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Review

The Mechanism and Kinetics of Degradation of Phenolics in Wastewaters Using Electrochemical Oxidation

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In recent years, there has been increasing interest in the search for better water treatment technologies for the efficient removal of contaminants. Phenols and its derivatives are considered an environmental problem due to their acute toxicity and due to their continuous input to the aquatic ecosystem. This paper reviews and discusses the effectiveness of electrochemical oxidation for the removal of phenols and its derivates from aqueous system. Research is directed towards the influence of the structure of such compounds, types of electrode materials as well as the media in which the electrochemical oxidation takes place on the efficiency of the removal of contaminants.

Keywords: electrochemical oxidation, wastewater, phenol, phenol derivatives

1. INTRODUCTION

Continual pollution of water bodies is a major environmental problem due to the greater industrial development. Phenols are one of the most important representatives of organic contaminants as they are toxic at low concentrations and their presence in water may lead to the formation of halogenated compounds [1, 2]. They are present in the effluents of various industries such as petrochemical industry (2.8 to 1220 mg/l), coke (28-3900 mg/l), refineries (6-500 mg/l), pharmaceuticals, plastics, paper (from 0.1 to 1600 mg/l) [3, 4] etc.

Efficient methods for the removal of phenolic compounds have been recently developed. They include phenol oxidation by catalytic wet oxidation, hydrogen peroxide, Fenton processes [5-8], electrochemical oxidation [9-11], oxidation using $KMnO_4$, Cl_2, H_2O_2 and O_3 [12-14]. Many researchers showed that non-biodegradable organic contaminants can be completely mineralized by using advanced oxidation processes, which are based on the production of highly reactive and non-selective hydroxyl radicals [7, 15-17]. Today, the electrochemical methods have become more efficient and compact and thus attract the attention of scientists interested in wastewater treatment because of their safety, selectivity, automation capabilities and environmental compatibility [18, 19]. Electrochemical methods have been widely used to remediate soil, sludge etc [20-22], have been used as corrosion inhibitors, having no harmful effect on the environment [23-27] and for the determination of pharmaceuticals [28-30]. Importance of electrochemical methods is reflected in their ability to quickly provide useful information about oxidation-reduction processes, the kinetic of heterogeneous reactions and the adsorption processes [31-33].

Destruction of organic pollutants by electrochemical oxidation include various species, such as hydroxyl radicals ($^{\cdot}OH$), $O_2^{\cdot}$, $HO_2^{\cdot}$ and $ROO^{\cdot}$ obtained *in situ* in the reaction medium. A hydroxyl radical, which results from decomposition of hydrogen peroxide, forms oxygen and water as by-products. It has a high reduction potential ($E_{(^{\cdot}OH/H_2O)}$ = 2,8 V vs. SVE) which allows it to react with a large number of organic compounds, regardless of their concentration, and has the ability to oxidize nearly all organic compounds to CO_2 and H_2O [4], or to simpler compounds such as acetic acid, oxalic acid and maleic acid, acetone, and chloroform [34]. Hydroxyl radicals can be prepared by direct decomposition of water on the anode [35]. They have the ability to eliminate the contaminants from the gas, liquid and solid forms. Non-selectivity of $^{\cdot}OH$ radicals helps prevent the formation of undesirable by-products. A short life span of $^{\cdot}OH$ radicals causes that the anodic oxidation process takes place near the surface of the electrode. However, very high oxidation capacity makes them a promoter of other oxidants of different types of chemical compounds contained in the wastewater [34].

This paper aims to present an overview of the published results of the electrochemical degradation of phenol and its derivatives. It was demonstrated that the electrochemical oxidation is a suitable technology for the treatment of wastewater effluents by different industry. The existing limitations and future research needs for wastewater treatment is also discussed.

2. ELECTROCHEMICAL OXIDATION OF PHENOLS AND PHENOL DERIVATIVES

Electrochemical oxidation of organic pollutants can be carried out in two ways: by direct or indirect oxidation. Direct oxidation of the pollutants first leads to their adsorption on the surface of the anode without the participation of other substances in the solution except electrons which are referred to as "pure reagent". Direct electrooxidation is theoretically possible at lower potential values before oxygen evolution but the reaction is usually slow and depends on the electrocatalytic activity of the anode. The higher speed of the electrochemical reaction is obtained by the use of noble metals such as Pt or Pd and anode based on metal oxides such as IrO_2, TiO_2-Ru, Ir-TiO_2, PbO_2.

However, the main problem of this type of oxidation is the fouling of electrodes which decreases its catalytic activity. This is because of the polymer layer formation on the surface of the anode. Deactivation of the anode depends on the adsorption properties of the surface, the nature and concentration of organic compounds and their degradation intermediates. Decline in the anode electrocatalytic activity is less pronounced when using electrode materials with lower adsorption capabilities, such as BDD (boron-doped diamond) anode. The effect of the anode fouling can be avoided by performing the oxidation process in the potential region in which decomposition of water takes place with simultaneous evolution of oxygen or indirectly by electrooxidation with the formation of the redox species *in situ* as chemical reactants that oxidize organic pollutants [36, 37].

Two reactions are possible during direct anodic oxidation of organic contaminants [38]:

a) Electrochemical conversion, where the organic compounds are partially oxidized according to the reaction:

$R \longrightarrow RO + e^-$ (1)

b) Electrochemical combustion, the organic compounds are decomposed to carbon dioxide, water and other inorganic compounds:

$R \longrightarrow CO_2 + H_2O + \text{salts} + e^-$ (2)

The idea of indirect electrochemical oxidation is to prevent fouling of the electrodes, avoiding direct exchange of electrons between the organic compound and the surface of the anode.

According to this, in the process of indirect electrolysis, contaminants are oxidized by electrochemically generated redox reagents that are actually intermediates in the transfer of electrons between the electrode and organic compound. Oxidation agents may be metal redox pairs with high oxidation potential, such as Ag (I/II) (E^θ=1.98 V vs. SHE), Ce (III/IV) (E^θ=1.44 V vs. SHE), Co (II/III) (E^θ=1.82 V vs. SHE), or strong oxidizing agents such as active chlorine, ozone, hydrogen peroxide, persulphate, percarbonate and perphosphate [36]. A different behavior is observed when wastewater contains chloride ions. This is because the active chlorine species such as Cl_2, HClO and/or ClO^-, ClO_2^- can decompose the organic compound. This procedure is called the electrochemical oxidation of active chlorine. It is based on the direct oxidation of Cl^- ions on the anode to soluble chlorine (reaction 3), which inturn diffuses from the anode to be ultimately transformed by hydrolysis into hypochlorite acid and hypochlorite ion (reaction 4) [39]:

$2Cl^- \longrightarrow Cl_2(aq) + 2e^-$ (3)

$Cl_2(aq) + H_2O \longrightarrow HClO + Cl^- + H^+$ (4)

Mediated oxidation with active chlorine species is faster in acidic than in alkaline media due to the higher standard potential of Cl_2 (E = 1.36V vs. SHE), and HClO (E = 1.49V vs. SHE) with respect to ClO^- (E = 0.89 V vs. SHE). The possibility of the formation and accumulation of toxic derivatives of chlorine, trihalomethane and chloramine present a major deficiency of electroxidation process in the presence of active chlorine species [40].

Different types of the anode materials have been examined for the destruction of phenols such as Ti/Pt-Ir, MnO_2, Pt-carbon black, carbon fiber. However, none of them showed sufficient activity and stability for the electrochemical oxidation process. Consequently, attention was drawn towards the following types of anodic materials: graphite, Pt, PbO_2, IrO_2, BDD, TiO_2, SnO_2 [41]. The major flaw for these types of materials is the formation of a polymer film on the surface of the anode during the process of degradation. They also have different values of potential for the evolution of oxygen (Table 1). The most convenient electrodes turned out to be BDD anodes.

Table 1. The oxygen evolution potential values of the electrode [41, 42]

Type of anode	Potential value, V	Experimental conditions	Reference electrode
Pt	1.3	0.5 M H_2SO_4	SHE
IrO_2	1.6	0.5 M H_2SO_4	
Graphite	1.7	0.5 M H_2SO_4	
PbO_2	1.9	1.0 M $HClO_4$	
SnO_2	1.9	0.5 M H_2SO_4	
Ti/BDD	2.7	0.5 M H_2SO_4	

Good characteristics of BDD anode for the use in the process of electrochemical oxidation of organic compound has been demonstrated by numerous researchers like Iniesta et al., [43], Canizares et al., [44]. They examined degradation of phenol under different conditions, in the potential region of water stability ($E < 2.3$ V vs. SHE) and in the potential region of water decomposition ($E > 2.3$ V vs. SHE). Iniesta et al., [43] examined electrochemical degradation of phenol in an acidic electrolyte (1 M $HClO_4$), while Canizares et al., [44], conducted studies in a solution of Na_2SO_4 ($5g/dm^3$), where pH value of the electrolyte was 2 and 12. The application of potential leads to direct or indirect degradation of phenol. When potential value of $E < 2.3$ V (vs. SHE) is applied there is direct electron transfer reaction on electrode surface that results in electrode fouling due to the formation of a polymeric film on its surface, which reduces its activity. In the case of application of $E > 2.3$V (vs. SHE) electrochemical oxidation of phenol takes place by means of hydroxyl radicals which are formed on the electrode surface. In this way, it is possible to avoid fouling of the electrodes. Electrochemical oxidation of phenolic wastewater using BDD anode, leads to the formation of quinone compounds (hydroquinone, benzoquinone) and carboxylic acids (usually maleic acid and oxalic acid) as intermediate products and CO_2 is generated as an end product. The high anodic potential of BDD anode (Table 1) for the process, allows performance of complete phenol mineralization without deactivating the anode. It was established that reaction is controlled by diffusion of phenol to the surface of the anode [43, 45].

Good performance was demonstrated by Ti/SnO_2-Sb, which was used in 0.25 M Na_2SO_4 solution as the electrolyte for degradation of phenol. Based on the voltammetric tests it was found that Ti/SnO_2-Sb has a high value of oxygen evolution potential (1.6 V vs. Ag/AgCl), and thus extends the presence of $^{\cdot}OH$ radicals, which inturn react with phenol [46]. The fact that BDD anode has good performance for the electrochemical oxidation of organic compounds was confirmed by Lv et al., [47], in his work. The high efficiency of the electrochemical degradation of phenol was achieved with BDD and SnO_2 anode. 0.25M Na_2SO_4 was used as the electrolyte and the current density of 10 mA/cm^2 was applied. After 6 hours of the process, the efficiency of phenol removal was 100% with the BDD anode and the same with SnO_2 anode was 95%. Cyclovoltammetric analysis was carried out in a solution with phenol concentration of 500 mg/l in order to determine the performance characteristics of both anode materials. The results are shown in Table 2.

Table 2. Cyclovoltammetric analysis of phenol solution (500 mg/ l) on BDD and SnO_2 anodes [47]

Phenol concentration, mg/l	Type of electrolyte	Type of electrode	Reference electrode	Anodic potential, V	Current density, mA/cm^2
500	0.25 M Na_2SO_4	BDD	Ag/AgCl	1.43	1.3
		SnO_2		1.03	2.1

It was concluded that direct electrochemical oxidation was obtained on SnO_2 anode (due to the higher current density). Indirect degradation of phenol was obtained on BDD anode due to the formation of $^{\cdot}$OH radicals having high oxidation capability. Slightly weaker characteristics were shown by the electrodes viz. Pt, PbO_2, IrO_2, Ti/RuO_2, Ti/RuO_2-Pt, Ti/IrO_2-Pt. The main problem of using PbO_2 as anode is the need for subsequent removal of dissolved lead from the treated solution [48]. It was found that PbO_2 electrode was not stable during the electrooxidation process [49]. PbO_2 and IrO_2 anodes lead to direct electrooxidation of phenol [48, 50, 51].

Li et al., [52], investigated the electrochemical degradation of phenol using two different anodes, Ti/RuO_2-Pt and Ti/IrO_2-Pt. They used a solution of NaCl as an electrolyte in concentration of 0.1g/l; 0.3g/l and 0.5g/l. It has been found that oxidation of phenol was carried out by an oxidant HOCl, generated by NaCl oxidation. Ti/RuO_2-Pt was shown to be more effective anode on whose surface the formation of polymer film was not observed, while polymeric film was formed on Ti/IrO_2-Pt. In addition, Ti/IrO_2-Pt anode has less potential for the evolution of oxygen (1.2 V vs. Hg/HgCl) with respect to Ti/RuO_2-Pt (1.58 V vs. Hg/HgCl). The low over-potential of the Ti/IrO_2-Pt anode would shorten the life span of ·OH radicals which would ultimately react with organic compounds. Many phenols are oxidized on the anode having a high potential for the evolution of oxygen, such as PbO_2 [53] and BDD [54, 55]. Panizza and Cerisola [55], found that ·OH radicals that are formed on PbO_2 anode have the ability to mineralize polymer film formed on the surface of the anode. On IrO_2 anode ·OH radicals react with the oxide of anode to form the IrO_3 which inturn demonstrates an active part in the oxidation of phenol on IrO_2 anode [56]. Hydroperoxyl radicals ($HOO^{\cdot-}$) are formed on Pt by water oxidation. Active types such as IrO_3 and $HOO^{\cdot}$ can oxidize polymer film formed on Ti/IrO_2 and Pt, which reduces their activity and prevents further oxidation of phenol [53].

In order to improve the process of electrochemical oxidation of organic compounds, a number of authors have used a modified electrode in their research [57-60]. It has been found that there is an increase in the active surface of modified electrodes, as well as in the increase in their stability. It was also noted that the modification of the electrode increases the value of potential of oxygen evolution. Hence, the potential of oxygen evolution is 2.19 V (vs. SCE) for Bi-PbO_2/PEG compared to 1.93 V (vs. SCE) for a Bi-PbO_2 [59]. The presence of surfactants in the medium may also lead to improvements in degradation of organic compounds. Sripriya et al., [61], investigated the effect of cetyl-trimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and polyoxyethylene lauryl ether (Brij-35) on the degradation of p-chlorophenol and p-nitrophenol in a chloride medium. Graphite and titanium in soluble anode (TSIA) were used in the analysis. The results are shown in Table 3. Improvement of electrochemical oxidation of phenolic compounds is obtained on TSIA in the presence of CTAB, as on the graphite anode. Cationic surfactants (CTAB) favor polymerization in liquid phase thereby blocking the adsorption of phenol electrogenerated cationic radicals on the surface of the anode. Adsorption of surfactants occurs on the graphite electrode, preventing oxidation of organic compounds.

Table 3. Comparison of the electrochemical oxidation efficiency of *p*-chlorophenol (PCP) and *p*-nitrophenol (PNP) in the presence of free surfactants [61]

Type of compounds	Type of electrolyte (0.1 M)	Type of surfactant (0.1%)	Type of anode	Removal efficiency, %
PCP	NaCl	/	TSIA	14
	NaCl	CTAB SDS Brij-35		57 6 16
PNP	NaCl	/	TSIA	48
	NaCl	CTAB SDS Brij-35		64 27 34
PCP	NaCl	/	Graphite	20
	NaCl	CTAB SDS		12 10
PNP	NaCl	/	Graphite	48
	NaCl	CTAB SDS		44 26

3. MECHANISM OF ELECTROCHEMICAL OXIDATION OF PHENOL AND PHENOL DERIVATIVES

The electrochemical oxidation of phenol and phenol derivatives was studied with different electrode materials and under different experimental conditions. Generally, degradation of phenol is carried out in several steps:

1. Cyclic intermediates are formed by oxidation of phenol and phenol derivatives,
2. Ring-opening reactions of cyclic intermediates where the organic acids are formed,
3. Mineralization of organic acids producing CO_2 as end product [54].

Based on the results of Chatzisymeon et al., [50], Wu et al., [62], Enache et al., [63], Arslan et al., [64] the electrochemical degradation of phenol is a single-step reaction resulting from the transfer of one electron and one proton to phenoxy radicals which inturn are thermodynamically unstable and can exist in the form of three isomers. The highest electron density of phenoxy radical is in the *ortho*- and *para*- positions. *Meta*- position is not favored for any type of chemical reaction due to instability of formed compound. Reactivity of the aromatic ring activated by -OH group, is increased when the group is in *ortho*- or *para*- position, because in the same time there is increase of electron density in these positions [63]. The mechanism of electrochemical oxidation of phenol and phenol derivatives was investigated by many authors [46, 51, 57, 58, 65-68] and it has been found that oxidation of examined organic compounds occurs faster on the "inactive" anodes (BDD, PbO_2, SnO_2) in regard to representatives of the "active" anodes (RuO_2, Pt). Electrophilic addition of ·OH radicals occurs during the electrochemical degradation of phenol on benzene ring in *ortho*-, *para*- and *meta*-position, and leads to the initial formation of the *o*-quinone and *p*-quinone, and later to *m*-quinone. These are then reduced to catechol, hydroquinone and resorcinol, respectively. The oxidation of intermediates leads to the formation of benzoquinone. The opening of benzoquinone’s aromatic ring leads to the formation of aliphatic carboxylic acids as intermediates. These organic acids are finally oxidized to CO_2 and H_2O as final products. Direct oxidation of phenol has been found while using PbO_2 [51] and BDD [43] as electrode material. During the oxidation of phenol, there is the formation of polymer film on the surface of the electrode, which covers the active sites of the electrode and thus prevents the further process of phenol oxidation. Electrochemical degradation of phenol derivative takes place via the carbon atom of aromatic ring to which the substituent is attached [69, 70]. In this way, the active chlorine atoms may occur if there is chlorinated phenol derivative [70]. The reaction intermediates, which are formed mainly by oxidation of phenolic compounds, are quinone products and short chain carboxylic acids. Oxidation of 4,4'-(propane-2,2-diyl) diphenol by ˙OH radicals initially forms hydroxylated derivatives of 4,4'-(propane-2,2-diyl) diphenol, which are further converted into a compound having one aromatic six-membered ring due to the breaking of isopropylidene connection. Aromatic compounds are then subjected to disintegration of the ring to form an aromatic acid, which is oxidized to the final product, CO_2 [71-73].

In addition to the experimental conditions under which the process is performed, degradation process of phenol derivatives is influenced by the position and properties of substituents attached to the aromatic ring of phenol. Liu et al., [69] investigated the effect of molecular structure of di-and tri-nitrophenol on their electrochemical degradation using Ti/PbO_2 electrode doped by bismuth. It has been found that nitrophenols are degraded by indirect oxidation and there is no formation of polymeric adhesive compound on the surface of the electrode. Electrooxidation follows the order: 2,6-dinitrophenol > 2,5-dinitrophenol > 2,4-dinitrophenol > 2,4,6-trinitrophenol. The effect of nitro group as substituent on BDD anode was examined in Jiang et al., [74] work. Studies included the electrochemical oxidation of three isomers of nitrophenol and phenol in alkaline medium: 2-nitrophenol, 3-nitrophenol and 4-nitrophenol. It was found that degradation process follows the order: 2-nitrophenol > 3-nitrophenol > 4-nitrophenol > phenol.

The OH- group is an electron donor and increases the electron density of the aromatic ring in *ortho*- and *para*-positions and the NO_2-group is an electron acceptor, and leads to deactivation of the aromatic ring. Based on the position of electron density, the favored positions of 2-nitrophenol, 4-nitrophenol and phenol aromatic ring are C2, C4 and C6. 3-nitrophenol in its structure has only one position of positive charge that may react with ·OH radical, which is C3 (-0.3639 eV). Since the reaction is electrophilic, ·OH radicals tend to react with the carbon atom having the highest electron density. For 2-nitrophenol the position with the highest density of electrons is C2 (-0.5403 eV), and as a result, 2-nitrophenol is degraded with highest efficiency. In 4-nitrophenol, it is the C4 position (-0.4600 eV) which has high electron density and consequently is degraded more slowly as compared to the 2-nitrophenol. In the case of phenols, ·OH radicals react primarily at the *para*- positions, because of operating steric effects at the *ortho*- positions. However, the *para*- position has a very low electron density (-0.1444 eV) and hence have the slowest disintegration of phenols having that kind of structure [74].

Cyclovoltammetric analysis showed that electrochemical oxidation of phenol nitro derivatives, occurs by a reversible reaction [74]. Two anodic peaks have been identified as representing the phenolate oxidation (the dominant form in alkaline medium) to phenoxy radicals and the further oxidation of phenoxy radicals to phenoxy cations [75, 76]. Resulting intermediates are very active and can couple to form polymers or undergo other chemical transformation, such as addition of hydroxyl and release of substituted groups [75]. Two cathodic peaks that also appear on the first scan are attributed to the reduction of the hydroxy amino phenol, nitrophenol and aminophenol [76]. New anodic and cathodic peaks were observed during the second scan, for 2Nitrophenol and 4Nitrophenol. Anodic peak represents the oxidation of dihydroxybenzene to benzoquinone, while the cathodic peak represents the opposite reaction, viz, the reduction of benzoquinone to dihydroxybenzene [77].

The simultaneous electrochemical oxidation of p-chlorophenol and p-nitrophenol in aqueous solutions was examined using PbO_2 electrode doped with bismuth [78]. During the simultaneous oxidation, p-nitrophenol inhibits oxidation of p-chlorophenol, since there is a stronger adsorption of p-nitrophenol on the electrode surface. First, there is a reduction in the concentration of p-chlorophenol, then it reaches the value corresponding to the attained adsorption equilibrium at interfaces electrode-solution. Adsorption can be described by Langmuir adsorption isotherms, and it was found that kinetics of adsorption of p-chlorophenol depends on the available adsorption places of free electrode surface. The adsorption speed of p-chlorophenol decreases with increasing of p-nitrophenol concentration, which is more strongly adsorbed on the surface of the electrode.

Torres et al., [79] found that order of reactivity of substituents in an acidic medium is as follows: $-NH_2 > -OH > -Cl > -H > -COOH > -NO_2$ but in basic medium the order is different: $-OH > -Cl > -COOH > -H > -NO_2$. In both media, phenol with electron-donor groups are more easily oxidized than those with acceptor (withdrawing) groups. Despite the deactivation characteristics of chlorine as substituent, p-chlorophenol is electrochemically more easily decomposed in comparison with unsubstituted phenol. In both acidic and basic media, degradation of p-chlorophenol was faster than expected, which was explained by the increase in phenol electrochemical reactivity with an increase of chlorinated substituents in its structure.

4. THE EFFECT OF ELECTROLYTE TYPE AND pH VALUE ON THE EFFICIENCY OF ELECTROCHEMICAL OXIDATION

Experimental parameters influence the electrochemical oxidation of phenol and phenol derivatives, and the most significant among these is the electrolyte type and pH of the applied electrolyte. Salts of chloride, sulfate and phosphate are the most commonly used electrolytes [80].

Based on the results obtained, Wu et al., [81] found that solution of Na_2CO_3 acts as an inhibitor and protects the organic compounds from the action of $^{\cdot}OH$ radicals. Concentration of generated $^{\cdot}OH$ radicals decreases with an increase in concentration of CO_3^{2-} because of the reaction where the incurred radicals are spent:

$$^{\cdot}OH + CO_3^{2-} \longrightarrow OH^- + CO_3^{\cdot\, 2-} \quad (5)$$

In the present medium there is HCO^{3-} ion, which also inhibits the action of $^{\cdot}OH$ radicals:

$$^{\cdot}OH + HCO_3^- \longrightarrow OH^- + HCO_3^{-\cdot} \quad (6)$$

Rabaaoui et al., [80], and Zaggout et al., [82], investigated the effect of electrolyte (NaCl, KCl, Na_2SO_4, Na_3PO_4) on electrochemical degradation of *o*-nitrophenol, while Chatzisymeon et al., [50] examined the effect of electroactive anion Cl^-, Br^-, SO_4^{2-} on the phenol degradation when they are added in concentration of 3.5 mM and 35 mM to a solution of an electrolyte (1 M $HClO_4$). Complete mineralization of *o*-nitorophenol was achieved in all four tested electrolytes (NaCl, KCl, Na_2SO_4, Na_3PO_4), but the process is the fastest in the presence of Na_2SO_4 as an electrolyte [80]. However, Murugananthan et al., [83] and Zaggout et al., [82] found that the highest efficiency of the *o*-nitrophenol's degradation was achieved in a solution of NaCl. The positive effect of chloride media on phenol degradation was observed also by Iniesta et al., [49], Chatzisymeon et al., [50], Park et al., [84], Rajkamar and Palanivelu [85], Bergman et al., [86], Sanchez-Carretero et al., [87] who have assumed that the Cl^- ions formed together with hydroxyl radicals, can oxidize the organic matter (R). The reaction between the water and radicals in the vicinity of the anode (M) in the acidic environment led to the formation of free chlorine or oxidizing species of chlorine (HClO, ClO_2^-, ClO_3^-, and ClO_4^-), which may react with the organic substances in the solution. The formation of free chlorine during the initial stages of reaction is disadvantageous, due to its characteristic strong odor and yellowish color. It is also important to note that large amount of NaCl may increase the toxicity of wastewater due to the formation of chlorinated compounds [88, 89]. Niu et al., [90] confirmed in their work, that the degradation process of phenolic compounds achieved a high efficiency in a chlorate electrolyte ($NaClO_4$), as compared to other tested electrolyte solutions (Na_2SO_3, $NaNO_2$, Na_2SO_4, $NaNO_3$).

High degradation efficiency of pentachlorophenol is primarily attributed to the oxidizing chlorine species, including Cl_2, HClO and ClO_2^-, resulting in the release of Cl^- from pentachlorophenol (reactions 3 and 4). Regarding the influence of electroactive anions, it can be said that the sulfate ion has practically no effect on the degradation in neither of the investigated concentrations. Addition of Br^- ions shows a slight effect on the process of degradation, probably because of the fact that the Br^-

ions act as scavenger of generated active species [91]. Conversely, Cl^- ions have a positive effect which has been observed for a concentration of 35 mM [50].

Since the solution of sulphate is an inert electrolyte, there is no formation of active species during electrolysis, except under special conditions where persulphate is formed [85]. It has been found that $S_2O_8^{2-}$ does not have the ability to degrade resistant molecules of the intermediates [71].

Some authors suggest that oxidation process is favored in acidic environments, while others claim that the higher efficiency is achieved in alkaline medium [92]. Based on these facts, it was concluded that pH value influences the process of electrochemical oxidation of analyzed organic compounds.

The work of Wu et al., [81] demonstrates that a pH of 11.0 showed the highest efficiency of phenol removal viz 100% after a time of 12 h and this was attributed to a large quantity of the radicals formed under alkaline conditions rather than under acidic and neutral environments. Since the electrodes of metal oxide are highly hydrophilic, the way of forming $^{\cdot}OH$ radicals is shown in the following reactions [93]:

$$2H_2O - 2e^- \longrightarrow 2^{\cdot}OH + 2H^+ \quad (7)$$

$$OH^- - e^- \longrightarrow {}^{\cdot}OH \quad (8)$$

When the initial pH value is 11.0, the formation of $^{\cdot}OH$ radical is probably extremely high, as described by reaction (8). It has been found that pH value of the electrolyte strongly influences the oxidation process of 4,4'-(propane-2,2-diyl) diphenol [71]. Trend observed in the rate of reaction at pH 10.0 can be explained by pKa value of 4,4'-(propane-2,2-diyl) diphenol molecule. 4,4'-(propane-2,2-diyl) diphenol (Bisphenol A) has two pKa values, 9.59 and 10.20, and is predominant in ionic form at pH 10.0. Additionaly, the attack will be more quickly performed by $^{\cdot}OH$ radicals which are electrophilic and oxidation occurs rapidly.

Based on the data available in the literature [62, 69, 82, 90, 94] it was found that acidic environment favors the process of the electrochemical oxidation of organic compounds. Increasing the pH value can be attributed to the production of hydroxyl ions at cathode and a decline in pH is caused by consumption of the hydroxyl anions as well as production of H^+ ions in dissociation reaction of HOCl. Since HOCl has been immediately used for the oxidation of high concentrations of phenol in phenol solution, the pH is in range of 9.0 to 9.3 for a long period. Moreover, the formation of different organic acids results in decreasing of pH. When phenol is completely removed from the solution, the pH reaches a value of 7.6 [69, 95, 96].

While performing electrolysis of an aqueous solution of *o*-nitrophenol at pH 3.6 and 10.0, it was revealed that more effective degradation was in acidic than in alkaline and neutral media [80]. It has been found that at pH 10.0 the solution becomes blurry after oxidation, which indicates the formation of polymer intermediate products by reaction of $^{\cdot}OH$ groups in the molecule of *o*-nitrophenol, and this makes the separation more difficult [97].

Niu et al., [90] also confirmed the low degradation efficiency under basic conditions. By increasing the pH, amount of generated $^{\cdot}OH$ radicals decreases. However, it is interesting that the rate of pentachlorophenol degradation increases again at very alkaline conditions (pH 11.0). At higher pH values, pentachlorophenol is in the form of an anion which is more easily adsorbed on the surface of the electrode.

The electrochemical oxidation of 4-chlorophenol was studied in acidic (pH of 1 M H_2SO_4 = 0.4), in neutral (1 M Na_2SO_4 pH = 6.9) and in alkaline media (1 M NaOH, pH = 12.9) on glass carbon electrodes at different temperatures of 25-85^{o}C by cyclovoltammetry. The first cycle of recording indicates analog changes of all three mediums [98]. It has been noted that oxidation peak of 4-chlorophenol moves towards less positive values of potentials with an increase of pH. Peak of 4-chlorophenol oxidation occurs at 0.98 V (SCE) in acidic medium, at 0.73 V (SCE) in neutral medium, and at 0.47 V (SCE) in alkaline medium. It should also be noted that current density in alkaline medium is significantly higher than in neutral and acidic solution. This may be related to the equilibrium dissociation of 4-chlorophenol:

$$C_6H_4ClOH \longrightarrow C_6H_4ClO^- + H^+ \quad (9)$$

At higher pH values, 4-chlorophenol is in the form of an anion which is more easily adsorbed on the surface of electrodes due to electrostatic forces. This inturn may facilitate the oxidation of 4-chlorophenol on a glass carbon electrode [98]. Kornienko et al., [99] examined the indirect electrochemical oxidation of phenol mediated by reactive oxygen species on Pb/PbO_2 anode in acidic and neutral media. Based on the results shown in the table 4, it was concluded that the higher efficiency of phenol degradation is achieved in an acidic medium and this was also confirmed by the fact that, increase in value of current density may lead to an increase in the efficiency of the process in both media.

Table 4. The results of the electrochemical oxidation of phenol in acidic and neutral medium [99]

Medium type	Initial phenol concentration, mg/l	The efficiency of the oxidation process	Current density, A/m^2
Acidic medium (1 M Na_2SO_4 + H_2SO_4 + $FeSO_4$)	200	84%	500
		92%	1000
Neutral medium (1 M Na_2SO_4)	200	48%	500
		77%	1000

5. KINETIC STUDIES OF ELECTROCHEMICAL OXIDATION OF PHENOL AND PHENOL DERIVATIVES

Based on the research of many authors like Duan et al., [51], Liu et al., [69], Rabaaoui et al., [80], , Wei et al., [100] it was found that degradation of phenol, chlorophenol, nitrophenol by electrochemical oxidation follows pseudo-first order kinetics. The results are shown in Table 5. Time required for the completion of oxidation reaction of phenol and its derivatives, depends on a number of variables such as: pH value of the electrolyte, the concentration of the organic compound, the current density and type of anode material [98, 101].

The reactions are carried out on the surface of the anode, and phenol degradation was attributed mainly to $^{\cdot}OH$ radicals, generated at the anode. Due to the strong oxidative power of $^{\cdot}OH$ radicals, they do not accumulate in the solution, but they react with the molecules of organic compound [65].

Table 5. Values of phenol degradation rate constant depending on the current density

Phenol concentration, mg/l	Current density (i), mA/cm^2	Degradation rate constant (k), min^{-1}	Literature
50	25	0.00083	[101]
50	100	0.003	
100	100	0.005	
500	10	0.003	[51]
	20	0.007	
	30	0.011	
	40	0.016	
	50	0.025	

While studying the degradation of p-nitrophenol on BDD [72] and PbO_2 anode doped with bismuth [69], it was found that the reaction was found to follow pseudo-first order kinetics (equation 10) [69, 74, 80, 102]. The obtained results are shown in Table 2.

$$\frac{dC}{dt} = -k \cdot C \quad (10),$$

where C is the concentration of *p*-nitro phenol (mg / l),
t- the reaction time (h),
k-degradation rate constant (h^{-1}).

It should be noted that the same time is necessary to remove the *o*-, *m*-, *p*-nitrophenol on the BDD anode, which was confirmed based on the reaction rate constants. The obtained values of reaction rate constants indicate that electro oxidation of nitrophenol follows the order: 2,6-dinitrophenol > 2,5-dinitrophenol > 2,4-dinitrophenol > 2,4,6-trinitrophenol, which also indicates that structure of nitrophenol affects degradation process [69]. Hydroxyl radicals formed on BDD anode remain generally free on the surface of anode. They are nonselective and directly interact with the molecules of organic compounds, while PbO_2 anode leads to their adsorption and therefore degradation of nitrophenols is slower and more time is needed for their degradation. Dependence of degradation rate on the number of nitro groups in the structure indicates on the one hand, that increasing number of nitro group leads to the reduction of reaction rate. On the other hand, if it is the same number of nitro groups, degradation rate is in accordance with the melting temperature of nitrophenol [69]. The obtained values of nitrophenol's degradation rate constants are shown in Table 6.

Table 6. Different values of reaction rate constants of nitrophenol's degradation according to the position of the nitro group in compound structure

Type of compounds	Degradation rate constant (k), (min^{-1})	Type of anode	Literature
o- nitrophenol	0.0988	$Bi\text{-}PbO_2$	[69]
m- nitrophenol	0.0709		
p- nitrophenol	0.0513		
2,4- nitrophenol	0.0286		
2,5- nitrophenol	0.0392		
2,6- nitrophenol	0.0489		
2,4,6- nitrophenol	0.0204		
o- nitrophenol	0.01158	BDD	[80]
m- nitrophenol	0.01134		
p- nitrophenol	0.01014		
2-nitrophenol	0.0162	BDD	[74]
3-nitrophenol	0.0095		
4-nitrophenol	0.0118		
phenol	0.0049		

The degradation rate of organic compounds is influenced by pH of the electrolyte and current density. Based on the values given in Table 7, it was found that increase in current density leads to increase of degradation rate, whether in acidic or alkaline medium [100].

Table 7. The values of reaction rate constants of p-nitrophenol electrochemical oxidation (60 mg/l) in acid and alkaline medium [100]

pH value of electrolyte	Current density (i), mA/cm^2	Degradation rate constant (k), h^{-1}
3	15	0.6562
	20	0.6954
	30	0.7208
9	15	0.6305
	20	0.7797
	30	0.8351

Niu et al., [103] investigated the electrochemical degradation of 2,4-dichlorophenol at Ti/SnO_2-Sb in pH range from 3.0 to 11.0. It has been found that degradation reaction follows pseudo-first order kinetics. The values of reaction rate constants (k) and half reaction time ($t_{1/2}$) were 0.21 min^{-1} and 2.8 minutes, respectively. Based on these results, it was found that degradation of 2,4-dichlorophenol was achieved at greater than 99.9% at different initial concentrations (5-200 mg/l).The k value of initial pH of 3.0 (k = 0.31 min^{-1}) was about 2 times higher than that in alkaline medium (pH 11.0, k = 0.18

min^{-1}), and half reaction time was in the range from 1.9 to 3.3 min. This suggests that faster degradation process takes place in acidic medium. Decomposition kinetic of 4,6-dinitro-2-methylphenol was tested using BDD and Pt anode, in acidic (pH 3.0) and in alkaline medium (pH 12.0), in current density range of 100-450 mA/cm^2 at 40°C. Degradation process of 4,6-dinitro-2-methylphenol was carried out faster in acidic than in alkaline medium. Obtained results are shown in Table 8. It was concluded that increase of current density increases the reaction rate constants of degradation [104].

Table 8. The values of reaction rate constants of 4,6-dinitro-2-methylphenol electro-oxidation in acidic medium depending on the applied current density [104]

Concentration of 4,6-dinitro-2-methylphenol, mg/l	Current density (i), mA/cm^2	Degradation rate constant (k), s^{-1}	Time required for removal of 4,6-dinitro-2-methylphenol, min
118	100	$1.6·10^{-4}$	200
	300	$3.7·10^{-4}$	160
	450	$5.0·10^{-4}$	140

Electrochemical oxidation of 2-, 3-, 4-methylphenol on BDD and PbO_2 anode was studied. It was determined that the same time is necessary to remove them from both types of investigated anodes [105]. A similar result was obtained in the work of Weiss et al., [106] where phenol electrochemical oxidation was examined. Yet BDD anode showed better properties due to more rapid removal of generated intermediate regarded to PbO_2 anode. Reaction values of phenol degradation rate constants are (k) 0.9, and 0.83 h^{-1} for BDD and PbO_2, respectively [106]. Degradation rate follows the order: 3-methylphenol > 2-methylphenol > 4-methylphenol. Increasing the removal rate of 3-methylphenol relative to the 2 - and 4-methylphenol may be due to lower stability of cationic radicals generated from 3-methylphenol. In addition, two *ortho*- and *para*- positions are available on 3-methylphenol for reaction with a reactive species, on 2-methylphenol, one *ortho*- and one *para*- position are available, while in the case of 4-methylphenol, two *ortho*- positions are available for the same reaction. The values of the reaction rate constants, and half reaction time of degradation, are shown in Table 9 [85].

Table 9. Half time of the reaction and reaction rate constants for cresol electrochemical oxidation, (2-, 3-, 4-methylphenol) at pH 9.0 and applied current density of 7.2 A/dm^2 [85]

Type of compound	Degradation rate constant (k), min^{-1} $·10^3$	$t_{1/2,}$ min
2-methylphenol	4.1	73.4
3-methylphenol	5.8	51.9
4-methylphenol	1.8	167.3

In the work of Murugananthan et al., [71] it was confirmed that degradation rate of phenolic compounds is dependent on the applied current density, where the increase of decomposition rate follows current density. The rate constant increases almost linearly with the increase of current density at constant initial concentration of 4,4'-(propane-2,2-diyl) diphenol, which indicates that process of degradation is bimolecular reaction between 4,4'-(propane-2,2-diyl) diphenol and $^{\cdot}OH$ radicals generated on BDD anode. The reaction follows kinetic of pseudo-first-order. However, other researchers [107] have argued that the degradation process of 4,4'-(propane-2,2-diyl) diphenol has complex kinetics, because of the competing reactions of $^{\cdot}OH$ radicals on the surface of BDD for the performance of parallel oxidation reactions with intermediate compounds.

6. CONCLUSION

Electrochemical oxidation process has proved to be an efficient technology and is suitable for the treatment wastewater. The advantage of direct oxidation reactions and indirect oxidation makes electrochemical oxidation an interesting treatment option for wastewater. The choice of the anode material is crucial as the specific interaction between the anode surface and the compounds in solution orients the degradation routes of these compounds.

The efficiency of the process depends on the nature of organic pollutants, on initial pH value and type of electrolyte. Degradation efficiency of phenols is related to the different positions of substituent group on the aromatic ring. It was found that substituent groups with electron donating ability are easier to remove than those with electron withdrawing groups.

The degradation of all phenols fitted the pseudo-first order kinetics.

The improvement of the electrochemical stability and electrocatalytic activity of the electrode materials is the basis for the direction for the future research, which will give better results and lower operational costs.

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