Effect of Sodium Sulphide Concentration on the Adsorption Kinetics and Photocatalytic Oxidation on Zinc Oxide

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Abstract

Adsorption and photocatalytic oxidation kinetics for sulphide ions on zinc oxide in aqueous solutions has been studied. It has been found that the rate constants of sodium sulphide adsorption and photocatalytic oxidation on zinc oxide decrease with increasing the substrate concentration, which indicates an auto-inhibition of these processes due to blocking the surface of zinc oxide by sodium sulphide.

Key words: sodium sulphide, zinc oxide, adsorption kinetics, photocatalytic oxidation kinetics

INTRODUCTION

Sulphides and hydrogen sulphide are widely used in various industrial processes. For example, Na_2S is used as a reducing agent for organic nitro compounds, for the preparation of sulphur dyes, alongside with other sulphides used in the leather and foot-wear industry, in the production of luminescent materials *etc*. Hydrogen sulphide is used in organic synthesis for the production of thio-compounds, such as thiophenes, mercaptans and others.

Hydrogen sulphide is a powerful nerve poison. The maximum the maximum allowable concentration is 0.01 mg/L, whereas in the presence of hydrocarbons this value amounts to 0.003 mg/L [1].

Sulphides of alkali and alkaline earth metal can cleave hydrogen sulphide within the gastrointestinal tract, which is the main cause of their toxicity. Furthermore, in the course of operating with these sulphides, the poisoning with gaseous H_2S should not be excluded [1]. In this regard, the removal of hydrogen sulphide and metal sulphides from waste industrial solutions is an important and urgent issue.

The present paper is devoted to studying the kinetics of the sorption and photocatalytic removal of sulphides from aqueous solutions using zinc oxide, depending on their concentration. It has been shown that sorption and photocatalytic processes on zinc are inhibited by the substrate.

EXPERIMENTAL

The objects under investigation were aqueous solutions of sodium sulphide. As a photocatalyst, finely dispersed zinc oxide with a specific surface area (S_{sp}) equal to 56 m^2/g was used. The irradiation was performed with the light of BUV-30 with the power of 30 W, the basic radiation of which is presented by UV light with the wavelength of 254 nm. Photocatalytic experiments were conducted via irradiating the solutions under investigation through a quartz reactor wall stirring the solution with a magnetic stirrer at frequency of about 100 min^{-1}.

In order to determine the concentration of sodium sulphide, we sampled the solution at

certain time intervals, and then the samples were centrifuged to remove the remainder zinc oxide. For determining the concentration of sulphur in the sodium sulphide solution, we chose a technique based on the formation of nanosized copper sulphide. Owing to this, we succeeded in sufficient shifting the light transmitted through the sample solution towards longer wavelength values, which is important if the solution contains any components (*e. g.*, surfactants) those can absorb UV light.

S^{2-} ion has a long-wavelength absorption band approximately centred at 230 nm [2]. In order to shift the absorption band of the system to a spectral range more convenient for registering longer wavelengths a method was used that is based on the formation of copper sulphide nanoparticles in the course of reaction between sodium sulphide and copper sulphate, taken in a slight excess in the presence of a stabilizer of the nanoparticles. As the stabilizers of researchers could use gelatine, polyethylene glycols, polyvinyl alcohol (PVA), albumin, sodium polyphosphate, surfactants and so on [3–8]. The studies of CuS nanocolloids stabilized with gelatine and polyethylene glycol in aqueous solutions, demonstrated the nanoparticles having an average size of about 10 nm to exhibit the crystal structure of covellite [6].

Polyvinyl alcohol with the molecular mass ranging within 85 000–12 4000 demonstrates an improved stabilization level of nanosized copper sulphide as to compare with other stabilizers. The nanoparticles stabilized in the solution thereof remain aggregation-resistant for several days (even for several weeks in the case of well-chosen stabilization conditions). The solution exhibits a slight scattering due to PVA, which can be easily compensated by using a solution of PVA as a reference solution.

Colloidal solutions of CuS with particle sizes of the order of several micrometers have the brownish black colour [5]. Depending on the concentration and the nature of a stabilizer the colour of nanosized CuS colloids varies from yellowish-brown to brown, which could be caused by a hypsochromic shift of the absorption edge due to the quantum size effect. However, in general, the absorption spectra of the solutions of nanosized copper sulphide insignificantly depend on the nature of the stabilizer (Fig. 1).
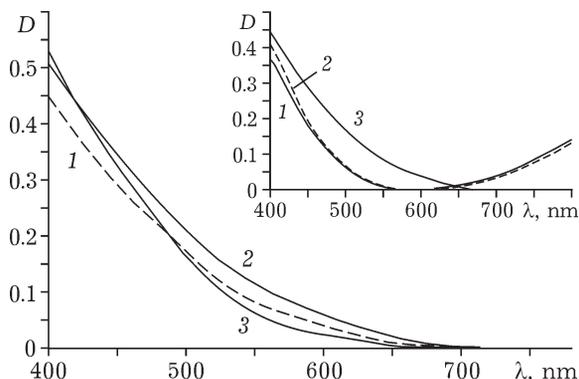

Fig. 1. Absorption spectra registered for the colloidal solutions of freshly prepared copper (II) sulphide with a formal concentration of $5 \cdot 10^{-4}$ mol/L, stabilized by 2.5 % PVA solution (*1*), by 2.5 % polyethylene oxide (*2*) solution and by 0.5 g/L methylbenzoethonium chloride solution (*3*). Inset: transformation of the absorption spectra of colloidal CuS stored at a room temperature in the presence of atmospheric oxygen (formal CuS concentration being equal to $5 \cdot 10^{-4}$ mol/L): *1* − fresh solution; *2*, *3* − the solution after 8 and 32 days passed, respectively.

Storing the nanosized copper sulphide solution in contact with air at room temperature, leads to the fact that its colour gets a green tint. This is caused by occurring the absorption band in the near infrared region of the spectrum (see inset in Fig. 1). It was suggested [3, 10] that a layer of copper (II) oxide could be formed on the surface of nanoparticles of copper sulphide due to the reaction with oxygen.

Based on the studies performed, we the following technique for determining the concentration of sodium sulphide in aqueous solutions was proposed. A sample portion of about 6 mL in volume was taken, then the reaction mixture was centrifuged to remove suspended ZnO from the solution, the transparent solution obtained was decanted. From this solution a 4 mL sample was taken, where to 1 mL of a 5 % PVA solution was added. The solution was thoroughly mixed, with adding thereto 200 μL of a saturated $CuSO_4$ solution, which resulted in appearing a brownish coloration caused by the formation of CuS* nanoparticles. The resulting colloidal solution of copper sulphide should

*The formation of nanoparticles apparently occurred in work [11] describing the method of the spectrophotometric identification of water-soluble sulphides by the addition of solutions of copper, silver mercury and other metals to aqueous of sulphides in the presence of gum Arabic that can function as a stabilizer of nanoparticles.

be kept no longer than one day, in order to eliminate the errors connected with the oxidation of copper sulphide in the course of determining the concentration of sodium sulphide.

The relative concentration of CuS was determined photometrically using the KFK-2MP photocolorimeter within the spectral range of 400−430 nm with a violet light filter in the cells with the optical path length $l = 10$ mm.

RESULTS AND DISCUSSION

Kinetics of sodium sulphide adsorption onto dispersed zinc oxide

Sodium sulphide is adsorbed onto zinc oxide. At the initial phase (less than 2000 s) the kinetics of this process obeys the equation of the first kinetic order (Fig. 2), regardless of the initial concentration of the sodium sulphide. The observed adsorption rate constant (k_{sorb}) decreases in a linear manner with increasing the initial concentration of sulphide. Decreasing the adsorption rate with increasing the concentration of sodium sulphide, could be, to all appearance, connected with decreasing the fraction of zinc oxide surface that can participate in the adsorption of sodium sulphide.

In the theory of monomolecular Langmuir adsorption it is assumed that the adsorption rate is expressed by the following equation

$v = \alpha\mu(1 - \theta)$

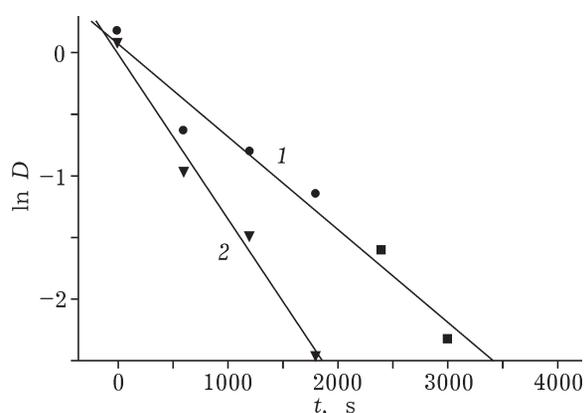where μ is the number of substrate molecules, impinging on the unit area within unit time (1 s);

Fig. 2. ln D value depending on time for the sorption (1) and for the photocatalytic oxidation (2) of Na$_2$S on zinc oxide. The initial concentration of Na$_2$S is equal to 12.92 mmol/L.

α is the fraction of molecules adsorbed during the collision with the surface (accommodation coefficient); θ is the fraction of the surface covered by the adsorbed molecules by the time moment t.

In case of autoinhibition, the observed adsorption rate constant could be a variable that decreases depending on time as the adsorption of sodium sulphide proceeds, but this is not observed in the experiments (see Fig. 2). At the time values <3000 s, an almost linear relationship between ln D and time is inherent in all the initial concentrations of sodium sulphide (see Fig. 2). Consequently, the rate constant does not change in the course of the substrate adsorption, whereas the substrate concentration could decrease to a great extent reduced due to the adsorption. For example, for the process that is described in Fig. 2, the concentration of sodium sulphide in the solution exhibits a more than three-fold decrease within 30 min after the addition of zinc oxide to the solution of sodium sulphide.

Since the adsorption of sodium sulphide the rate constant of adsorption remains constant, so we could assume that during the sodium sulphide adsorption process, the fraction $(1 - \theta)$ of zinc oxide surface unoccupied by the substrate does not change, too. To all appearance, this could be connected with the fact that the adsorption of sodium sulphide occurs in two stages. At the first stage, the substrate is adsorbed onto the zinc oxide surface to form a monomolecular layer of sodium sulphide. Further, there occurs a polymolecular (multilayer) adsorption of sodium sulphide onto zinc oxide when sodium sulphide is adsorbed onto a previously adsorbed substrate layer rather than onto a free surface. As a consequence, the fraction of zinc oxide surface not occupied by sodium sulphide does not change in the course of the adsorption process. From the energetic standpoint, the polymolecular adsorption of the salt onto the already adsorbed layer of sodium sulphide is more efficient as compared to the adsorption onto zinc oxide.

In case of the multimolecular adsorption of salts, is the Coulomb attraction between the molecular dipoles of salts is of great importance, whereby the formation of polymolecular adsorbed layer occurs. Because of the multilayer adsorption the rate constant is almost unchanged in the course of the substrate ad-

sorption, because the surface area of the sorbent occupied by sodium sulphide, remains constant to a considerable extent during the adsorption of sodium sulphide. In moving to systems with a greater initial concentration of sodium sulphide sulphide the surface occupied by adsorbed sodium sulphide expands and, accordingly, the constant of the adsorption rate decreases.

Kinetics photocatalytic oxidation
of sodium sulphide on zinc oxide

The irradiation of an aqueous suspension of finely dispersed zinc oxide in the presence of sodium sulphide results in the oxidation of the latter in a photocatalytic process with the formation of sulphur, and, to all appearance, the products of a deeper oxidation. Thus, UV irradiation can be used in order to remove soluble sulphides from aqueous solutions. The long irradiation of sodium sulphide solution without zinc oxide with UV light mentioned above the concentration of Na_2S in the solution decreases.

The specificity of the photocatalytic system is the fact that sorption is relatively fast and profound, in comparison with, for example, the case of the photocatalytic conversion of dyes and dichromate ions on TiO_2 [8, 12]. Upon reaching the sorption equilibrium, the residual concentration of sulphide ions approaches the sensitivity limit of a spectrophotometer, and the study of the photocatalytic process kinetics becomes impossible. For this reason, in this work we did not perform any pre-adsorption of the substrate, whereas the irradiation was started immediately after the preparation of the reaction mixture. Thus, the adsorption and photocatalytic processes run in parallel, whereas the kinetic curves obtained actually reflect general decrease in the concentration of sulphide ions in solution as a result of both processes.

The kinetics of photocatalytic conversion of sulphide on zinc oxide obeys the first order kinetic equation (see Fig. 2). The photocatalytic reaction rate constant measured according to a decrease of sulphide concentration in solution exceeds the rate constant of adsorption (as measured in an independent dark experiment), although it is close in value to the latter (see Fig. 2). This could be explained by the fact that the pho-

tocatalytic stage competes with the dissociation of the S^{2-} and zinc oxide sorption complex:

$$S^{2-} + ZnO \rightleftarrows S^{2-}...ZnO \xrightarrow{h\nu} Product$$
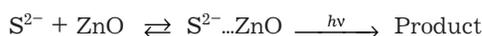
True rate constants inherent in the photocatalytic process, determined as the difference between the observed rate constants of the photocatalytic process and the adsorption rate constant almost linearly depend on the initial concentration of sodium sulphide solution.

The observed rate constant of sodium sulphide conversion in a solution upon irradiation with UV light, that is equal to the sum of the rate constant of adsorption and the rate constant of the "true" photocatalytic process, decreases with increasing the concentration of sodium sulphide in the solution. In a similar manner, the photocatalytic component of this process, too, which is equal to the difference between the rate constant of the overall process and the adsorption rate constant decreases (Fig. 3). In both cases, there is almost linear dependence of the rate constant on the concentration of sulphide. Decreasing the rate constant of the photocatalytic process with increasing the initial concentrations of sodium sulphide, according to [12], is caused by the photocatalytic autoinhibition process. The authors of [12] first revealed that in the case of an initially low concentration of safranin the photocatalytic safranin reduction rate constant exhibits an increase with increasing the safranin concentration with further decreasing. In the case of potassium dichromate, there was no
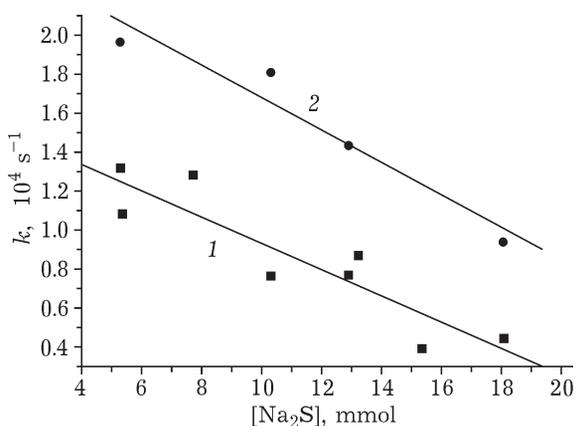

Fig. 3. Sorption rate constants (*1*) and the rate constant of sodium sulphide photocatalytic oxidation (*2*) depending on the initial concentration of sodium sulphide in the reaction mixture.
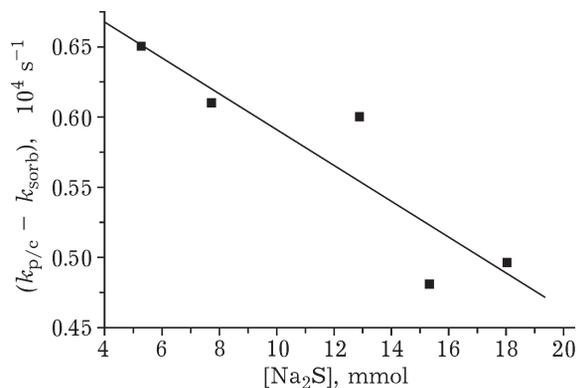
Fig. 4. Rate constant of sodium sulphide consumption in the photocatalytic process $k_{p/c} - k_{sorb}$ depending on the concentration of sodium sulphide. The initial concentration of sodium sulphide $18.09 \cdot 10^{-3}$ mol/L.

initial increase in rate constant observed with increasing the concentration thereof. The decrease of constant rate only with the increase of the substrate concentration is observed both for this system and the photocatalytic oxidation of sodium sulphide.

Undoubtedly, the phenomenon of autoinhibition is due to the sorption of the substrate by a photocatalyst. The fact is that in the course of the sorption of sodium sulphide onto the surface of zinc oxide, a part of zinc oxide surface becomes inaccessible, which makes difficult both the sorption and the photocatalytic process. It is quite possible that the sulphur formed in the course of the photocatalytic oxidation of S^{2-} anions also has the inhibitory effect. Figure 2 shows that at $t < 2000$ the ln D almost linearly dependence on time, that characterizes the overall process, is observed.

There are contradictory data in the literature concerning the role of adsorption in photocatalytic processes. For example, the authors of [14, 15] observed a correlation between photocatalytic reaction rates and the values of sorption. However, it is known [16] that rhodamine 6G is rapidly destroyed in the photocatalytic processes, but it is not adsorbed onto titanium dioxide. The data presented in Fig. 4 demonstrate a correlation between the rate constant of the photocatalytic oxidation of sodium sulphide and the constant of its adsorption onto ZnO (correlation coefficient 0.915). Thus, sodium sulphide adsorption represents a stage required for the photocatalytic oxidation of the

mentioned substrate. On the other hand, decreasing the concentration of sulphide could not be explained by the only sorption, which follows from the kinetic dependences for dark sorption and photocatalysis.

The detailed analysis of products of oxidation of sulphide at the photocatalysis on ZnO was not included in the objectives of this investigation, primarily owing to the fact that the probable primary product that is elementary sulphur can be quite difficult to separate from zinc oxide. Nevertheless, additional experiments allow to judge about some products: after the end of the photocatalytic process, the reaction mixture was separated from the precipitate (ZnO and, possibly, sulphur), whereas the supernatant was precipitated using barium chloride. The precipitate formed upon acidification with nitric acid dissolved partially with a gas evolution, which indicates the presence of sulphate (a part of precipitate, insoluble in the acid), thiosulphate (decomposing, as it is well known, with the evolution of sulphur dioxide) and, probably sulphite.

CONCLUSIONS

1. A method for the photometric determination of the concentration of sulphide anion in aqueous solutions has been modified, basing on the formation of stabilized nanosized copper sulphide that exhibits absorption from UV to IR range.

2. Sodium sulphide adsorption onto zinc oxide obeys the first order kinetic equation, therewith the observed adsorption rate constant depends on the initial sulphide concentration (decreasing in a linear manner with increasing the sulphide concentration), but remains really constant (within experimental error) in each experiment. Thus, at all the initial concentrations of sodium sulphide, ln D depends on time in an almost linear manner. This indicates that the process of substrate adsorption substrate does not affect the rate constant.

3. The irradiation of the aqueous suspension of finely dispersed zinc oxide in the presence of sodium sulphide results in the oxidation of the latter with the formation of sulphur and the products of more profound oxidation. The rate constant of sodium sulphide

photocatalytic conversion decreases with increasing the initial concentrations sodium sulphide. The mentioned decrease in the rate constant represents a manifestation of photocatalytic process autoinhibition.

4. A correlation between the rate constant of sodium sulphide photocatalytic oxidation and the constant of adsorption thereof onto ZnO has been revealed, which indicates that the adsorption of the substrate is a necessary stage in the photocatalytic oxidation of sodium sulphide.

Acknowledgement

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