Galvanochemical Oxidation of 2-Chlorophenol

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Abstract

Results of the galvanochemical oxidation (GCO) of 2-chlorophenol (2-CP) in aqueous solutions at pH_{in} 3 are discussed. A more substantial decrease in the concentration of 2-CP ($C_{2\text{-CP}}$ = 1.55 10^{-4} mol/l) and intermediates, absorbing within the region 250–260 nm, during GCO in comparison with Fenton's reagent points to oxygen activation in oxidation reactions participated by the iron-carbon charge. Photoactivation of 2-CP galvanochemical oxidation promotes additional increase in the rate of its oxidation and in conversion degree. Almost complete oxidation of phenol occurs with the molar ratio H_2O_2 : 2-CP » 3 : 1, which is 22 % of the amount of H_2O_2 necessary for complete mineralization. It was established that with alkalization to pH 8.5 the intermediate products of GCO of 2-CP can undergo coagulation deposition with iron hydroxides. Such an operation allows one to decrease the time of solution treatment and the consumption of oxidizing reagent for the implementation of the technology of impurity oxidation in wastewater.

INTRODUCTION

Chlorinated phenols are toxic compounds having extremely unfavourable effect on the vital functions of animal and plant organisms exhibited even in the case of low concentrations of these compounds in water. In addition to the high toxicity, chlorophenols are the direct precursors of more dangerous compounds – polychlorinated dibenzodioxins [1].

The main source of chlorinated phenols in the environment is the plants of pulp and paper industry where these compounds are formed the stage of cellulose bleaching during lignin destruction. In addition, chlorinated phenols are intermediate products in the processes involved in the production of dyes, pesticides, herbicides, plastics, *etc.*

One may decrease the amount of chlorophenols entering the environment by developing and introducing new efficient technologies of purification of wastewater formed at the plants. Chlorophenols are removed from waste water by means of destruction using mainly ozone or hydrogen peroxide in the form of Fenton's reagent (H_2O_2 + Fe^{2+}) as oxidizers or combining these oxidizers with ultraviolet (UV) irradiation, as well as radiolysis – Advances Oxidation Processes (AOPs) [2–10]. The essence of AOPs is liquid-phase chain oxidation of organic compounds with highly reactive active oxygen particles, first of all ˙OH radicals, generated using various procedures. A special role in these processes is played by iron-containing compounds acting as the catalysts of H_2O_2 decomposition.

According to the classical notions of Haber and Weiss [3], the reaction between H_2O_2 and Fe^{2+} in aqueous solutions at pH £ 3 leads to the formation of ˙OH radicals:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (1)$$
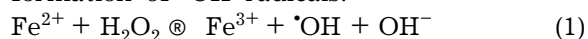
Then they attack organic molecules, H_2O_2 and Fe^{2+}.

Numerous investigations of oxidation processes participated by Fenton's reagent in the aqueous solutions of various organic compounds including phenols showed that the analysis of results should necessarily take into account the possibility of reactions between the initial organic compounds, intermediates (intermediate unstable oxidation products) and active inorganic particles like $\cdot OH$, $HO_2^{\cdot}$, $\cdot O_2^-$ *etc.*, and the reactions of iron ions with intermediates and stable products of the oxidation of organic compounds. The possible processes involve both the acceleration of the reduction of Fe^{3+} ions formed in reaction (1) and deactivation of Fe^{2+} and Fe^{3+} by means of the formation of stable organometallic complexes [11]. The concentration of free Fe^{2+} ions in solution usually decreases, which results in a rapid decrease in the rate of destruction of organic compounds, even in the presence of H_2O_2. A deficiency in Fe^{2+} is compensated for by reducing Fe^{3+} under UV irradiation of solutions [4, 5], electrochemical [6] or galvanochemical dissolution of Fe^0 [12, 13].

The galvanochemical method is based on the anode oxidation of Fe^0 into Fe^{2+} at the moment of the formation of a large number of microgalvanic pairs during the contact of iron chips with crushed coke while water and air are passed through this charge. In the presence of H_2O_2, destruction of organic compounds occurs according to the mechanism of radical chain oxidation, followed by chemisorption of a part of the formed intermediates on the surface of hydroxo compounds of Fe^{3+}, which are formed in water as a result of the oxidation of Fe^{3+} with oxygen of the air. The efficiency of the method of galvanochemical oxidation (GCO) of organic compounds exceeds the classical Fenton's procedure; however, the effect of dissolved oxygen, pH, salt content and other parameters on the reaction mechanisms has not been investigated in full.

The goal of the present work was to investigate the regularities of GCO of organic compounds for chlorinated phenol as an example, and to reveal the possibility to intensify this process using UV irradiation.
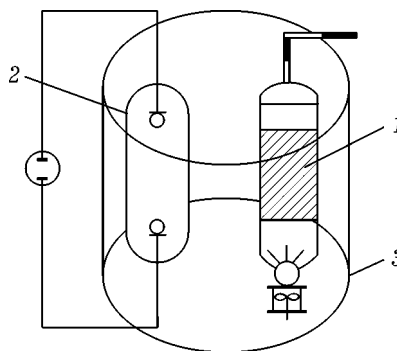

Fig. 1. Scheme of the experimental set-up for the galvanochemical treatment of solutions: *1* − reactor; *2* − DB-30 lamp; *3* − reflector.

EXPERIMENTAL

Model solutions of 2-CP were chosen as the subject of investigation. GCO processes were carried out in the reactor (Fig. 1) charged with a mixture of iron chips and coke in the presence of hydrogen peroxide (HP). The source of UV radiation in the experiments on photochemical oxidation was a quartz mercury low-pressure lamp DB-30 with the maximal radiation at 254 nm. The lamp and the reactor were placed inside a reflector made of stainless steel. The shape of the reflector and the manner in which the radiation source and the reactor were placed in the foci of ellipse provided high UV irradiation use factor [14]. The completeness of chlorophenol oxidation processes was monitored by means of spectrophotometry and gas chromatography using the Agilent 8453E UV-visible spectroscopy system and Hewlett-Packard HP 6890 gas chromatograph (electron-capture detector with a microcell, HP 5 capillary column 30 m long with the inner diameter of 0.32 mm). To eliminate the influence of iron, butyl acetate extracts of solutions were used for photometry.

RESULTS AND DISCUSSION

The electron spectra of 2-CP after oxidation with Fenton's reagent and after GCO in the reactor with iron-carbon charge for 1 and 30 min at pH_{in} 3 are shown in Fig. 2. In both cases, $C_{2\text{-}CP} = 1.55 \cdot 10^{-4}$ mol/l, $C_{HP} : C_{2\text{-}CP} \gg 3 : 1$. The concentration of Fe^{2+} in Fenton's reagent

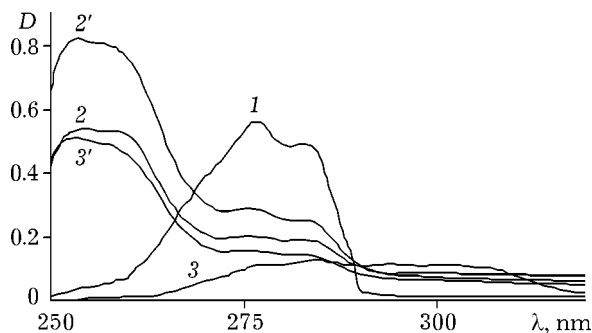Fig. 2. Electron spectra of 2-chlorophenol (*1*) after GCO for 1 (*2*) and 30 min (*3*) and oxidation with Fenton's reagent for 1 (*2'*) and 30 min (*3'*). Here and in Figs. 3−5: $C^0_{2\text{-CP}} = 1.56\ 10^{-4}$ mol/l, $C_{HP} : C_{2\text{-CP}} \gg 3 : 1$, $C_{Fe(total)} = 3.6\ 10^{-4}$ mol/l, pH_{in} 3, $t = 20\ ^{\circ}C$.

Fig. 3. Electron spectra of 2-chlorophenol (*1*) after GCO for 5 min with argon (*2*) and air (*3*) bubbled through the solution. For conditions, see Fig. 2.

corresponded to $C_{Fe\ total} = 3.6\ 10^{-4}$ mol/l as determined by the chemical analysis of the solution of 2-CP after treatment in the reactor with iron-carbon charge for 30 min. So, oxidation of 2-CP with Fenton's reagent was carried out under the conditions when the kinetics of phenol oxidation was almost independent of Fe^{2+} concentration and was determined only by the ratio $C_{HP} : C_{2\text{-CP}}$.

One can see that within 1 min we observe a decrease in the concentration of 2-CP by 48 % for oxidation with Fenton's reagent and by more than 65 % for GCO, which is evidenced by a decrease in the intensity of absorption bands at 277 nm. At the same time, bands at 250−260 and 280−290 nm appear; they correspond to the formation of quinones, diphenols and their halogenated derivatives [11, 15−17]. Since the initial H_2O_2 : 2-CP ratio was only 3 : 1, oxidation of 2-CP becomes then much slower. According to the data of spectral analysis, the major oxidation products are aromatic intermediates and final non-aromatic products the stability of which increases due to the formation of complex with Fe^{2+} and Fe^{3+}.

A more substantial decrease during GCO in the concentration of 2-CP and organic compounds absorbing within the range 250−260 nm points to the change of the mechanism of reactions participated by the iron-carbon charge. The galvanochemical oxidation of iron according to reactions
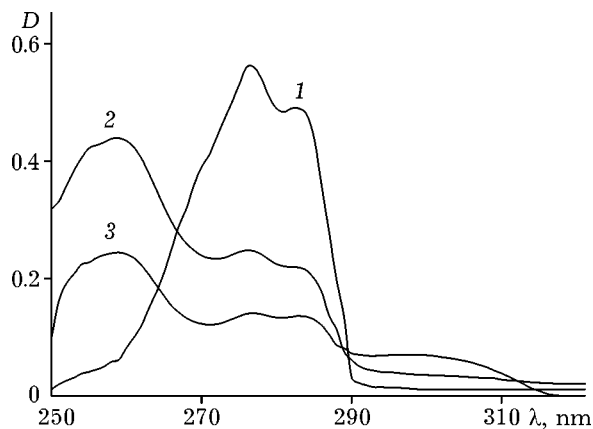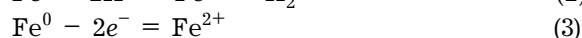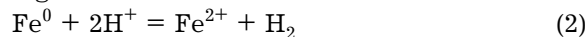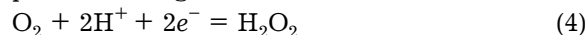
$$Fe^0 + 2H^+ = Fe^{2+} + H_2 \qquad (2)$$

$$Fe^0 - 2e^- = Fe^{2+} \qquad (3)$$

permanently compensates for a deficiency in Fe^{2+} ions in solution; two-electron reduction of oxygen at the cathode of iron − coke galvanic pair according to the reaction

$$O_2 + 2H^+ + 2e^- = H_2O_2 \qquad (4)$$

is accompanied by the synthesis of an additional amount of HP and further on, according to reaction (1), results in the formation of ·OH radicals and, as a consequence, causes complete oxidation of the intermediates (see Fig. 2). The role of oxygen in GCO reactions of organic compounds is confirmed in the experiments on the treatment of 2-CP with HP bubbling argon through the solution and the iron-carbon charge (Fig. 3).

The ratio of the concentrations of H_2O_2 and chlorophenol in the reaction mixture has a substantial effect both on the conversion degree and on the initial oxidation rate (Table 1). The degree of chlorophenol conversion increases from 30 to 100 % while $C_{HP} : C_{2\text{-CP}}$ changes from 0.58 to 5.8, which makes 45 % of the amount of HP needed for its complete mineralization according to the reaction

$$C_6H_5OCl + 13H_2O_2 \circledR 6CO_2 + 15H_2O + HCl \quad (5)$$
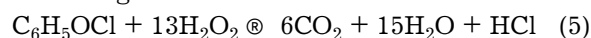
For the same $C_{HP} : C_{2\text{-CP}}$ values, the initial rate of 2-CP oxidation is higher for larger C_{HP}. However, the degree of 2-CP conversion decreases.

The intermediate products of GCO of 2-CP with H_2O_2 added can undergo coagulation deposition with ferric hydroxides. This follows from Fig. 4, which shows the electron spectra of 2-CP solution after GCO for 1 min followed by alkalization of the solution to pH 8.5 and sep-

TABLE 1

Dependence of the initial rate of 2-chlorophenol (2-CP) oxidation ($W_{2\text{-CP}}$) on the concentrations of reagents. pH_{in} 3, $t = 20\,^{\circ}C$

C^0_{HP}, 10^{-4} mol/l	$C^0_{2\text{-CP}}$, 10^{-4} mol/l	$C_{HP} : C_{2\text{-CP}}$	Conversion degree, %		$W_{2\text{-CP}}$, 10^{-4} mol/(l min)	
			GCO	GCO + UV	GCO	GCO + UV
2.26	1.55	1.40	52	77	0.4	1.0
4.5	1.55	2.90	83	100	0.6	1.2
6.75	1.55	4.35	85	100	0.8	1.5
9.0	1.55	5.80	100	100	0.8	1.6
18.0	1.55	11.6	100	100	1.5	1.6
4.5	0.77	5.84	100	100	0.5	0.8
4.5	1.55	2.90	83	100	0.6	1.2
4.5	3.8	1.18	47	50	0.8	1.6
4.5	7.7	0.58	40	45	1.2	2.1

Note. HP is hydrogen peroxide.

aration of the solid phase. Absorption bands at 250−260 disappeared; absorption at 277 nm and in the long-wavelength region of the spectrum decreased substantially, which is likely to be connected with adsorption of hydroxylated chlorophenol on the surface of ferric hydroxides. At the same time, alkalisation of 2-CP solution to pH 8.5 after 30 min GCO in the reactor with iron-carbon charge without H_2O_2 added results in precipitation of ferric hydroxides alone; the concentration of 2-CP in solution does not change.

So, the galvanochemical process of the oxidative destruction of 2-CP can be interrupted at the stage of formation of intermediates by dosing H_2O_2 added, alkalization of solution followed by coagulation deposition of the formed compounds with ferric hydroxides. Due to this, one may substantially decrease the time of solution treatment and the consumption of the oxidizing agent in implementing the technology of impurity oxidation in wastewater.

It is known that the joint treatment of solutions with Fenton's reagent and UV irradiation allows one to intensify the oxidation of organic compounds and to achieve almost complete mineralization. This is accompanied by an additional formation of the active oxygen forms. Mainly hydroxyl radicals, both due to the decomposition of H_2O_2 and due to the reduction of Fe^{3+} from inactive Fe^{3+} intermediates:

$$H_2O_2 + h\nu = 2^{\bullet}OH \qquad (6)$$

$$[Fe^{3+}, (COOH)_2] + h\nu = Fe^{2+} + (COOH)_2$$
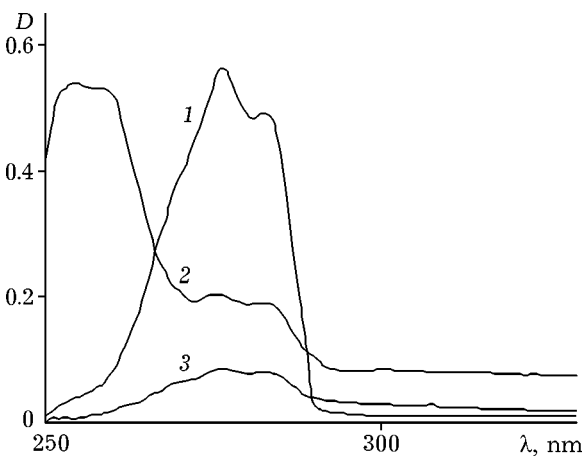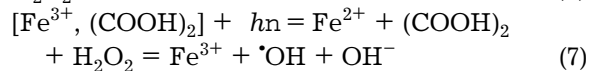$$+ H_2O_2 = Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (7)$$

Fig. 4. Electron spectra of 2-chlorophenol (1) after GCO for 1 min (2) and of the solution 2 after alkalisation to pH 8.5 (3). For conditions, see Fig. 2.
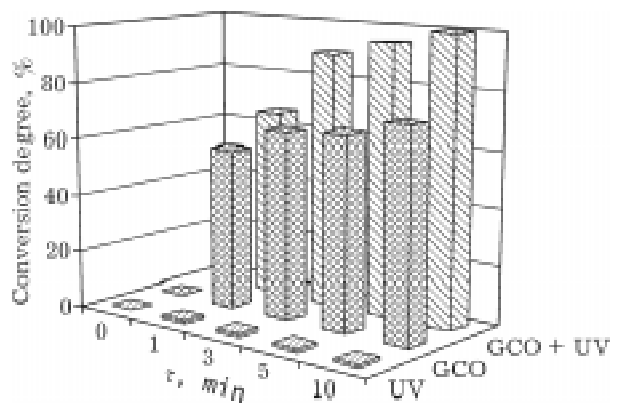

Fig. 5. Comparative estimation of the efficiency of combined oxidation procedures for 2-CP. For conditions, see Fig. 2.
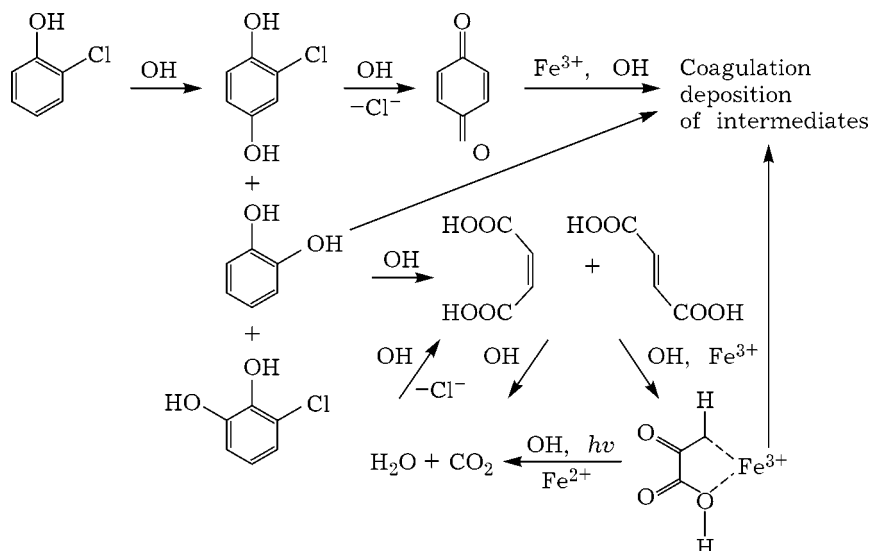
Fig. 6. Possible reactions of galvanochemical and photogalvanochemical oxidation of 2-CP.

Photoactivation of the process of GCO of 2-CP (see Table 1, Fig. 5) helps increasing 2-CP oxidation rate and the conversion degree due to reactions (6), (7). Almost complete oxidation occurs with the molar ratio $C_{HP} : C_{2-CP} \sim 3 : 1$, which makes 22 % of the amount necessary for complete mineralization according to equation (5). A combination of UV irradiation and GCO causes synergism and an increase in the initial rate of 2-CP oxidation almost by a factor of 2 within a broad range of 2-CP concentrations.

CONCLUSIONS

Analysis of the literature data and the experimental results obtained by us allow us to formulate the most probable routes of the reactions of galvanochemical and photogalvanochemical oxidation of 2-chlorophenol (Fig. 6). At the first stage of oxidation, hydroxylation of 2-CP molecules occurs; intermediates are formed which then are attacked by $^{\bullet}OH$ radicals and get oxidized to maleic (fumaric) and oxalic acids. Under the action of UV radiation, the formed complexes $[Fe^{3+}, (COOH)_2]$ are rapidly destroyed, which helps more profound oxidation of chlorophenol and the intermediates.

The results of our investigations provide evidence that a more profound oxidation of chlorinated phenol in comparison with Fenton's reagent during GCO occurs due to the activation of the oxygen of the air at iron − coke galvanic pairs and permanent compensation of the lack of Fe^{2+} ions due to the anode dissolution of iron.

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