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PROCESSES AND EQUIPMENT OF CHEMICAL INDUSTRY

Liquid-Phase Oxidation of Hydrogen Sulfide in Centrifugal Bubbling Apparatus

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Abstract—Liquid-phase oxidation of H_2S in centrifugal-bubbling apparatus in the presence of catalysts [manganese(II) chloride, cobalt phthalocyanine disulfonic acid, and a catalytic system including cobalt phthalocyanine disulfonic acid and $MnCl_2$] was studied.

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Sulfides, and hydrogen sulfide in particular, widely occur in nature, being present in water of many natural mineral springs and in volcanic gases, and are obtained in production of oil and natural gas and in mining of coal and ores of heavy and nonferrous metals. Sulfides (in particular, H_2S) are formed in anaerobic decomposition of natural sulfur-containing organic substances, fungicides, pesticides, and fertilizers and are discharged in large amounts into the natural environment with wastewater from plants of pulp-and-paper, oil-refining, chemical, and tanning industries.

The content of sulfides in wastewater formed in chrome tanning at tanneries may be as high as 1000 mg l^{-1}. One of methods for their detoxication is oxidation to nontoxic sulfur-containing compounds with atmospheric oxygen in aqueous–alkaline solutions, which is commonly performed in bubble columns. In this case, the oxidation of sulfides is rather slow even in the presence of highly active catalysts because of the low rate of oxygen dissolution in a solution. Mn(II) compounds are most frequently used as catalysts. For example, wastewater from tanneries, with an initial concentration of sulfides in the range 700–1400 mg l^{-1}, are oxidized to a residual content of 0.5–1.5 mg l^{-1} in bubble columns in the course of 6–12 h. In this case, the specific air expenditure is 30–35 $m^3 m^{-3}$ [1]. The considerable expenditure of the catalyst (Mn^{2+}/HS^- mass ratio may be as high as 0.4–0.5) is due both to the high concentration of sulfides and to the presence in wastewater of a large amount of suspended and colloidal substances. These substances adsorb on their surface insoluble manganese compounds formed in oxidation of sulfides and thereby make lower the activity of the catalyst.

The oxidation of sulfides can be intensified and the expenditure of the catalyst can be lowered by changing the processing technology of spent solutions and wastewater.

Because more than a half of all the contaminants and more than 90% of sulfides (COD 15–35 g l^{-1}, HS^- 4–6 g l^{-1}, pH 8–12) is discharged into the wastewater disposal system from the liming process, it is advisable to collect and purify separately spent solutions and the most concentrated wastewater. The suspended and colloidal substances are removed by coagulation precipitation from a liming wastewater acidified to pH 4–4.5, and hydrogen sulfide formed in acidification is removed by bubbling of air through the solution. Then, H_2S-containing air is purified to remove H_2S in a centrifugal-bubbling apparatus (CBA) with a circulating aqueous–alkaline solution containing a dissolved catalyst, with simultaneous catalytic oxidation of the caught hydrogen sulfide to nontoxic products, sulfates and thiosulfates.

As catalysts were suggested Mn(II) salts [1], frequently used at tanneries, and also cobalt phthalocyanine disulfonic acid (CPDA) and a catalytic system constituted by a mixture of a Mn(II) salt and CPDA [2].

In an absorbing aqueous solution containing sodium carbonate, the CPDA catalyst is converted to a disodium cobalt phthalocyanine disulfonate, $\{CoPc(SO_3Na)_2\}$, a macrocyclic complex having the form of a planar symmetric 18-π-electron aromatic macroring with a cobalt atom situated in the central cavity and retained there by chemical bonds formed by unoccupied orbitals of the cobalt atom and lone-pair electrons of central nitrogen atoms [3]. In complexes of this kind, the metal plays the role of a redox center.

Previously, an attempt has been made to use CBA for oxidation with atmospheric oxygen of aqueous–alkaline solutions of sodium sulfide in the presence of a catalyst, tetrasodium cobalt phthalocyanine tetrasulfonate, $CoPc(SO_3Na)_4$ [4]. With CBA, a sharp increase in the oxidation rate of hydrosulfide ions by oxygen was observed, compared with oxidation of the same aqueous–alkaline solution in a rocking static "duck" reactor and in a bubbling reactor. According to [4], HS^- ions are oxidized by oxygen in both the "duck" and bubbling reactors under diffusion control. The product formed in CBA in oxidation of aqueous–alkaline solutions of hydrogen sulfide in the presence of $CoPc(SO_3Na)_4$ is sulfur. It should be noted that oxidation of sulfides in CBA to pure sulfur has a significant disadvantage: in prolonged operation, finely dispersed sulfur that accumulated in the absorbing solution settles on the walls of the swirling chamber of the reactor, altering the operation parameters of the apparatus and thus making its work impossible. Therefore, hydrogen sulfide removed from a spent liming solution was oxidized in CBA so as to prevent formation of elemental sulfur and obtain soluble salts, thiosulfates and sulfates, as a result of oxidation.

In weakly alkaline and alkaline aqueous solutions, oxidation of soluble sulfides by atmospheric oxygen may occur to give S^0, $S_2O_3^{2-}$, SO_3^{2-}, and SO_4^{2-}. The extent and rate of oxidation depend on the pH value, concentration ratio of HS^- ions and dissolved oxygen, temperature, and ionic strength of the solutions.

The oxidation of HS^- ions is strongly affected by the choice of a catalyst. The liquid-phase oxidation of H_2S by atmospheric oxygen in the presence of soluble salts of Mn(II) occurs at a high rate to give mainly $S_2O_3^{2-}$ and SO_4^{2-} ions. It should be noted that, at *Eh* of 0.3–0.4 V and pH 8–12, Mn(II) is rather easily oxidized to MnO_2 [5], whose activity in oxidation of sulfur compounds is substantially lower. In addition, it is to be taken into account that soluble salts of manganese are unstable in the presence of hydrosulfide ions and can coagulate to give manganese sulfides.

It has been found in an analysis of oxidation of HS^- ions with dissolved oxygen in the presence of cobalt phthalocyanine sulfonates $\{CoPc(SO_3Na)_n\}$ that there exist various redox forms of $CoPc(SO_3Na)_n$, containing cobalt in oxidation states I–III [6].

In a strongly alkaline medium (pH ≥ 11), hydrosulfide ions are oxidized with oxygen by the mechanism [7, 8] involving formation of a paramagnetic superoxocomplex $[Co(III)Pc(SO_3Na)_n \cdot O_2^-]$ and its subsequent interaction with the substrate:

$$[Co(III)Pc(SO_3Na)_n \cdot O_2^-] + HS^- \rightarrow [HS^- \cdot Co(III)Pc(SO_3Na)_n \cdot O_2^-]. \quad (1)$$

Further, this complex decomposes:

$$[HS^- \cdot Co(III)Pc(SO_3Na)_n \cdot O_2^-] \rightarrow Co(II)Pc(SO_3Na)_n + HSO_2^-, \quad (2)$$

and then HSO_2^- undergoes noncatalytic transformations to give thiosulfate, sulfite, and sulfate ions.

At pH 7.3–8.0, sulfides contained in a solution as hydrosulfide ions are oxidized with oxygen in the presence of $CoPc(SO_3Na)_n$ at a high rate mostly by the polysulfide mechanism [6]. The main oxidation product is elemental sulfur. HS^- ions are oxidized at the expense of redox transitions $Co(II)Pc(SO_3Na)_n \rightleftarrows Co(I)Pc(SO_3Na)_n$.

A transition from one oxidation mechanism of sulfides to another can occur upon a comparatively slight change in the reaction conditions (pH value; concentration ratio of hydrosulfides and dissolved O_2; catalyst concentration; presence in a solution of hydrosulfide oxidation products that favor or hinder accumulation of polysulfides in the reaction mixture [6, 9]). Changing the reaction conditions and choosing cobalt phthalocyanine disulfonate as the most appropriate catalyst make it possible to achieve the required hydrosulfide oxidation intensity and composition of the products obtained.

EXPERIMENTAL

Figure 1 schematically shows a laboratory rig for studying the kinetics of liquid-phase catalytic oxidation of easily volatile compounds, with hydrogen sulfide as example. A Na_2S solution or a spent liming solution is delivered by a pump from tank *1* to bubbling column *2*, to be acidified there by an H_2SO_4

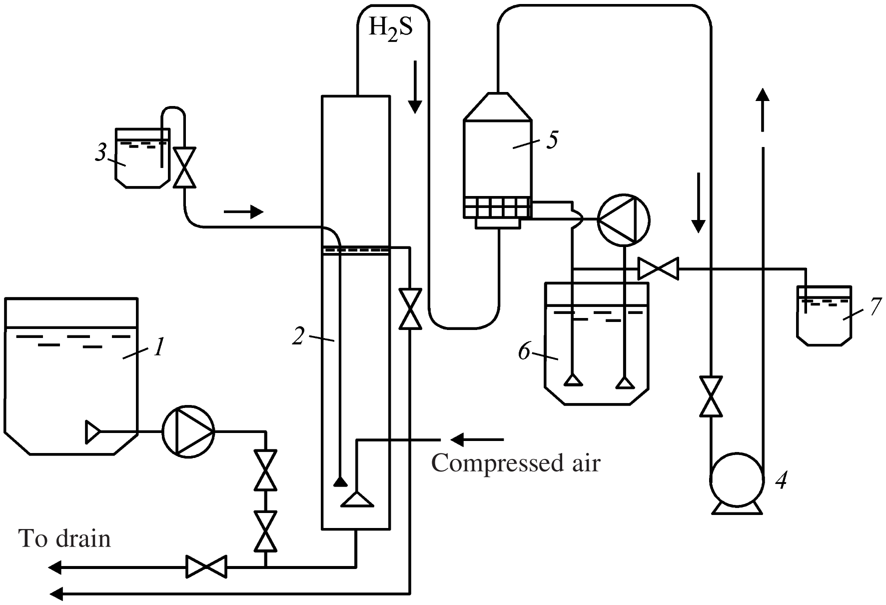

Fig. 1. Laboratory rig for liquid-phase oxidation of volatile compounds in CBA: (*1*) tank with an absorbing solution, (*2*) bubbling column, (*3*) vessel with H_2SO_4, (*4*) ventilator, (*5*) CBA, (*6*) vessel with an absorbing solution, and (*7*) vessel with a catalyst solution.

solution from vessel *3*. The forming hydrogen sulfide is removed from the column and is supplied, together with air, by sucking-in ventilator *4* into CBA *5* and is absorbed there by the circulating aqueous–alkaline solution *6* and rapidly oxidized upon delivery of the catalyst from vessel *7*.

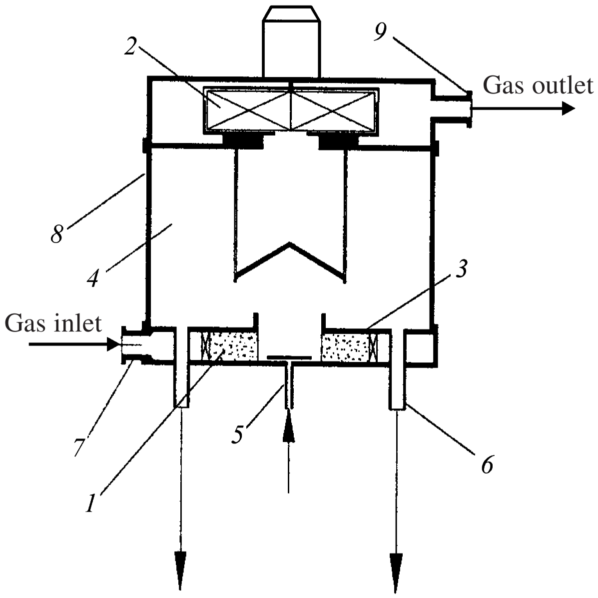

Fig. 2. Schematic of a centrifugal-bubbling apparatus: (*1*) rotating gas–liquid layer, (*2*) ventilator, (*3*) swirler, (*4*) separation zone, (*5, 6*) pipes for liquid delivery and discharge, (*7*) gas supply pipe, (*8*) cylindrical case, and (*9*) gas discharge pipe.

The operation principle of CBA (Fig. 2) is based on passing a gas through a rotating liquid layer *1*, which is retained within the swirling chamber by the gas flow. After ventilator *2* is switched on, gas passes through swirler slits, acquires a rotary motion, and involves the liquid in this motion. As a result, a gas–liquid layer with a developed and instantaneously renewed phase contact layer is formed within the apparatus. The gas and liquid are delivered from the swirling chamber into separator *4* and then discharged from the reactor. The air expenditure in the CBA is 100 Sm^3 h^{-1} (Sm^3 is m^3 under normal conditions). The circulation rate of the absorbing solution in the CBA is 50 dm^3 h^{-1}.

In the stage of desorption, in contact of an acidified spent liming solution with air, hydrogen sulfide is virtually not oxidized at all. This occurs because the rate of noncatalytic oxidation of dissolved hydrogen sulfide is very low. The caught hydrogen sulfide is oxidized at a very high rate in CBA, because the absorbing solution contains catalysts that can diminish the time of oxidation of the forming hydrosulfide ions at room temperature and atmospheric pressure from several hours or even days to several seconds.

Hydrogen sulfide mixed with air was delivered into the CBA at rates of 2.8×10^{-2}, 5.3×10^{-2}, and 1×10^{-1} mol min^{-1} counting on H_2S. The presence of hydrosulfide ions in the solution discharged from the CBA and of hydrogen sulfide in the purified air at

Results of experiments on catching of hydrogen sulfide and its oxidation in CBA. Flow rate of the gas mixture 100 $Sm^3 h^{-1}$; solution circulation rate 50 $l h^{-1}$; H_2S concentration in purified air less than 5 $mg m^{-3}$; no HS^- ions in the absorbing solution discharged from CBA. T = 25°C, P = 0.1 MPa

Run no.	Content of H_2S in gas mixture, vol %	Catalyst	$H_2S/MnCl_2$, mol/mol	Installation operation time,** min	pH of absorbing solution	Amount of caught H_2S, mol (g)
1	0.04	$MnCl_2$	86.83	72	11.5	2.16 (73.4)
2	0.07	$MnCl_2$	86.83	48	11.5	2.41 (81.9)
3	0.07	$MnCl_2$	17.36	78	11.5	3.96 (134.6)
4	0.14	$MnCl_2$	86.83	24	11.5	2.41 (81.9)
5	0.14	$MnCl_2$	17.36	43	11.5	4.41 (149.9)
6	0.15	$CoPc(SO_3Na)_2$		24	8.2–8.3	2.71 (92.1)
7	0.15	$MnCl_2$, $CoPc(SO_3Na)_2$		36	8.2–8.3	4.05 (137.7)
8	0.15	$MnCl_2$ $CoPc(SO_3Na)_2$	86.83	40	8.2–8.3	4.59 (156.1)

* Run no. 6: content of $CoPc(SO_3Na)_2$ in the absorbing solution 1.28 × 10^{-6} M (1.0 mg dm^{-3}); run no. 7: $MnCl_2$ content 1.28 × 10^{-6} M (0.16 mg dm^{-3}), $CoPc(SO_3Na)_2$ content 1.28 × 10^{-6} M (1.00 mg dm^{-3}); run no. 8: $CoPc(SO_3Na)_2$ content 1.28 × 10^{-6} M (1.00 mg dm^{-3}), $MnCl_2$ is batched into solution simultaneously with delivery of the gas mixture being purified.

** Operation time of the installation until appearance (breakthrough) of HS^- in the absorbing solution.

the CBA outlet was checked using lead indicator paper. The concentrations of hydrosulfide, thiosulfate, and sulfite ions were found by iodometric titration [10]. The concentration of sulfate ions in this absorbing solution was determined by complexometry [10] and gravimetry [11]. UV/Vis spectra of absorbing solutions containing CPDA and the catalytic system CPDA + $MnCl_2$ were recorded with an Agilent 8453 spectrophotometer.

An aqueous solution containing sodium carbonate, into which catalysts were introduced, served as an absorbing solution. In the case of a CPDA catalyst and a catalytic system containing CPDA and $MnCl_2$, a 0.001 M aqueous solution of Na_2CO_3 (pH 8.2–8.3) was used. With $MnCl_2$ serving as a catalyst, a 0.1 M Na_2CO_3 solution was used (pH 11.5).

The results of the experiments performed demonstrated (see table) that acidification of sulfide-containing wastewater to pH 4–4.5 and subsequent evaporation of H_2S in CBA enables virtually complete removal of sulfides from spent liming solutions. Hydrogen sulfide is completely caught by the absorbing solution and oxidized (oxidation of HS^- ions) in this apparatus at a high rate and low catalyst expenditure.

The main products formed in catalytic oxidation of hydrosulfide ions by atmospheric oxygen were sodium sulfate and thiosulfate.

The experiments demonstrated that the time during which the $MnCl_2$ catalyst remains in the working state (until appearance of HS^- ions) strongly depends on the method of its introduction into the absorbing solution. In the case of fractional batching of $MnCl_2$ into the reaction zone of the CBA, the amount of oxidized H_2S is 28–56% higher than that in a single-portion introduction of the same amount of $MnCl_2$ into the absorbing solution before the beginning of H_2S delivery into the CBA. Apparently, if the whole amount of the catalyst is introduced in a single portion, excess Mn^{2+} favors fast formation of a precipitate of low-active MnO_2.

The UV/Vis spectra of CPDA and Mn(II) solutions (Fig. 3) show that no chemical interaction occurs between these substances.

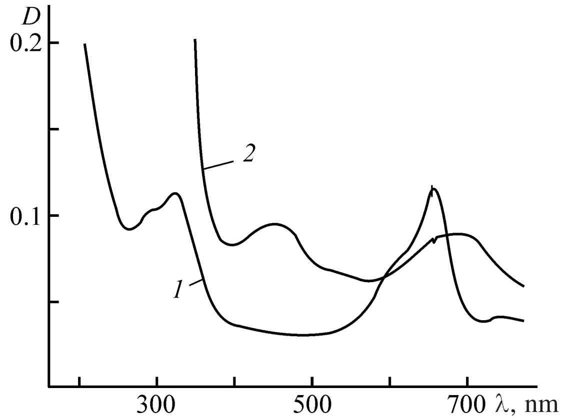

Fig. 3. UV/Vis spectra of CPDA. (D) Optical density and (λ) wavelength. Solution: (*1*) absorbing with CPDA + $MnCl_2$, 1.28 × 10^{-6} M each, after run no. 8 (see table); (*2*) Na_2S (0.45 M) with CPDA (0.86 × 10^{-6} M) after 60 min of oxidation in a bubbling column.

The spectrum of a CPDA solution obtained upon oxidation of H_2S in a CBA in run no. 8 contains two strong absorption bands at 655 and 320 nm, associated with π–π^* transitions from the ground state to the first excited singlet state. The additional bands appearing in the absorption spectrum of cobalt phthalocyanine disulfonate can be attributed to metal $\rightleftarrows$ ligand charge transfer or to appearance of weak π bonds between molecules of the complex to give dimers [12]. Oxidation of a sodium sulfide solution in the bubbling column in the presence of CPDA gives rise to a weak band at 450 nm in the absorption spectrum, associated with Co(I) $\rightleftarrows$ Co(II) transitions [6]. In oxidation of caught H_2S by atmospheric oxygen in a CBA under conditions of a developed phase contact area in a CPDA-containing absorbing solution both with and without $MnCl_2$, no absorption band at 450 nm is observed in the absorption spectrum of CPDA. In this case, the intensity of the absorption band at 320 nm, associated with Co(II) $\rightleftarrows$ Co(III) transitions, sharply increases.

CONCLUSIONS

(1) Liquid-phase oxidation of H_2S in centrifugal-bubbling apparatus in the presence of catalysts ($MnCl_2$, cobalt phthalocyanine disulfonic acid, and a catalytic system consisting of cobalt phthalocyanine disulfonic acid and $MnCl_2$) occurs at a high rate. The oxidation of hydrosulfide ions is not controlled by dissolution of oxygen in the contacting absorbing solution because of the large, and rapidly changing, area of the gas–liquid mass-exchange surface.

(2) Sulfates are the main oxidation products.

(3) It is recommended to use these catalysts in oxidation of hydrogen sulfide formed in acidified liming solutions from plants manufacturing half-finished leather articles by chrome tanning.

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REFERENCES

1. Laskov, Yu.M., Fedorovskaya, T.G., and Zhmakov, G.N., *Ochistka stochnykh vod predpriyatii kozhevennoi i mekhovoi promyshlennosti* (Purification of Wastewater from Plants of Tanning and Fur Industries), Moscow: Legkaya i Pishchevaya Prom–st., 1984.
2. Faddeenkova, G.A. and Kundo, N.N., *Zh. Prikl. Khim.*, 2003, vol. 76, no. 12, pp. 1995–1999.
3. Berezin, B.D., *Koordinatsionnye soedineniya porfirinov i ftalotsianinov* (Coordination Compounds of Porphyrins and Phthalocyanines), Moscow: Nauka, 1978.
4. Zavarukhin, S.G., Kuvshinov, G.G., Gogina, L.V., and Kundo, N.N., *Khim. Prom–st.*, 1999, no. 2, pp. 26–30.
5. Pourbaix, M., Zhang, H.M, and Yang, X.Z., *Atlas of Chemical and Electrochemical Equilibria in the Presence of a Gaseous Phase*, Brussels: CEBELCOR, 1996.
6. Kundo, N.N. and Keier, N.P., *Kinet. Katal.*, 1970, vol. 11, no. 1, pp. 91–99.
7. Hoffmann, M.R., *Environ. Sci. Technol.* 1991, vol. 25, pp. 1153–1162.
8. Abel, E.W., *Chem. Commun.*, 1971, no. 9, pp. 449–450.
9. Kundo, N.N. and Faddeenkova, G.A., *Khim. Inter. Ustoich. Razv.*, 2003, no. 11, pp. 619–625.
10. Lur'e, Yu.Yu., *Analiticheskaya khimiya promyshlennykh stochnykh vod* (Analytical Chemistry of Industrial Wastewater), Moscow: Khimiya, 1984.
11. Privalov, V.E., Khlopkova, L.I., and Popkov, G.I., *Analiz stochnykh vod koksokhimicheskikh zavodov* (Analysis of Wastewater from Coke-Chemical Plants), Moscow: Metallurgiya, 1976.
12. Hanack, M., Heckmann, H., and Polley, R., in *Methoden der Organischen Chemie* (Houben–Weyl), Stuttgart: Thieme, 1997, 4th ed., vol. E9d.