Chemistry for Sustainable Development **10** (2002) 291–295

Thiocyanate Oxidation by Hydrogen Peroxide Generated in Gas Diffusion Electrode in Alkaline Medium

TATIANA A. KENOVA and VASILY L. KORNIENKO

Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Ul. K. Marksa 42, Krasnoyarsk 660049 (Russia)

E-mail: chem@krsk.infotel.ru

(Received October 11, 2001; in revised form November 19, 2001)

Abstract

Results of the indirect electrochemical oxidation of thiocyanates in an alkaline medium at different current densities, with Pt anode and gas diffusion cathode generating hydrogen peroxide from oxygen in electrolyzers with cation exchange membranes and without a membrane, are reported.

INTRODUCTION

Environmental protection puts forward the necessity to search for new ecologically safe methods to purify industrial waste waters from hazardous impurities [1, 2].

The method most frequently used to dispose the wastes from gold mining industry by removing such toxic substances as cyanides, thiocyanates (rhodanides), metals in the form of cyanide complexes is chlorination. Other methods, for example treatment with a mixture of sulphur dioxide and air (INKO technology) do not allow one to dispose thiocyanates efficiently [3]. In Russia, unlike many western countries, thiocyanate content is strictly standardized; maximum permissible thiocyanate concentration practically coincides with that for cyanides accounting for 0.1 mg/l in water for household purposes and drinking.

Advantages of chlorination are accessibility and instrumentation simplicity of purification procedure, efficiency of purification from such a difficultly oxidized impurity as a thiocyanate. However, this method has also some substantial shortcomings, among which is the danger of poisoning the environment with chlorinated agents and the products of their interaction with cyanides, substantial increase of the hardness salts in waste water, and rapid corrosion wear of metal equipment.

Recently, attention to electrochemical methods of waste water treatment has increased. Along with direct decomposition of impurities at the cathode and (or) anode, their indirect oxidation by electrolysis products (O_2, O_3, H_2O_2, Cl_2) or highly reactive intermediates (HO, HO_2, O_2, ClO, Cl, H) is also possible [4, 5].

Direct oxidation of cyanides at different anode materials [6] demonstrated that this method had low efficiency for water containing less than 20 g/l CN^-. In order to dispose waste water containing small amounts of cyanides, it is more reasonable to oxidize them by electrochemically generated hypochlorite.

Depending on electrolysis conditions, electric oxidation of thiocyanates can proceed forming cyanide or cyanate ions. It is demonstrated in [3] that the solutions with high NCS^- concentration (1000–3000 mg/dm^3) can be treated electrochemically with the formation of CN^- and its subsequent isolation. At lower concentration of thiocyanate ions, they are oxidized to form less toxic CNO^-.

Destructive oxidation of cyanides and thiocyanates proceeds rather efficiently with the participation of $HO^{\cdot}$ radicals formed in the systems $Fe^{2+} - H_2O_2$, $Fe^{3+} - H_2O_2$ (Fenton and Raff systems) [7]. It should be noted that this method requires acidification to pH 2–4, which leads to the release of toxic hydrogen cyanide from solution; it is necessary to utilize it.

It is known that the radicals $HO^{\cdot}$, $HO_2^{\cdot}$ are formed in the presence of hydrogen peroxide in alkaline media at Pt, Pb/PbO_2, Sn/SnO_2 anodes; these radicals are able to destructively oxidize various organic impurities [8–10]. Since the technological solutions have pH $\geq$ 11 after the isolation of precious metals from them, it is interesting to investigate the oxidation of cyane-containing compounds under these conditions.

In the present study we report the results of investigation into thiocyanate oxidation in alkaline medium using Pt anode and gas diffusion cathode generating hydrogen peroxide from oxygen in electrolyzers with cation exchange membrane and without it.

EXPERIMENTAL

Model alkaline solutions with the initial NCS^- concentration about 1 g/l, NaOH 20 g/l were used in the investigation.

Electrolysis was performed in a cell with separation and without separation of the cathode and anode space. Cathode was gas diffusion hydrophibized electrode; platinum plate was used as anode. Ion exchange membrane MF-4SK-100 was used to separate the cathode and anode space. For electrolysis, 1 M H_2SO_4 solution was used as anolyte in the cell equipped with a membrane.

Gas diffusion electrodes were made of acetylene carbon black (A 437-E grade) with the mass fraction of hydrophobizing agent (fluoroplastics 4D) 20 % shaped as flat single-layer discs 33 mm in diameter, their total porosity being 65–66 % and thickness 0.8–0.9 mm; the procedure is described in [11]. The area of the visible frontal surface of the cathode in contact with electrolyte was 5 cm^2, the area of immersed part of platinum anode was 3.6 cm^2. Oxygen was let into the gas diffusion electrode from the reagent chamber through the back side of the electrode.

Electric oxidation of thiocyanates was carried out at the constant current of electrolysis of 250 and 500 mA in a cell with membrane, and 100, 250, 500 mA in a cell without a membrane. The volume of solution was 30 ml in all the cases. Electrolysis temperature was maintained within the range 15–20 °C.

Gas diffusion electrode was activated at a potential of −1.65 V with respect to the reference silver chloride electrode (SCE) before each experiment.

The NCS^- content of solution was determined by photometry of thiocyanate complexes of iron (III) [12], while the residual concentration of thiocyanates was determined after complete decomposition of hydrogen peroxide.

RESULTS AND DISCUSSION

It is known that the efficiency of cyanide oxidation by hydrogen peroxide depends on a series of factors, such as concentrations of the oxidizing agent and substrate, pH, temperature, presence of acceptors of oxyl radicals, *etc.* [7]. Specific consumption of H_2O_2 for thiocyanate oxidation in alkaline medium is more than 10 mol/mol NCS^- [13]. Thiocyanate oxidation products may be cyanates, ammonium ions, sulphites or sulphates, carbonates, and water [7].

For homogenous oxidation of thiocyanates in the catholyte volume, the rate of their oxidation will likely depend on the current density at the cathode, which defines hydrogen peroxide concentration at its electrosynthesis.

Thiocyanate oxidation by hydrogen peroxide generated electrochemically in gas diffusion electrode was performed in a cell with cation exchange membrane at the cathode current density of 50 and 100 mA/cm^2 (total current being 250 and 500 mA). The initial concentration of NCS^- was 1065 mg/l.

Figure 1 shows kinetic curves of thiocyanate oxidation by hydrogen peroxide generated electrochemically at current density of 50 and 100 mA/cm^2. The rate constant of the process, determined from the tangent of the slope

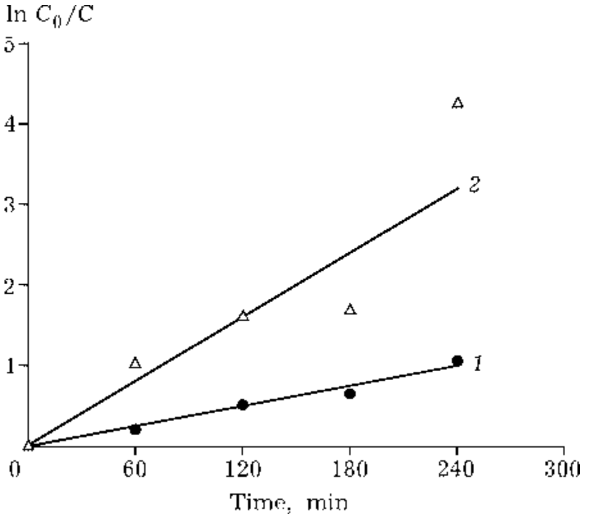

Fig. 1. Kinetic dependences of the oxidation of thiocyanates by hydrogen peroxide generated electrochemically from oxygen in alkaline medium in an electrolyzer with cation exchange membrane. *I*, mA: 250 (*1*), and 500 (*2*).

of logarithmic dependence, the residual concentration and efficiency of NCS^- oxidation are listed in Table 1.

One can see from these results that with increasing total current from 250 to 500 mA, the oxidation rate constant increases about three times. The efficiency of thiocyanate destruction for identical quantity of electricity (1 A h) was 64.7 and 80.2 %, at the current of 250 and 500 mA, respectively. This is the evidence of the dependence of NCS^- oxidation depth on HO_2^- concentration within the electrolyte, which was noted in [13, 14]. Practically complete thiocyanate oxidation (98.6 %) was observed only after electrolysis for 4 h at the current of 500 mA.

When performing the process in a cell without cation exchange membrane, along with the oxidation of NCS^- by hydrogen peroxide generated in the gas diffusion electrode, its direct oxidation at the Pt anode is also possible. Besides, the oxidation of the generated HO_2^-, as well as water or hydroxyl ions, is possible at the anode; the following reactions may occur:

$$HO_2^- \rightarrow HO_2^{\cdot} + e^- \qquad (1)$$

$$HO_2^{\cdot} \rightarrow O_2 + H^+ + e^- \qquad (2)$$

$$2H_2O \rightarrow 2HO^{\cdot} + 2H^+ + 2e^- \qquad (3)$$

$$OH^- \rightarrow HO^{\cdot} + e^- \qquad (4)$$

It is known that the perhydroxyl and hydroxyl radicals formed in the system possess substantially higher reactivity in comparison with HO_2^- ions [15]. In the absence of hydrogen peroxide in the system, the oxidation of NCS^- can proceed either at the anode or in the near-anode layer with the participation of $OH^{\cdot}$ radicals formed according to the reactions (3), (4) [9, 10] . In the case when hydrogen peroxide is added into the system, it is most probable that the substrate is oxidized both by $OH^{\cdot}$ and by $HO_2^{\cdot}$ radicals, along with direct oxidation at the anode.

In order to confirm the occurrence of a chemical reaction of the substrate with $HO_2^{\cdot}$ radicals, we performed comparative investigation of the thiocyanate oxidation kinetics in the case when HO_2^- was formed in the gas diffusion cathode and in the case of its absence. In the latter case, oxygen was not admitted into gas diffusion electrode. Electric oxidation was carried out at the current of 100,

TABLE 1

Oxidation of thiocyanates by electrothermally generated peroxide ion

Total current *I*, mA	τ, min	*q*, A · h	Residual NCS^- concentration, mg/l	Efficiency, %	*k*, 10^{-2}min^{-1}
250	60	0.25	862.6	19.0	0.42
	120	0.5	636.0	40.3	
	180	0.75	543.3	50.0	
	240	1.0	375.5	64.7	
500	60	0.5	378.6	64.5	1.4
	120	1.0	210.7	80.2	
	180	1.5	195.2	81.7	
	240	2.0	15.0	98.6	

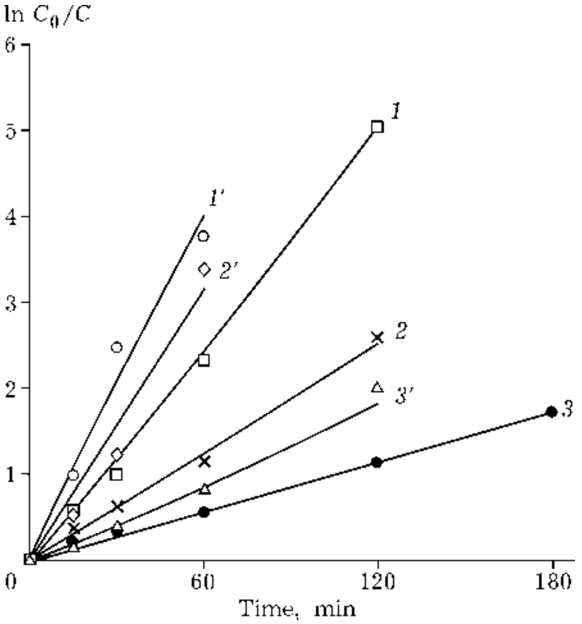

Fig. 2. Kinetic dependences of thiocyanate oxidation in an electrolyzer without a membrane. *I*, mA: 500 (*1*, *1′*), 250 (*2*, *2′*), and 100 (*3*, *3′*); *1–3* – in the absence of hydrogen peroxide; *1′–3′* – in electric synthesis of hydrogen peroxide.

250, and 500 mA. Results of these investigations are shown in Fig. 2. Calculated rate constants and efficiencies of the destruction of thiocyanates are presented in Table 2.

These data are the evidence that the increase of electrolysis current leads to the increase of thiocyanate destruction, both in the presence of peroxide ions in the system and in their absence. Since the analysis of kinetic curves indicates the first order of the reaction, the reaction rate can be represented by the following equation:

$$\omega = (k_1[\text{HO}^\cdot] + k_2[\text{HO}_2^\cdot])\,[\text{NCS}^-] = k[\text{NCS}^-] \qquad (5)$$

where k, the rate constant of anode decomposition of NCS^-, is a function of the concentrations of $\text{HO}^\cdot$ and $\text{HO}_2^\cdot$. At the increase of current, the concentrations of these particles increase causing the acceleration of thiocyanate oxidation.

TABLE 2

The anode oxidation of thiocyanates in the presence and in the absence of peroxide ions

Total current *I*, mA	τ, min	*q*, A · h	Residual NCS^- concentration, mg/l	Efficiency, %	*k*, 10^{-2} min^{-1}
			Without HO_2^-		
500	15	0.125	611.5	42	3.4
	30	0.25	398.5	62	
	60	0.50	105.4	90	
	120	1.0	7.0	99	
250	15	0.063	740.3	30	2.0
	30	0.125	570.3	46	
	60	0.25	338.6	68	
	120	0.50	81.1	92	
100	15	0.025	878.0	17	0.97
	30	0.05	769.9	27	
	60	0.10	616.7	42	
	120	0.20	348.9	67	
	180	0.30	195.5	81	
			In the presence of HO_2^-		
500	15	0.125	400.4	62	7.3
	30	0.25	42.5	96	
	60	0.50	21.5	98	
250	15	0.063	637.3	40	4.1
	30	0.125	313.5	70	
	60	0.250	36.2	97	
100	15	0.025	888.3	16	1.37
	30	0.05	723.6	31	
	60	0.10	467.3	56	
	120	0.20	76.0	93	
	180	0.30	30	99	

A deviation from the linear dependence at long electrolysis time and current of 500 mA is likely to be connected with imperfectness of the procedure of determining residual NCS^- concentration at substantial excess of hydrogen peroxide. It is known that the efficiency of the anode oxidation of NCS^- decreases substantially at increased electrolysis current because of the competing processes [16]. It is most probable that such a process occurring in alkaline medium is the discharge of water molecules of hydroxyl ions. Since the efficiency decreases only insignificantly in the case under consideration being 62–71 % after passing 0.25 A h, one can assume that $HO^\cdot$ radicals participate in thiocyanate oxidation.

The appearance of $HO_2^\cdot$ as an additional oxidizing agent leads to the increase of both rate and efficiency of thiocyanate oxidation process. After electrolysis for 30 min at the current of 500 mA, the efficiency was 96 %, while at the anode oxidation in the absence of hydrogen peroxide it was 62 %.

CONCLUSIONS

1. It is stated that the rate of indirect oxidation of thiocyanates in a cell with cation-exchange membrane is substantially lower than in the cell without membrane.

2. It is stated that the rate and efficiency of thiocyanate destruction increases noticeably in the presence of hydrogen peroxide generated from oxygen in gas diffusion electrode.

REFERENCES

1 M. B. Arkhipova, L. Ya. Tereshchenko, I. A. Martynova, Yu. M. Arkhipov, *Zhurn. prikl. khimii*, 4 (1994) 458.

2 V. V. Goncharuk, *Chemistry for Sustainable Development*, 5 (1997) 321.

3 M. A. Meretukov, A. M. Orlov, Metallurgiya blagorodnykh metallov: zarubezhny opyt, Metallurgiya, Moscow, 1991.

4 L. M. Yakimenko, G. A. Seryshev, Elekyrokhimicheskiye protsessy v khimicheskoy promyshlennosti: elektrokhimicheskiy sintez neorganicheskikh soyedineniy, Khimiya, Moscow, 1984.

5 D. M. Stanbury, *Adv. Inorg. Chem.*, 33 (1989) 69.

6 T. A. Kharlamova, G. A. Tedoradze, *Khim. prom-st'*, 2 (1981) 21.

7 B. A. Tsybikova, A. A. Ryazantsev, S. Ts. Khahkhasaeva *et al.*, *Khimiya v interesakh ustoychivogo razvitiya*, 8 (2000) 445.

8 E. Brillas, R. M. Bastida and E. Liosa, *J. Electrochem. Soc.*, 142, 6 (1995) 1733.

9 Ch. Comminellis and C. Pulgarin, *J. Appl. Electrochem.*, 21 (1991) 703.

10 O. J. Murphy, G. D. Hitchens, L. Kaba and C. E. Verotsko, *Wat. Res.*, 27 (1992) 443.

11 V. L. Kornienko, G. A. Kolyagin, Yu. V. Saltykov, *Zhurn. prikl. khimii*, 72 (1999) 353.

12 Yu. Yu. Lurie, Analiticheskaya khimiya promyshlennykh stochnykh vod, Khimiya, Moscow, 1984.

13 I. R. Wilson and G. M. Harris, *J. Am. Chem. Soc.*, 82 (1960) 4515; *Ibid.*, 83 (1961) 286.

14 M. K. Chaudhuri and N. S. Islam, *Indian J. Chem.*, 24A (1985) 447.

15 N. A. Vysotskaya, *Uspekhi khimii*, 10 (1973) 1843.

16 Yu. Yu. Lurie, V. E. Genkin, Ochistka promyshlennykh stochnykh vod, Gosstroyizdat, Moscow, 1962.