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Citation: **1772**, 040004 (2016); doi: 10.1063/1.4964563

View online: <http://dx.doi.org/10.1063/1.4964563>

View Table of Contents: <http://aip.scitation.org/toc/apc/1772/1>

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Electro-Fenton-Like Reactions of Transition Metal Ions with Electrogenerated Hydrogen Peroxide

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Abstract. We evaluated and compared the hydroxyl radical-generating ability of chromium, iron, cobalt, nickel, copper, lanthanum, and cerium ions when reacted with electrogenerated hydrogen peroxide by usage the voltammetry. There was reproduced an electro-Fenton-like reaction in electrochemical cell when metal salt added. The nature of metal ions determined the appearance and increasing of current of hydroxyl radicals cathodic reduction due to individual rate of the redox cycling of metal ions with ongoing cathodic regeneration of Fenton-active metal ions oxidation state. The approximated current magnitude growth in relation to metal ions concentration was calculated for each tested metal. It expressed in $\mu A \cdot ml \cdot \mu mol^{-1}$ and is equal to HO[•]-generating ability of metal ions. Results are usable for improvement of advanced oxidation processes (AOPs) through enhancement of exploitation of electro-Fenton-like processes with selecting metals that are more active. Besides, in accordance with concept of metal-induced hydroxyl radical stress in biological systems, the hydroxyl radical-generating ability of metal ions is equal to their pro-oxidant capacity.

INTRODUCTION

Transition metal ions-catalyzed hydrogen peroxide decomposition with generation of hydroxyl radicals HO[•], known as Fenton and Fenton-like reactions [1], has been extensively developed as advanced oxidation processes (AOPs) for removal of taste and odor compounds from aqueous media [2], for textile wastewater treatment [3], for treatment of water pollutants [4], for remediation of soils contaminated with organic compounds [5]. On the other hand, in biological systems redox-active metals such as iron and copper as well as other transition metals can undergo redox cycling reactions and produce reactive oxygen species (ROS), and one of the most damaging ROS occurring in biological systems is the hydroxyl radical formed via the Fenton reaction [6, 7].

The reaction of ferrous iron ions Fe²⁺ with hydrogen peroxide H₂O₂, generated via electrochemical technologies (by cathodic reduction of molecular dioxygen O₂), known as electro-Fenton process, applied in AOPs [8]. Lisetskij and coworkers [9] showed that voltammetry is method allowing the detection of hydroxyl radicals.

The purpose of our study was to evaluate and compare the HO[•]-generating ability of certain transition metal ions when reacted with electrogenerated hydrogen peroxide by usage the voltammetry.

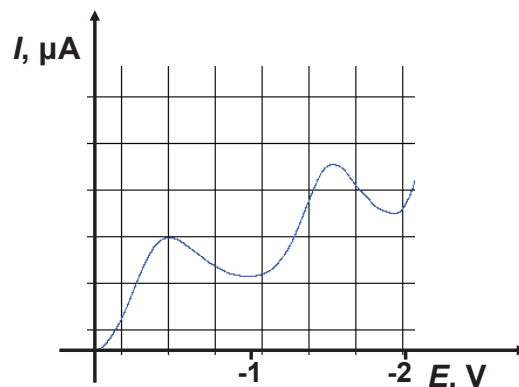
EXPERIMENTAL PART

Equipment

We used the voltammetric analyzer STA-1 (OOO "ITM", Tomsk, Russian Federation, Fig.1a) with output on digital interface. Mercury film working electrode and silver chloride reference electrode were adapted. The electrochemical cell was filled with 10 ml 0.1 mol/l Na₂SO₄. Working electrode polarization was in cathodic region from zero to -2 V with scanning speed 0.04 V/sec.



(a)

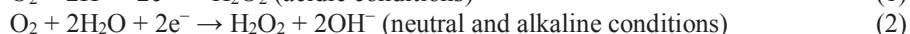
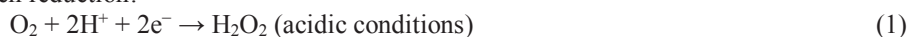


(b)

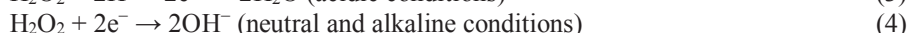
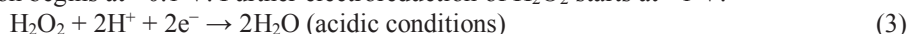
FIGURE 1. The used voltammetric analyzer (a) and voltammogram (b) of molecular dioxygen electroreduction on mercury film cathode in 0.1 mol/l Na₂SO₄

Molecular Dioxygen Cathodic Reduction

The dissolved molecular dioxygen is electrochemically reduced in two steps [10]. First, the hydrogen peroxide is generated by two-electron oxygen reduction:



Hydrogen peroxide generation begins at -0.1 V. Further electroreduction of H₂O₂ starts at -1 V:

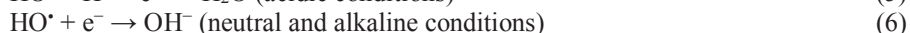
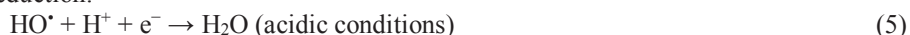


Voltammogram of oxygen reduction on mercury film electrode in 0.1 mol/l Na₂SO₄ (Fig.1b) is two-wave curve. The first wave in the voltage range from zero to -1 V corresponds to reactions (1) and (2). The second wave between -1 and -2 V is the electric current of two-electron hydrogen peroxide reduction in according with reactions (3) and (4).

Voltammetric Detection of Hydroxyl Radicals

When hydrogen peroxide added in electrochemical cell, we watched amperage increasing between -1 and -2 V. The electric current is proportional to hydrogen peroxide concentration in cell, and there are no changes in the shape of second wave of voltammetric curve (Fig.2a).

We used acidified aqueous solutions of inorganic salts of some transition metals: chromium(III) chloride CrCl₃·6H₂O, ferrous sulfate FeSO₄·7H₂O, ferric chloride FeCl₃, cobalt(II) sulfate CoSO₄·7H₂O, nickel(II) chloride NiCl₂·6H₂O, copper(II) sulfate CuSO₄·5H₂O, cerium(IV) sulfate Ce(SO₄)₂, and lanthanum(III) chloride LaCl₃·7H₂O. When the aliquot of any of them added in electrochemical cell, there was change in the shape of H₂O₂ reduction wave (Fig.2b). Regardless of metal ions nature, there was appearance of a new wave in the voltage range between -1.4 and -1.8 V with current maximum near -1.6 V. According with [9] this wave is the current of hydroxyl radicals one-electron cathodic reduction:



Foundation for Evaluation of Hydroxyl Radical-Generating Ability of Metal Ions

The nature of metal ions determines the changing of HO[•] electroreduction current magnitude. Appearance of this analytical signal as well as its further increasing depends on metal ions concentration in electrochemical cell variously for different metals (Fig.3). One can notice that ferrous iron ions Fe²⁺ and ferric iron ions Fe³⁺ produce identical results.

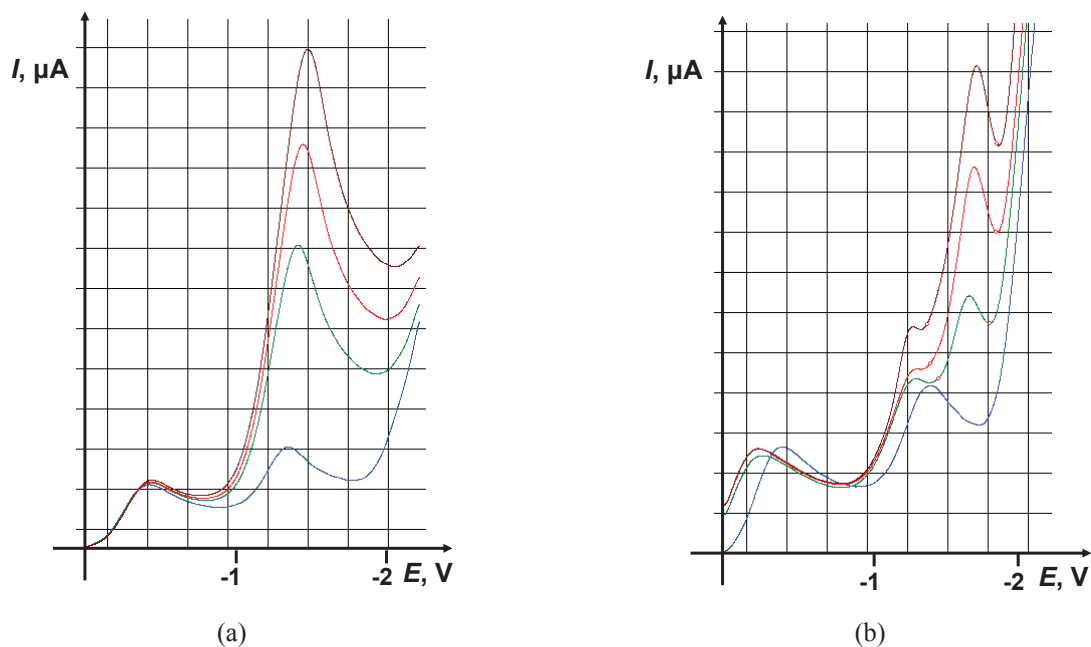


FIGURE 2. Voltammograms when hydrogen peroxide added (a) and when transition metal ions added (b)

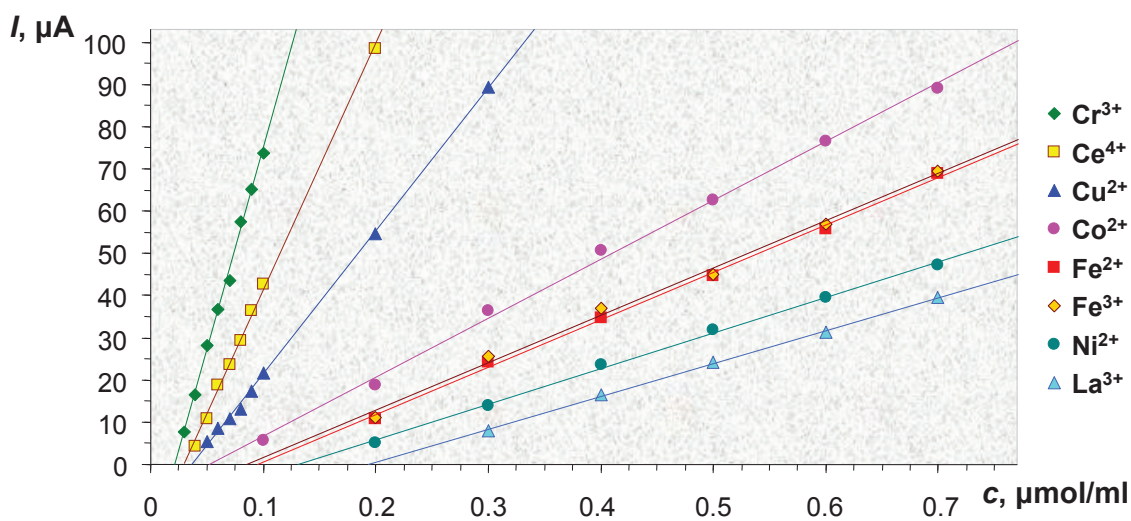
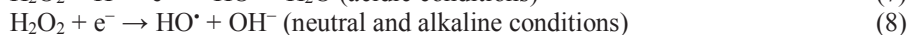


FIGURE 3. The dependence of hydroxyl radicals electroreduction current magnitude I on metal ions concentration c in electrochemical cell

RESULTS AND DISCUSSION

When transition metal salt adding in solution, the appearance of hydroxyl radicals cathodic reduction current is a result of one-electron reduction of electrogenerated hydrogen peroxide:



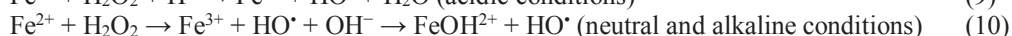
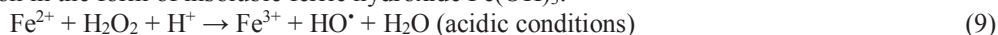
Metal ions serve as one-electron carriers. In Table 1, electron configurations of tested metals in non-ionized states (atoms) are presented.

TABLE 1. Electron configurations of non-ionized atoms of tested metals

Metal	Electron Configuration	Metal	Electron Configuration
Chromium	[Ar]3d ⁵ 4s ¹	Copper	[Ar]3d ¹⁰ 4s ¹
Iron	[Ar]3d ⁶ 4s ²	Lanthanum	[Xe]4f ⁰ 5d ¹ 6s ²
Cobalt	[Ar]3d ⁷ 4s ²	Cerium	[Xe]4f ¹ 5d ¹ 6s ²
Nickel	[Ar]3d ⁸ 4s ²		

Iron

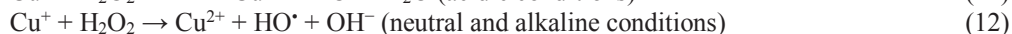
Iron in ferrous ion state Fe²⁺ is a classical Fenton catalyst [1]. Its using in AOPs requires strict acidic conditions to prevent precipitation in the form of insoluble ferric hydroxide Fe(OH)₃:



In our study the current of HO[•] reduction appeared when Fe²⁺ used as well as Fe³⁺ used, and the dynamics of analytical signal was identical (Fig.3). Iron in ferric ion state Fe³⁺ has next electron configuration: [Ar]3d⁵4s⁰. Thus, its energy 3d-sublevel is in a stable half-filled state, and Fe³⁺ itself is unable to provide an electron to hydrogen peroxide. According with [8] there is cathodic Fe²⁺ regeneration by one-electron reduction of ferric iron ions. Our results confirm this view and indicate on iron redox cycling (Fig.4a).

Copper

We used copper in divalent oxidation state Cu²⁺ (cupric), but the Fenton-active form is monovalent Cu⁺ (cuprous) ion [1]:



We proposed similar redox cycling for copper in electrochemical cell (Fig.4b).

Cobalt and Nickel

We used cobalt and nickel in divalent oxidation states. Their electron configurations are [Ar]3d⁷4s⁰ for Co²⁺ and [Ar]3d⁸4s⁰ for Ni²⁺. Thus, ions have on 3d-sublevel some transferable electrons. There is possible at least one-electron redox cycling (Fig.4c and d).

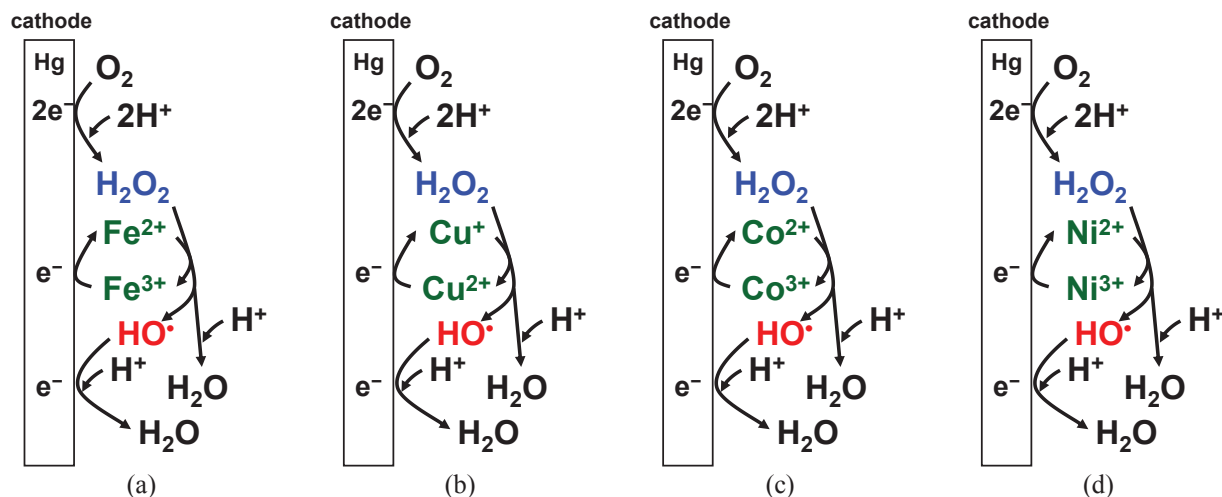


FIGURE 4. Proposed redox cycling (coloured in green) for iron (a), copper (b), cobalt (c), and nickel (d) when reacting with electrogenerated hydrogen peroxide (coloured in blue) with hydroxyl radical formation (coloured in red) in acidic conditions

Chromium

We used chromium in trivalent oxidation state Cr^{3+} with the next electron configuration: $[\text{Ar}]3d^34s^0$. There is possible three-electron oxidation to the highest hexavalent state. According with [1] each step of one-electron oxidation from Cr(III) to Cr(VI) is capable to generate HO^{\bullet} by H_2O_2 reduction. Thus, there is possible three-electron redox cycling on cathode: $\text{Cr(III)} \leftrightarrow \text{Cr(IV)} \leftrightarrow \text{Cr(V)} \leftrightarrow \text{Cr(VI)}$. This view is supported by greatest dynamics of hydroxyl radical electroreduction current in our study when chromium added in electrochemical cell (Fig.3).

Cerium and Lanthanum

According with [1] among all lanthanoids, cerium is the only element capable of activating H_2O_2 by Fenton-like mechanism. In trivalent oxidation state Ce^{3+} (cerous) it has next electron configuration: $[\text{Xe}]4f^15d^06s^0$. Cerous ion is a strong reducing agent and readily gives its electron from 4f-sublevel to hydrogen peroxide.

Since we used cerium in Fenton-inactive tetravalent (ceric) oxidation state Ce^{4+} , we proposed its cathodic reduction and redox cycling $\text{Ce}^{4+} \leftrightarrow \text{Ce}^{3+}$ similarly to other metals.

Surprisingly, we watched HO^{\bullet} reduction current when added lanthanum(III) chloride in electrochemical cell, although its dynamics was least compared to other metals tested (Fig.3). Lanthanum precedes cerium in Periodic System of Elements and has no electron on 4f-sublevel. Its usual trivalent oxidation state is stable. There are no literature data about Fenton-like activity of this metal. When looking at its electron configuration (Table 1), one can notice the distinct nature of valence 5d-electron. We proposed the one-electron cathodic reduction $\text{La}^{3+} + e^- \rightarrow \text{La}^{2+}$ ($[\text{Xe}]5d^16s^0$), Fenton-like reaction of La^{2+} with H_2O_2 , and redox cycling $\text{La}^{3+} \leftrightarrow \text{La}^{2+}$.

Evaluation and Comparison of Hydroxyl Radical-Generating Ability of Metal Ions

As illustrated in Fig.3, the correlation $I = f(c)$ is linear. In Table 2, results of regression analysis are presented.

TABLE 2. Results of regression analysis of correlation between HO^{\bullet} reduction current and tested metal ions concentration

Metal	Fenton-active state	Regression Equation	R ²	Metal	Fenton-active state	Regression Equation	R ²
Chromium	Cr^{3+}	$I = 953c - 21$	0,997	Iron	Fe^{2+}	$I = 112c - 10$	0,998
Cerium	Ce^{3+}	$I = 584c - 17$	0,998	Nickel	Ni^{2+}	$I = 84c - 11$	0,998
Copper	Cu^+	$I = 338c - 12$	0,999	Lanthanum	La^{2+}	$I = 78c - 15$	0,999
Cobalt	Co^{2+}	$I = 140c - 7$	0,997				

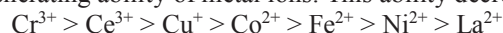
The template of regression equation is:

$$I = kc - I_0 \quad (13)$$

The coefficient $-I_0$ is the calculated coordinate of intersection of trendline with current magnitude axis. Consequently:

$$k = \frac{(I_0 + I)}{c} \quad (14)$$

Hence, coefficient k is the approximated amperage growth in relation to metal ions concentration. It expressed in $\mu\text{A}\cdot\text{ml}\cdot\mu\text{mol}^{-1}$ and is equal to HO^{\bullet} -generating ability of metal ions. This ability decreases in the next sequence:

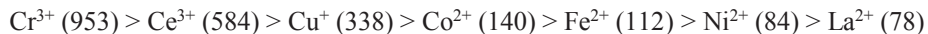


Differences in the hydroxyl radical-generating ability of tested metal ions are based on the individual kinetics of each electro-Fenton-like reaction. The nature of metal ions determines the rate of one-electron transfer from cathode to hydrogen peroxide through the redox cycling of metal ions, see equations (7) and (8), and Fig.4. As supporting date, the rate constant of cuprous-dependent one-electron H_2O_2 reduction, see equations (11) and (12), is equal to $10^4 \text{ l}\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$ [1], while the rate constant of classical (ferrous-dependent) Fenton reaction, see equations (9) and (10), is less than $10^2 \text{ l}\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$ [1]. In our study, copper-dependent hydroxyl radical formation from electrogenerated hydrogen peroxide also prevails over the HO^{\bullet} generation via the iron-dependent electro-Fenton reaction: $338 \mu\text{A}\cdot\text{ml}\cdot\mu\text{mol}^{-1}$ versus $112 \mu\text{A}\cdot\text{ml}\cdot\mu\text{mol}^{-1}$.

CONCLUSION

In our study, we evaluated and compared the hydroxyl radical-generating ability of certain transition metal ions when reacted with electrogenerated hydrogen peroxide by usage the voltammetry. Metals tested were chromium, iron, cobalt, nickel, copper, lanthanum, and cerium. There was reproduced an electro-Fenton-like reaction in electrochemical cell when metal salt added. The nature of metal ions determined the appearance and increasing of current of hydroxyl radicals cathodic reduction due to individual rate of the redox cycling of metal ions with ongoing cathodic regeneration of Fenton-active metal ions oxidation state.

The approximated amperage growth in relation to metal ions concentration was calculated for each tested metal. It expressed in $\mu A \cdot ml \cdot \mu mol^{-1}$ and is equal to HO[•]-generating ability of metal ions. This ability decreases in the next sequence of metal ions in Fenton-active oxidation state:



To our knowledge, this is the first report about electro-Fenton-like activity of lanthanum.

The results are of interest in two aspects. At one side, results are usable for improvement of advanced oxidation processes (AOPs) through enhancement of exploitation of electro-Fenton-like processes with selecting metals that are more active. The most important benefit of electrochemical technologies is uninterrupted generation of required reagents. First, there is flow and in situ formation of hydrogen peroxide by electroreduction of readily available molecular dioxygen. Second, there is ongoing regeneration of Fenton-active metal ions oxidation state.

On the other hand, results have biomedical application. In accordance with conception of metal-induced hydroxyl radical stress in biological systems, there is possible the redox cycling of metal ions in the body. The hydroxyl radical-generating ability of metal ions is equal to their pro-oxidant capacity that has mainly toxicological significance, but can find also pharmacological application, for example, in oncology.

ACKNOWLEDGMENTS

Our Best Regards to the Organizers of the XIII International Conference of Students and Young Scientists “Prospects of Fundamental Sciences Development” (Russia, Tomsk, April 26–29, 2016).

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