rate was 120 l.h^{-1} , corresponding to 10 vv min^{-1} . The experiments were carried out in a stirred cell at different temperatures (20, 30 and 60°C) maintained by thermostat. The volume of the solution in the cell was 200 ml. A sketch of the experimental set-up is shown in Fig. 1.

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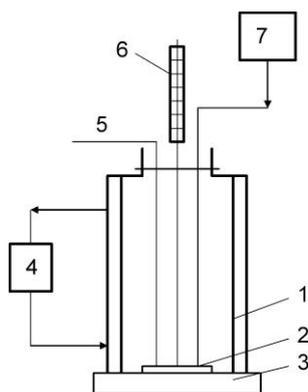


Fig. 1. Scheme of thermostated cell. 1- thermostated cell; 2,3- magnetic stirrers; 4- thermostat; 5- sampling outlet; 6- thermometer; 7- aerator.

The experiments were carried out in model solutions imitating sea water prepared by dissolving NaCl to attain a concentration of 16.5 g.l^{-1} , corresponding to the Black Sea salinity (i.e. $15\text{-}17 \text{ g.l}^{-1}$) [10, 11]. Sulfide was added by dissolving sodium sulfide nonahydrate ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ reagent ACS $\geq 98\%$) in the model sea water. The experiments were performed with concentrations of $25\text{-}120 \text{ mg.l}^{-1}$ which is 5-20 times higher than the actual concentration of sulfides (i.e. between 5 and 15 mg.l^{-1}) [2, 12].

The catalysts obtained and incorporated in the matrix of activated carbon were characterized by iodine adsorption. The specific surface area of the ZrO_2 - catalyst is $780.66 \text{ m}^2.\text{g}^{-1}$.

Analyses. Samples from the reacting solution were taken periodically. The concentration of the total sulfur-containing reducing substances was determined iodometrically. The sulfide (S^{2-}) content was determined photometrically [13] and the presence of sulfate ions was detected qualitatively by addition of barium chloride solution. Sulfates were determined quantitatively by addition of barium chloride and back-titration of the excess of Ba^{2+} ions with EDTA using Eriochrome Black T as indicator.

RESULTS AND DISCUSSION

Kinetic parameters of the reactions

A comparison of the oxidation rate for both regimes at 120 mg.l^{-1} , and different temperatures is represented in Fig. 2. It shows that the process at constant stirring is about 2 times slower than that with aeration.

The amount of the catalyst used was the same (0.5 g.l^{-1}) for all experiments.

Fig. 2 shows the oxidation of sulfide ions in both hydrodynamic regimes –aeration and stirring with a constant stirring rate. The rate of oxidation without the use of catalyst is shown for comparison.

There is about 10 % decrease of the sulfide ions in the first sixty minutes in the case without the use of catalyst. The addition of the catalyst into the reactor volume leads to a considerable acceleration of the process (from 50 to 90% reduction of the sulfide ions in the first sixty minutes) in both regimes.

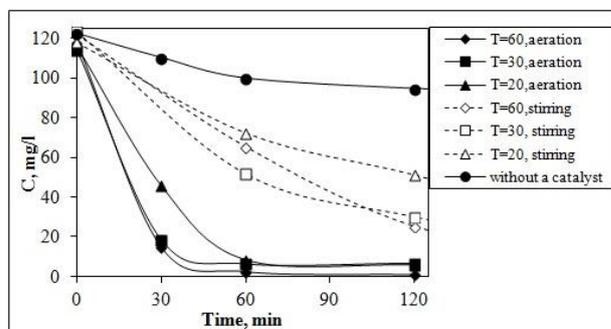


Fig. 2. Comparison of catalytic oxidation of sulfide ions in the presence of light in both hydrodynamic regimes.

Formation of elemental sulfur was not observed during all experiments. Sulfates are the desirable product because they are naturally present in the sea. The reaction products are 90% sulfate ions relative to the initial quantity of sulfides. Since sulfate ions are naturally present in seawater they can be returned into it without harming the environment, restoring the sulfur cycle.

In the second case with continuous stirring (Fig. 3) at constant rate for the same temperatures the reaction products are stable reducers which are determined iodometrically and should not be returned into the sea water.

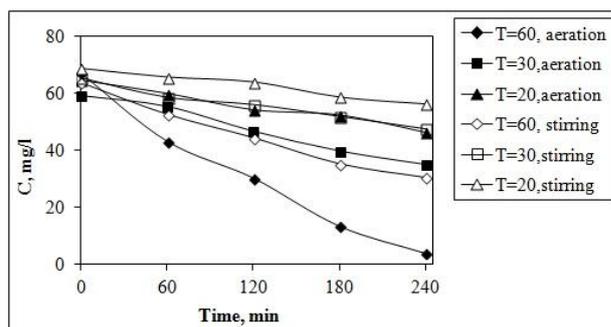


Fig. 3. Comparison of the non-catalytic oxidation of sulfide ions in the presence of light in both hydrodynamic regimes.

Fig. 4 shows that for the processes with continuous aeration in absence of light, the catalytic oxidation of sulfide ions is 2 to 3 times slower than the oxidation in the presence of light. The reaction products in this case (in the dark) are generally sulfite ions.

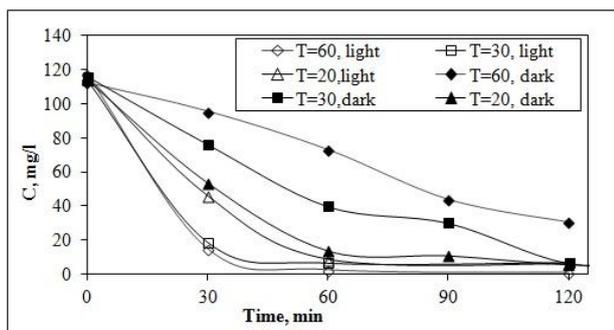


Fig. 4. Catalytic oxidation of sulfide ions with and without light and aeration.

The oxidation with aeration follows the kinetics of a first-order reaction.

The rate constants of the process were calculated from the data for different temperatures and concentrations and are given below. The rate constants for the regime with stirring at constant rate were not alike for the different concentrations, i.e. the process is limited by the amount of dissolved oxygen in the cell.

Based on experimental data obtained from the kinetic curve, the activation energy of the reaction was calculated as 22 kJ.mol⁻¹.

Rate constant of the oxidation of sulfide without catalyst by:

Aeration	Stirring
$k=0.0021 \text{ min}^{-1}$ for 20 °C	$k=0.00115 \text{ min}^{-1}$ for 20 °C
$k=0.0027 \text{ min}^{-1}$ for 30 °C	$k=0.0013 \text{ min}^{-1}$ for 30 °C
$k=0.0044 \text{ min}^{-1}$ for 60 °C	$k=0.0030 \text{ min}^{-1}$ for 60 °C

Rate constant of the oxidation of sulfide with catalyst and aeration:

Light	Dark
$k=0.0269 \text{ min}^{-1}$ for 20 °C	$k=0.011 \text{ min}^{-1}$ for 20 °C
$k=0.0358 \text{ min}^{-1}$ for 30 °C	$k=0.012 \text{ min}^{-1}$ for 30 °C
$k=0.0813 \text{ min}^{-1}$ for 60 °C	$k=0.014 \text{ min}^{-1}$ for 60 °C

Experiments with structured catalysts

As it was mentioned above, for the use of ZrO₂ in practice it is incorporated over activated carbon padding by the same procedure as the powder catalyst is produced. Fig. 5 shows a comparison of

the changes in the concentration of sulfide ions by the use of pyrolyzed and non-pyrolyzed padding. The reduced exploitation characteristics of the pyrolyzed padding are probably due to the decreased surface area owing to the losses during the pyrolyzation process. However, for three hours both paddings show an acceptable rate of depletion – 80 % for the non-pyrolyzed and 70 % for the pyrolyzed one. This rate is slower than that of the powdered catalyst because of diffusion limitations.

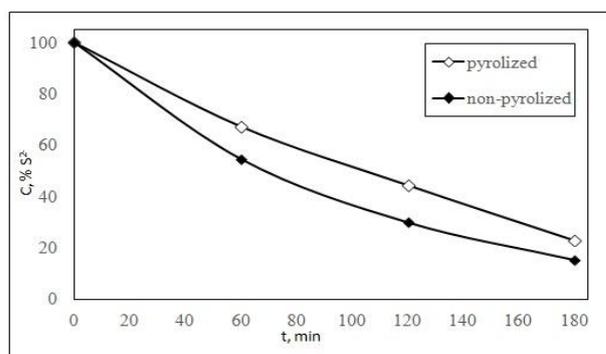


Fig. 5. Catalytic oxidation of sulfide ions with pyrolyzed and non-pyrolyzed padding.

In order to use the prepared catalyst in multiple oxidation steps or in continuous mode of operation six successive experiments were carried on (Fig. 6). It can be seen that during all of them, except the first one, the padding does not change its properties. This could be explained with diffusion limitations connected with the process of wetting and reaching the active sites of the catalyst in the first cycle.

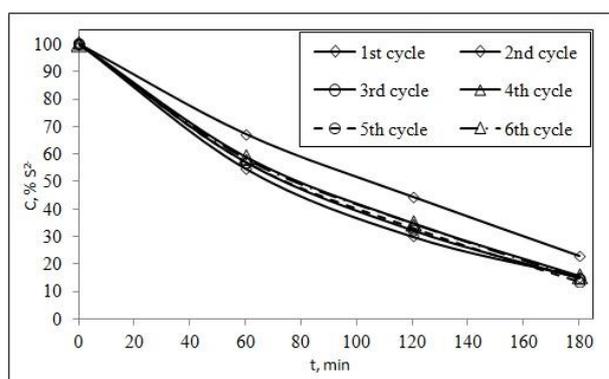


Fig. 6. Number of cycles of use of the ZrO₂ catalyst.

CONCLUSIONS

In all experiments no elemental sulfur was observed. In the case of continuous aeration with light, the conversion of sulfide into sulfate was over 90% according to the initial sulfide concentration whereas at continuous stirring without aeration the products of the reaction were stable reducers but no sulfate. The reaction products in case of continuous

aeration and catalytic oxidation without light were generally sulfite ions. The oxidation follows the kinetics of a first-order reaction with relatively small activation energy – 22 kJ.mol⁻¹. In the presence of light the catalytic process with constant stirring is about two times slower than that with continuous aeration. The non-catalytic process, as expected, had a very low rate of oxidation and did not depend significantly upon the operating conditions. Only at 60°C with aeration there was 60% reduction of the initial sulfides for the first two hours, whereas in all other cases this reduction was only about 15-25%. Rate constants of the processes carried out without catalyst are comparable for both hydrodynamic regimes. Rate constants of catalytic process are by an order of magnitude higher than those without catalyst in all cases. The presence of light and aeration increases the rate constant two to three times. The padding can be used repeatedly and is economically viable.

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