Chemistry for Sustainable Development **17** (2009) 201–205

UDC 628.543+628.349.094.3

Photogalvanochemical Oxidation of 2.4-Dichlorophenol

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(Received July 22, 2008; revised November 27, 2008)

Abstract

Results of photoactivated galvanochemical oxidation of 2,4-dichlorophenol in aqueous solutions in a flow film-type photoreactor are discussed. It is established that the photoactivation promotes an increase in the rate constant of 2,4-dichlorophenol oxidation by a factor of 1.7 due to acceleration of the destruction of intermediate products and allows achieving almost complete mineralization of the substrate.

Key words: galvanochemical oxidation, ultraviolet irradiation, 2,4-dichlorophenol

INTRODUCTION

Chlorinated phenols are toxic compounds having extremely unfavourable effect on the life activities of organisms and plants. The effect of these compounds is exhibited even in the case of their insignificant content in water. In addition to high toxicity, chlorophenols are direct precursors of more dangerous compounds, for example such stable organic pollutants as polychlorinated dibenzodioxins that have been included in the list “Dirty dozen” [1].

The main anthropogenic sources of chlorophenols entering water ecosystems are the waste waters from chemical, pharmaceutical, pulp-and-paper, oil-processing and other branches of industry [1, 2].

Biological processes of chlorophenol destruction are ineffective due to the inhibition of the growth of microorganisms and relatively low decomposition rate. Even well acclimatized microorganisms are unable to neutralize waste water with chlorophenol concentration above 20 mg/L. The processes of adsorption on activated carbon and the use of ozone as an oxidizer turned out to be economically unprofitable. At present, one of the most promising methods of chlorophenol destruction is considered to be combined oxidation technologies Advance Oxidation Processes (AOP) that combine the advantages of different oxidation processes. They are more ecologically sound and promote complete mineralization of difficultly oxidized pollutants [2].

Previously the authors of [3] demonstrated that the use of galvanochemical oxidation is promising for the purification of waste water containing various organic compounds. This method is based on the use of the effect of a number of short-circuited microgalvanocouples that arise in the contact of iron chips with crushed coke during passing water and air through this charge.

The mechanism of galvanochemical purification of waste water is determined by the processes that are realized during the contact of water to be purified and air with the charge [4]. It is known that oxygen gets reduced on graphitized carbon materials to form hydrogen peroxide (Berl process). On the “oxygen” electrode, which is an indifferent support saturated with gaseous oxygen – coke, oxygen reduction occurs according to the reaction

$$O_2 + 2H^+ + 2\bar{e} \rightarrow H_2O_2\ (pH \le 7) \qquad (1)$$

At the anode, oxidation of iron scrap takes place:

$$Fe^0 - 2\bar{e} \rightarrow Fe^{2+} \qquad (2)$$

Due to the difference of electrochemical potentials at the contacts of the particles, iron gets anode-polarized, and coke gets cathode-polarized. As a result, short-circuited galvanic element iron–coke is formed; it promotes the origination of galvanocoagulation at the contact site and in the direct vicinity of it. In other words, a set of electrochemical and physical processes appears: dissolution of the anode material (iron) and its transition into water (mainly in the form of divalent aqua ions), electrolysis of water, resulting in simultaneous acidifying of the near-anode layer and substantial alkalization of the near-cathode layer causing an increase in pH of the whole water volume. Then iron is oxidized to Fe(III), and hydrated forms of various iron-containing compounds are formed.

When hydrogen peroxide is added into the system, the conditions for the existence of Fenton and Raff reagents in the flow mode are realized. The method of GCO of organic compounds surpasses the classic Fenton method in efficiency [5].

GCO of organic compounds may be intensified substantially by using additional UV irradiation of the system, which is accompanied by the rise of synergistic effect [6].

The goal of the present work was to study the regularities of GCO of organic compounds in a flow film-type photoreactor with 2,4-dichlorophemol as an example.

EXPERIMENTAL

A model solution of 2,4-dichlorophenol (2,4-DCP) was chosen as the object of investigation. The reagent of 99 % purity (Merck, Germany) was used to prepare the initial solution. The concentration of 2,4-DCP in experiments was 0.12 mmol/L, the concentration of hydrogen peroxide was 0.36 mmol/L. The acidity of the medium was corrected by adding 10 % solution of sulphuric acid (kh. ch. reagent grade) to pH 3.0.

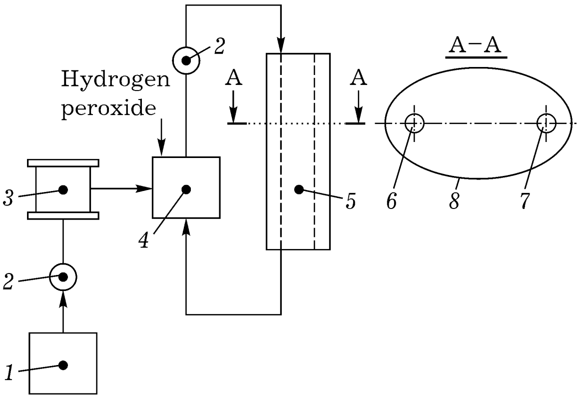

Fig. 1. Scheme of the experimental set-up: *1* – initial vessel, *2* – pump, *3* – galvano-coagulator, *4* – intermediate reservoir, *5* – unit for the UV irradiation of water flow, *6* – quartz tubular reactor, *7* – UV radiation source, *8* – reflector.

The experimental set-up (Fig. 1) includes the units that are sequentially connected in the direction of the flow of water under treatment: initial vessel *1*, intermediate vessel *4*, galvano-coagulator *3*, and unit *5* for UV irradiation of water in flow. The latter unit is composed of a quartz tubular reactor *6*, radiation source *7* (low-pressure mercury lamp with the power of 30 W, the maximum of radiation being at 254 nm), reflector *8*, which is made as a shell (elliptical in the section). The source of radiation and the reactor are placed in the zones corresponding to the foci of the ellipse. In addition, the tubular reactor is equipped with a special injector to feed in the solution under treatment, which provides the uniform distribution of the liquid over the walls of the quartz tube and its downstream flow in the form of a thin film. Thus we succeeded in increased the efficiency of solution treatment with the ultraviolet radiation, because the screening of UV radiation by the molecules of difficultly oxidizable organic compounds is thus minimized. The specific dose of radiation obtained by the solution in this reactor was determined by means of chemical actinometry described in [7]; it was 1.64 W/cm^2. Solutions were fed in with the help of chemical peristaltic pumps of Etatron Co. (Italy).

Water treatment was carried out in two stages. At the first stage, water to be purified was supplied from the initial vessel *1* at a rate of 1 L/h to galvano-coagulator *3* in which

0.09 mmol/L Fe^{2+} was generated during the contact of water and air with the charge (Fe^0/coke). Then the solution enriched with iron entered the intermediate reservoir *4* equipped with a magnetic mixer.

At the second stage, hydrogen peroxide was added into the solution under treatment (V = 0.2 dm^3); then the solution was UV irradiated. The rate of solution circulation was 1 L/min. Time of treatment was reckoned from the moment when the oxidizer was added into the solution to be purified.

To estimate the contribution from different oxidation processes, additional experiments were carried out with the set-up described above. The GCO process was carried out according to the two-step scheme with the UV radiation source switched off. The UV irradiation was carried out in the circulating contour without oxidizer avoiding the first step of treatment, while other conditions were kept constant. Peroxide treatment was carried out under similar conditions adding doses of oxidizer into the treated solution without switching the source of UV radiation. Experiments aimed at the investigation of combined system UV + H_2O_2 were carried out under the same conditions but switching on the source of UV radiation.

Sampling for analysis was carried out from the intermediate reservoir *4*. The concentration of chlorophenol determined from the integral intensity of the band with λ_{max} = 288 nm (ε = 1205 L/(mol · cm) using the UV-Vis Agilent 8453 spectrophotometer. To eliminate the effect of iron during photometry, we used butylacetate extracts of solutions. The concentration of hydrogen peroxide was determined by means of permanganatometry [8]. The concentration of total iron was determined by means of photometry using sulphosalicylic acid [9]. The acidity of the solution was determined using pH-150M instrument with combined glass electrode.

RESULTS AND DISCUSSION

Fenton reagent (H_2O_2 and Fe^{2+}) generates highly reactive species – OH radicals – under normal conditions. According to the classical interpretation by Haber and Weiss [10], the following process takes place in aqueous solutions in the acid medium in the presence of Fe^{2+}:

$$H_2O_2 + Fe^{2+} \rightarrow FeOH^{2+} + {}^{\bullet}OH \qquad (3)$$

It is evident that the concentrations of Fe^{2+} and H_2O_2 to a substantial extent determine the amount of the formed OH radicals that oxidize organic substrates. The formed aqua ion Fe^{3+} may interact with any active particle (H_2O_2, HO_2 or R radicals) getting reduced to Fe^{2+}, and participating in further oxidation reactions [11]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad (4)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \qquad (5)$$

$$Fe^{3+} + R^{\bullet} \rightarrow Fe^{2+} + R^+ + \text{products} \qquad (6)$$

In course of these reactions, both acceleration of the reduction of Fe^{3+} ions formed according to reaction (3) or deactivation of Fe^{2+} and Fe^{3+} by the formation of stable organometallic complexes are possible [12].

Usually the concentration of free Fe^{2+} ions in solution decreases, which leads to a rapid decrease in the rate of destruction of organic compounds, even in the presence of hydrogen peroxide. Oxidation of chlorophenols proceeds until H_2O_2 and Fe^{2+} ions are completely consumed.

The lack of Fe^{2+} ions is compensated by reducing Fe^{3+} under the action with UV radiation of solutions [13], by means of electrochemical [14] or galvanochemical dissolution of Fe^0 [15].

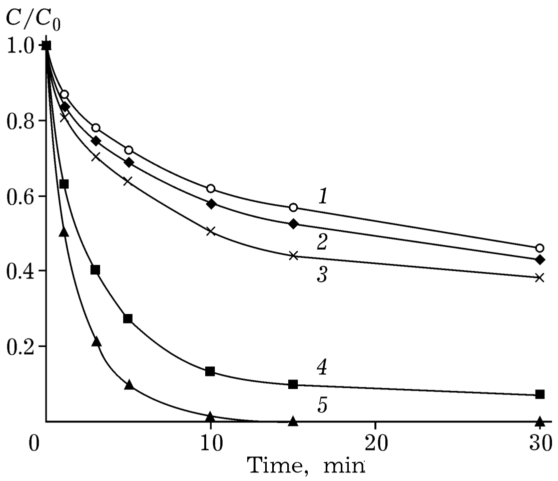

Fig. 2. Degree of 2,4-DCP conversion in different oxidative systems: *1* – UV irradiation, *2* – H_2O_2, *3* – UV + H_2O_2, *4* – GCO, *5* – GCO + UV.

Figure 2 shows the kinetics of oxidation of 2,4-DCP in different oxidizing systems: UV irradiation, treatment with hydrogen peroxide, simultaneous treatment with H_2O_2 and UV radiation, GCO in the presence of H_2O_2, photoactivated GCO in the presence of H_2O_2. The initial concentration of hydrogen peroxide in the experiments was 0.36 mmol/L, which accounts for 30 % of the amount necessary for stoichiometry calculated according to the hypothetical equation

$$C_6H_4OCl_2 + 12H_2O_2 \rightarrow 6CO_2 + 13H_2O + 2HCl \quad (7)$$

Evidently, oxidation of 2,4-DCP in systems without catalysts (see Fig. 2, curves *1–3*) occurs insignificantly and reaches the maximum of 50 % after treatment for 30 min. The simultaneous action of UV radiation and H_2O_2 does not allow achieving event he additive effect. With the introduction of catalyst Fe^{2+} generated by passing the solution through the galvanocoagulating set-up, the process accelerates substantially, and the degree of substrate conversions reaches 95 %. Additional photoactivation accelerates the destruction of the intermediate products of reaction and leads to complete mineralization of 2,4-DCP, which is evidenced by the analysis of electron absorption spectra of 2,4-DCP (Fig. 3).

The kinetic dependence of the oxidation of 2,4-DCP can be represented by a one-side reaction of the second order:

$$\mathrm{d}C/\mathrm{d}t = -k_{2,4\text{-DCP}}C_{2,4\text{-DCP}}C_{\mathrm{OH}^\bullet} \quad (8)$$

where $k_{2,4\text{-DCP}}$ is the rate constant of the one-side second-order reaction; $C_{2,4\text{-DCP}}$ is the concentration of 2,4-DCP; $C_{\mathrm{OH}^\bullet}$ is the concentration of OH radicals at moment *t*.

If we accept that OH radicals are generated in excess and their concentration is constant in time, the kinetic equation may be simplified to the equation of the pseudo-first order:

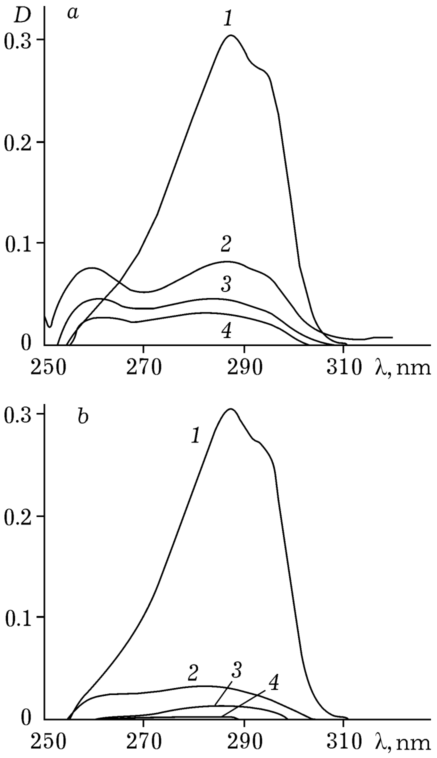

Fig. 3. Electron spectra of 2,4-DCP after GCO (*a*) and photoactivated GCO (*b*): *1* – initial, *2–4* – after treatment for 5 (*2*), 10 (*3*) and 15 min (*4*).

$$\mathrm{d}C/\mathrm{d}t = -k'_{2,4\text{-DCP}}C_{2,4\text{-DCP}} \quad (9)$$

where $k'_{2,4\text{-DCP}}$ is the rate constant of the reaction of pseudo-first order.

Integrating equation with the initial conditions $C_{2,4\text{-DCP}} = C_{0\ 2,4\text{-DCP}}$ and $t = 0$ we obtain

$$\ln\frac{C_{2,4\text{-DCP}}}{C_{0\ 2,4\text{-DCP}}} = -k'_{2,4\text{-DCP}}t \quad (10)$$

A similar simplification is widely used for comparative estimation when considering complicated combined systems [11, 16, 17].

TABLE 1

Data on the initial rate, time of half-transformation and rate constant of pseudo-first order for the reaction of 2,4-DCP oxidation in different oxidative systems

Oxidative system	k, min^{-1}	W_0, 10^{-2} mmol/L	$\tau_{1/2}$, min
UV irradiation	0.054	1.66	12.8
H_2O_2	0.062	2.05	11.2
UV + H_2O_2	0.076	2.38	9.1
GCO	0.279	4.59	2.5
GCO + UV	0.481	6.13	1.4

The data on the initial rate and the time of half-transformation for the oxidation of 2,4-DCP, as well as the pseudo-first-order rate constants of 2,4-DCP oxidation in different oxidizing systems are presented in Table 1. It is evident that the additional photoactivation during GCO of 2,4-DCP leads to an increase in the reaction rate constant by a factor of 1.7 and therefore a decrease in the time of half-transformation; the initial reaction rate increased by a factor of 1.3. The reaction rate is about an order of magnitude lower in the oxidative systems without catalyst.

We assume that under the conditions of our experiment oxidation of 2,4-DCP is accompanied by hydroxylation and dechlorination of the initial substrate, the formation of the compounds of quinoid type that are further on decomposed to form organic acids of aliphatic series. The UV irradiation causes additional formation of highly reactive hydroxyl radicals due to the reduction of Fe^{3+} and additional disproportionation of hydrogen peroxide, which promotes complete mineralization of 2,4-DCP.

CONCLUSION

We demonstrated the possibility to realize photoactivated galvanochemical oxidation of 2,4-dichlorophenol in a flow film-type photoreactor. It was established that additional photoactivation causes an increase in the reaction rate constant by a factor of 1.7 and increase in the initial rate by a factor of 1.3. In addition, the UV irradiation allows achieving complete mineralization of the organic substrate.

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