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The removal of chlorophenols from aqueous solutions using activated carbon adsorption integrated with H_2O_2 oxidation

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Abstract The removal of eight chlorophenols (2-CP, 3-CP, 4-CP, 2,3-DCP, 2,4-DCP, 2,5-DCP, 2,6-DCP and 2,4,6-TCP) using adsorption on activated carbon and adsorption in the presence of hydrogen peroxide was investigated. The influence of the pH, activated carbon dosage and hydrogen peroxide concentration were studied. The effects of the chlorine atom position and the chlorine content in the chlorophenol molecules on their degradation were also studied. The results revealed that the integration of the activated carbon and H_2O_2 treatment was more effective for the removal of the chlorophenols than using the activated carbon alone. The adsorption kinetics and adsorption efficiency increased with the increasing substitution of chlorine on the aromatic ring. The degradation rate and degradation efficiency of the chlorophenols using the activated carbon integrated with H_2O_2 decreased with the increasing chlorine atoms in the molecule. The combination of the activated carbon with hydrogen peroxide may significantly enhance the process and could offer an interesting alternative in wastewater treatment.

Keywords Chlorophenol · Activated carbon · Hydrogen peroxide · Adsorption

Introduction

Chlorophenols (CPs) are among the most widespread pollutants of wastewater and natural waters. The presence of chloroorganic compounds in the aqueous environment including drinking water [1, 2] is a consequence of their use in a variety of industrial processes such as wood, fibre, paint and leather preservatives, for the manufacturing of pesticides and resins as well as for water disinfection [3].

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Chlorophenols cause serious environmental problems, due to their high toxicity, strong odor emission, persistence in the environment and carcinogenic properties [4]. Thus, it is important to prevent their release into the environment and to study methods for their removal from contaminated sites.

Several methods are available for the removal of chlorinated phenols from water. Among them, biodegradation [5], oxidation by advanced oxidation processes [6] and adsorption [7, 8] are the most widely used. Advanced oxidation processes (AOPs) are based on the generation and use of powerful hydroxyl radicals ($^{\cdot}$OH) by means of chemical, photochemical or photocatalytic methods (Fenton, photo-Fenton, H_2O_2/O_3, H_2O_2/UV, UV/O_3, UV/TiO_2) [6]. Adsorption has proven to be one of the most attractive and effective methods for removing chlorophenols from water, due to its low maintenance costs, high efficiency, simplicity of operation as well as the no or lower generation of toxic substances. Activated carbons (AC) are now the most commonly used adsorbents of the proven adsorption efficiency for organic pollutants due to their high surface area, pore volume, and pore size distribution [7, 8]. Activated carbons have also been used as heterogeneous catalysts and supports of catalysts [9]. It is well known that the hydrogen peroxide can be activated by AC (Eqs. 1 and 2) forming reactive free radicals that are able to oxidize organic contaminants.

$$AC + H_2O_2 \rightarrow AC^+ + OH^- + \, ^{\cdot}OH \tag{1}$$

$$AC^+ + H_2O_2 \rightarrow AC + HO_2^{\cdot} + H^+ \tag{2}$$
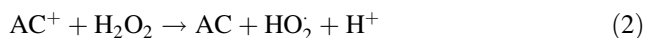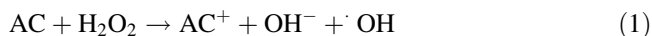
In recent years, several authors reported that H_2O_2 in the presence of activated carbon could oxidize some pollutants such as methyl *tert*-butyl ether [10], trichloroethene [10], fulvic acids [11], dyes [12, 13], paraquat [14], cyanide [15], ethylene glycol [16], ampicillin [17] and chlorophenols [10, 18–20].

The effectiveness of the organic compound degradation depends on many factors, including the pH, temperature, H_2O_2 concentration as well as the physicochemical properties of the activated carbons, which affect the decomposition of the hydrogen peroxide. The H_2O_2 decomposition on the activated carbon is followed by the exchange of a hydroxyl group at the AC surface with a hydrogen peroxide anion (Eq. 3). The formed surface peroxide is regarded as having an increased oxidation potential which enables the decomposition of another hydrogen peroxide molecule releasing oxygen and regenerating the activated carbon group (Eq. 4) [10].

$$AC-OH + H^+OOH^- \rightarrow AC-OOH + H_2O \tag{3}$$

$$AC-OOH + H_2O_2 \rightarrow AC-OH + H_2O + O_2 \tag{4}$$
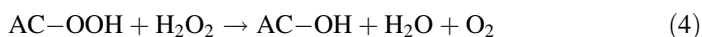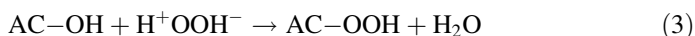
The degradation of the hydrogen peroxide depends on the nature of the activated carbon surface. The activated carbons of basic character promote a faster hydrogen peroxide decomposition whereas the presence of acidic surface oxygen groups inhibits the reaction [12, 18, 21]. Huang et al. [19] found that the decomposition of the H_2O_2 decreased with an increasing content of the acidic groups on the AC

surface. The catalytic activity of AC toward the 4-CP followed the inverse sequence of the activity toward the H_2O_2. The acidic functional groups on the AC surface, decreased the loss of the H_2O_2 and reduced the effect of surface scavenging resulting in the increase of the 4-CP degradation efficiency [19]. A similar phenomenon was observed in the oxidation of the 2-chlorophenol [20]. Lücking et al. [18] reported that the decomposition of H_2O_2 during the oxidation of 4-chlorophenol in the AC/H_2O_2 system was slower than in the absence of 4-CP. This fact was a consequence of the adsorption of 4-CP which reduces the surface area of the AC available for the decomposition of the hydrogen peroxide. The decreasing of the particle size of the activated carbon also accelerates the kinetics of the hydrogen peroxide decomposition [22]. The porosity of the activated carbons (the extended surface areas or large pore volumes) did not enhance the decomposition of H_2O_2, but in fact reduced it [19, 21]. Nevertheless, the catalytic activity of some carbonaceous materials (carbon blacks and carbon nanotubes) toward 2-CP was enhanced with an increase in the specific surface area of the catalysts [20].

In most of the works, the authors studied the oxidation by hydrogen peroxide in the presence of the activated carbon or compared the catalytic properties of various activated carbons. These studies, however, concern only one compound (comparative studies for several compounds were rare). The effectiveness of the AC/H_2O_2 process was investigated only for a few selected chlorophenols including 2-CP [20], 4-CP [18, 19] and 2,4,5-trichlorophenol [10]. However, to the best knowledge, the other chlorophenols were not studied and were not compared to each other.

The aim of this study was to investigate the adsorption as well as the adsorption integrated with the H_2O_2 oxidation of eight chlorophenols. The effects of the pH, activated carbon dosage and hydrogen peroxide concentration were studied. The effects of the chlorine atom position and chlorine content in the chlorophenols molecules on their degradation were evaluated and discussed.

Materials and methods

Chemicals and reagents

The chlorophenols: 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), 2,3-dichlorophenol (2,3-DCP), 2,4-dichlorophenol (2,4-DCP), 2,5-dichlorophenol (2,5-DCP), 2,6-dichlorophenol (2,6-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) were purchased from Sigma-Aldrich (St. Louis, USA). Sodium hydroxide, hydrogen peroxide (30 %), sulfuric acid (95 %), acetic acid (99 %) and HPLC-grade acetonitrile were from Avantor Performance Materials (Gliwice, Poland).

The L2S powdered activated carbon (Ceca, France) was used in this experiment. The specific surface area (S_{BET}), the micropore (V_{mi}) and the mesopore (V_{me}) volumes were 925 $m^2\,g^{-1}$, 0.245 and 0.235 $cm^3\,g^{-1}$ [23]. Prior to use, the activated carbon was dried in an oven at 120 °C to a constant weight and kept in a desiccator for further study.

Adsorption/oxidation procedure

The experiments were carried out in Erlenmeyer flasks containing 0.05 L of chlorophenol solution (0.5 mmol L^{-1}) as well as appropriate amounts of hydrogen peroxide and activated carbon at various pH (3–11) and an agitation speed of 200 rpm at 25 °C. The effects of the pH, activated carbon dosage and hydrogen peroxide concentration were investigated. These experiments were conducted only for the 3-chlorophenol. It was established that the best conditions for the degradation of 3-CP will be optimal also for the other chlorophenols. Aqueous samples were taken at different intervals of time and the concentrations of chlorophenols were measured by high performance liquid chromatography. The amounts of adsorption/oxidation at the time t (q_t, mmol g^{-1}) and at equilibrium (q_e, mmol g^{-1}) were calculated by the following equations:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{5}$$

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{6}$$

Here C_0, C_t and C_e are the initial concentration, concentration at time t and equilibrium concentration (after 6 h) of chlorophenol in the solution (mmol L^{-1}), V is the volume of the solution (L) and m is the mass of the activated carbon (g).

   All the experiments were carried out in triplicate under identical conditions and the average values were used for further calculations. The mean and standard deviation of the three replicates were reported and the data obtained were analyzed using t test and/or ANOVA with a Tukey test. The differences between any pair of the treatment means were tested using the least significant difference test with the significance level at 0.05.

Analytical method

The concentrations of the chlorophenols were measured by high performance liquid chromatography with UV detection (Shimadzu LC-20, Kyoto, Japan). The chromatographic conditions were as follows: mobile phase—acetonitrile/water adjusted to pH 3.0 with acetic acid (50/50, v/v), flow rate 0.25 mL min^{-1} and analytical wavelength 280 nm. The chromatographic analyses were carried out on a Phenomenex Luna C18, 2.0 × 150 mm, 3 µm column (Torrance, USA).

Results and discussion

In order to investigate the optimal chlorophenol degradation conditions, the effects of the pH, the activated carbon dosage and the hydrogen peroxide concentration were studied. 3-Chlorophenol was used as a model compound throughout the study.

Effect of pH

The effect of the pH on the 3-CP degradation was studied by varying the initial pH of the solutions from pH 3 to 11. The pH was adjusted (prior to the addition of the H_2O_2 and the AC) using 0.1 mol L^{-1} H_2SO_4 or 0.1 mol L^{-1} NaOH and was measured using a pH meter. The mass of the AC was fixed at 0.01 g and the initial concentrations of 3-CP and H_2O_2 were 0.5 and 5.0 mmol L^{-1}, respectively. The results are presented in Fig. 1.

For the description of the experimental data, the equations of the pseudo-first [24] (Eq. 7) and pseudo-second order [25] (Eq. 8) were considered.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{8}$$

Here k_1 is the pseudo-first order rate constant (h^{-1}) and k_2 is the pseudo-second order rate constant (g $mmol^{-1}$ h^{-1}). The values of k_1 and k_2 were calculated from the plots of $\log(q_e - q_t)$ versus t and t/q_t versus t, respectively. All of the results obtained from the pseudo-first order kinetic model were weaker in each case, and therefore they were not taken into account and are not shown. For the comparison and interpretation of the results only the pseudo-second order rate constants were used.

The degradation rate of the 3-CP decreased with an increase in the pH from 3 to 11. The k_2 values obtained for the initial pH solutions of 3, 5, 7, 9 and 11 were 0.775, 0.554, 0.513, 0.267 and 0.156 g $mmol^{-1}$ h^{-1}. As can be seen, the pH affects not only the degradation rate of 3-CP but also its effectiveness. After 6 h, at pH 3, about 80 % of 3-CP was removed while at pH 11 only 10 %.

Fig. 1 Effect of pH on the removal of 3-chlorophenol by AC/H_2O_2. Experimental conditions: [3-CP] = 0.5 mmol L^{-1}, [H_2O_2] = 5.0 mmol L^{-1}, AC = 0.01 g, temperature: 25 °C
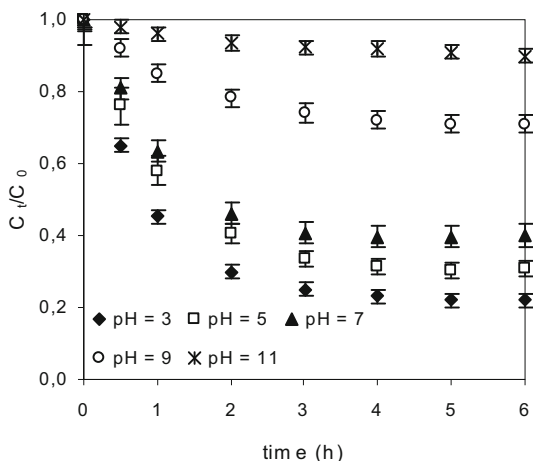
The relationship between the initial solution pH and the adsorption/oxidation of 3-CP at equilibrium (q_e) is presented in Fig. 2. For comparative purposes, the experiments of the 3-CP adsorption on the activated carbon in the absence of hydrogen peroxide were also carried out under the same conditions (Fig. 2).

The removal of the 3-CP in the absence of H_2O_2 was almost constant at the acidic pH range of 3-7 and decreased with the further increasing in the pH (from pH 7 to 11). The q_e value decreased with an increase in the pH from 3 to 11 from 0.997 to 0.190 mmol g^{-1}. This dependence is associated with the pK_a of the adsorbate (8.8) and pH$_{PZC}$ of the adsorbent. The point of zero charge (pH$_{PZC}$) was determined by the pH drift method and was found to be 7.0. At a pH greater than the pK_a value, 3-CP existed predominantly in anionic forms as a negatively charged phenolate anions. At the pH below the pH$_{PZC}$, the surface of the AC was positively charged, while at a pH greater than pH$_{PZC}$, the surface had a net negative charge. The results showed that the non-dissociated form of 3-CP was preferred by the positively charged surface of the activated carbon. The large reduction in 3-CP adsorption at highly basic conditions can be attributed to the electrostatic repulsion between the negatively charged AC and the dissociated 3-CP molecules. Similar results were reported for the adsorption of the 4-chlorophenol on the activated carbon prepared from rattan sawdust [26] and the Norit R3-ex granular activated carbon [27].

The influence of the pH on 3-CP removal by the AC/H_2O_2 is different, because the pH of the solution affects the nature of the chemical surface of the activated carbon but also the stability of the hydrogen peroxide. In acidic media, hydrogen peroxide is more stable; the higher decomposition is observed under the basic conditions. These facts explain the removal of 3-CP at different pH (Fig. 2). The results showed that 3-CP degradation using activated carbon and H_2O_2 decreased by increasing the pH. The best results were observed in the acid environment (pH 3) as a result of the higher stability and the higher *redox* potential of the hydrogen peroxide [18] as well as the high adsorption capacity of the activated carbon at low pH values. Similar observations (the most effective degradation of the 4-CP by AC/

Fig. 2 The relationship between the solution pH and the removal of 3-CP at equilibrium (after 6 h) on activated carbon (AC) and activated carbon in the presence of H_2O_2. Experimental conditions: [3-CP] = 0.5 mmol L^{-1}, [H_2O_2] = 5.0 mmol L^{-1}, AC = 0.01 g, temperature: 25 °C
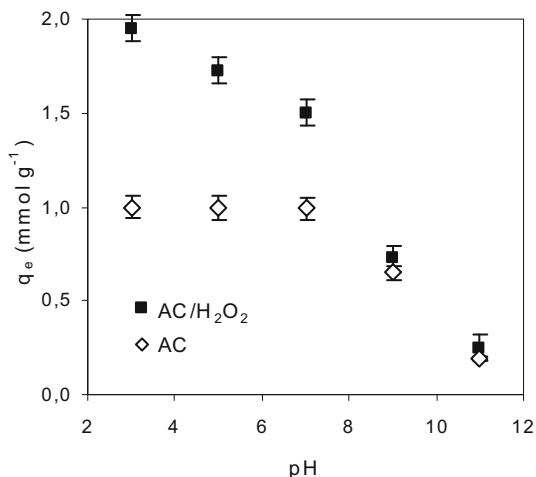
H_2O_2 at pH 3) have previously been described by Lücking et al. [18]. Khorramfar et al. [13] also reported that the Acid Red 18, Direct Red 80 and Reactive Red 194 dyes oxidation using the AC/H_2O_2 increased by decreasing the pH.

Since the lower pH favored the removal efficiency, in the following, chlorophenols degradation were studied at pH 3.

Effect of activated carbon dose

To investigate the effect of the activated carbon dosage on the chlorophenol degradation, different amounts of AC (0.005, 0.010, 0.015 and 0.020 g) were added to the Erlenmeyer flasks containing 0.05 L 3-CP solution (0.5 mmol L^{-1}) and hydrogen peroxide (5.0 mmol L^{-1}). The pH of the solution was set as 3.0 prior to the addition of the H_2O_2 and AC. The results are presented in Fig. 3.

The removal efficiency increased with an increase in the initial AC dosage from 50 % (0.005 g) to about 85 % (0.02 g). The degradation kinetics followed a pseudo-second order and the k_2 rate constants were found to increase with the AC dosage (0.281, 0.911, 1.522 and 1.788 g mmol^{-1} h^{-1} for the initial AC concentration of 0.005, 0.010, 0.015 and 0.020). An increase in 3-CP removal with the AC dosage can be attributed to the greater surface area and the availability of more adsorption sites. Moreover, the higher AC concentration leads to an increase in the number of active catalytic sites available for H_2O_2 decomposition.

Effect of H_2O_2 concentration

The effect of the hydrogen peroxide concentration was studied with an initial 3-CP concentration of 0.5 mmol L^{-1}, for different $[H_2O_2]/[3-CP]$ molar ratios equal to 1, 10, 50 and 100. The AC concentration was constant for all of the experiments (0.015 g) and the pH was 3.0. It can be observed in Fig. 4 that the removal efficiency of 3-CP raises with the increase of the H_2O_2 molar excess from 1 to 10. A

Fig. 3 Effect of activated carbon dosage on degradation of 3-CP using AC/H_2O_2. Experimental conditions: [3-CP] = 0.5 mmol L^{-1}, $[H_2O_2]$ = 5.0 mmol L^{-1}, pH = 3.0, temperature: 25 °C
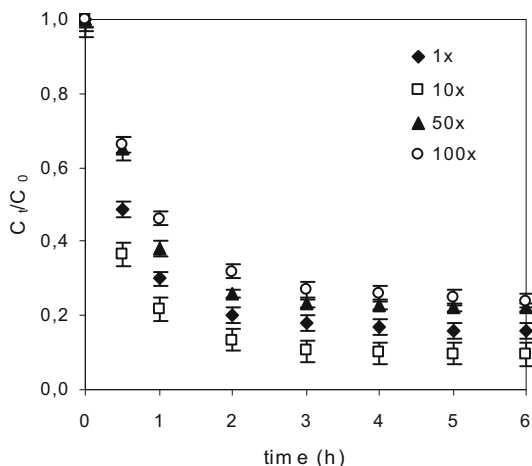
further increase of the H$_2$O$_2$ dosage did not achieve a higher removal rate and efficiency. For the molar ratios of 1, 10, 50 and 100, 3-CP removal after 6 h was 84, 91, 78 and 76 %, and the k_2 values were as follows: 2.430, 3.275, 1.522 and 1.223 g mmol^{-1} h^{-1}. These results agree with the earlier studies, which reported that an excessive concentration of hydrogen peroxide decreases the degradation efficiency of the organic compounds including ampicillin [17] and paraquat [14] by AC/H$_2$O$_2$. It may be due to the fact that some of the organic compounds and oxidation by-products were quickly removed by the adsorption and did not react with the H$_2$O$_2$, so they did not consume H$_2$O$_2$. Also, the more resistant by-products generated during the oxidation process could only be removed by the activated carbon, and as a result, a further increase of the H$_2$O$_2$ concentration did not improve the removal efficiency [17]. Dhaouadi and Adhoum [14] reported that the decrease in the oxidation efficiency observed at high H$_2$O$_2$ dosages may be due to its scavenging effect towards the hydroxyl radicals according to the following reactions:

$$H_2O_2 + \cdot OH \leftrightarrow HO_2^{\cdot} + H_2O \tag{9}$$

$$HO_2^{\cdot} + \cdot OH \leftrightarrow O_2 + H_2O \tag{10}$$
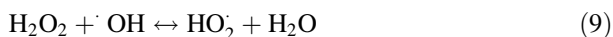
This phenomenon causes a dramatic loss of hydrogen peroxide leading to oxidation inefficiency [14]. A negative impact of the excessive H$_2$O$_2$ concentration has previously been described by Ku et al. [28] who studied the decomposition rate of the 3-CP by sonolysis in the presence of hydrogen peroxide. The degradation rate of 3-CP (20 mg L^{-1}) was kept high in the presence of 700 mg L^{-1} of H$_2$O$_2$. However, the degradation rate was slightly decreased for the experiment conducted with the presence of 1000 mg L^{-1} of hydrogen peroxide [28]. On that basis, a 5.0 mmol L^{-1} concentration of H$_2$O$_2$ was used for subsequent studies.
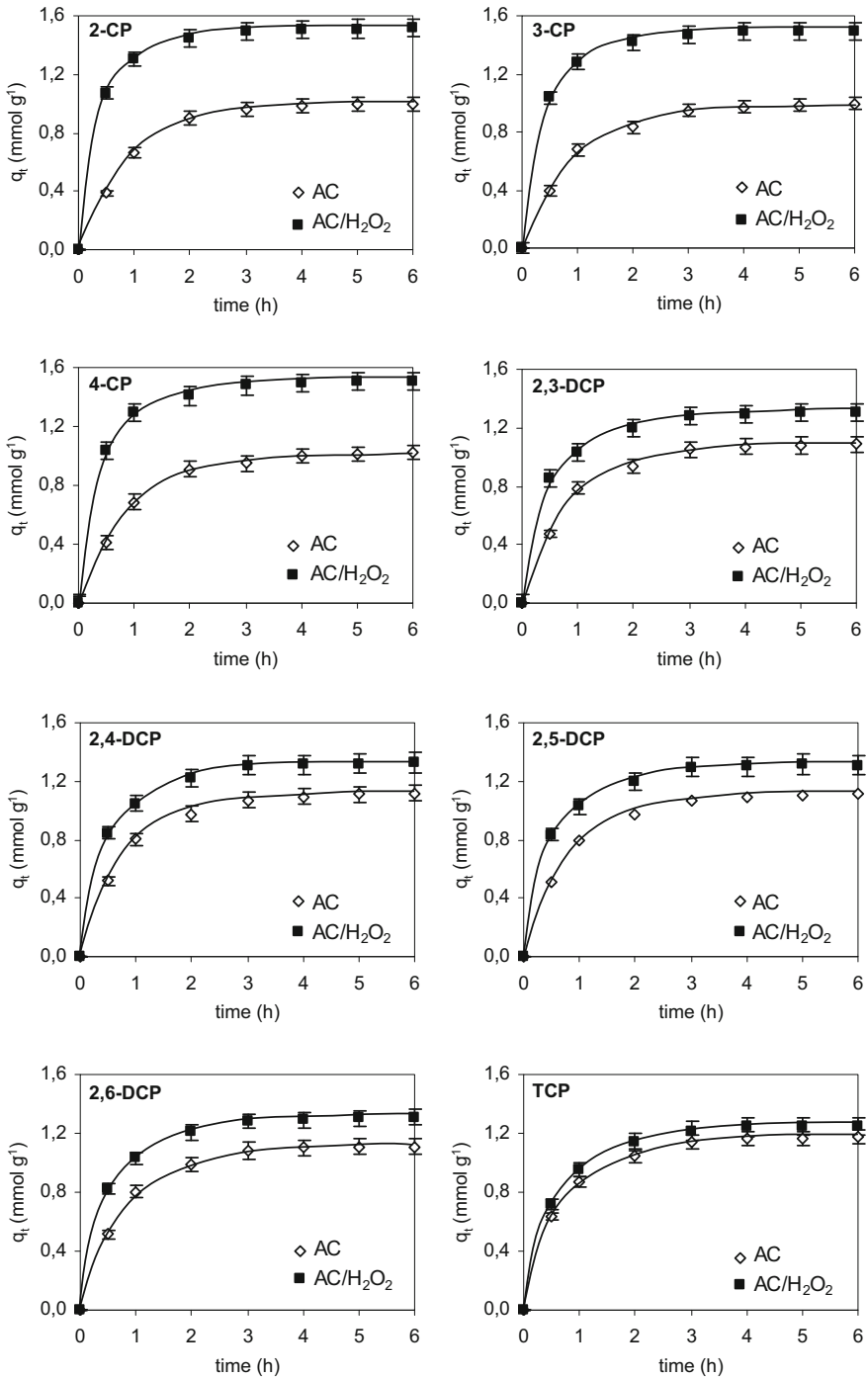
Removal of chlorophenols by AC and AC/H$_2$O$_2$

The removal efficiency and kinetics of eight chlorophenols in aqueous solution were investigated. The effects of the chlorine position and chlorine content in the chlorophenol molecules on their degradation were evaluated. All of the experiments were conducted under the same conditions (temperature 25 °C, agitation rate 200 rpm, pH 3.0, mass of the AC = 0.015 g, initial concentration of the CP = 0.5 mmol L^{-1}, initial concentration of H$_2$O$_2$ = 5.0 mmol L^{-1}). The non-catalytic oxidation with H$_2$O$_2$, the adsorption on the activated carbon, as well as the oxidation with H$_2$O$_2$ in the presence of the activated carbon were studied. The hydrogen peroxide decomposition by the activated carbon was not tested because in all of the experiments only one AC was used (L2S Ceca).

The oxidation of the chlorophenols with H$_2$O$_2$ in the absence of the activated carbon was not significant [data not shown]. During the considered period of time (6 h), the amounts of the CPs in the solution were constant. The concentrations varied ±3 %, which was due to the measurement error rather than the oxidation of the chlorophenols by the hydrogen peroxide. The removal of the chlorophenols by the AC and the AC/H$_2$O$_2$ as a function of time is presented in Fig. 5. The values of the k_2 kinetic constants, the q_e and percentage removal after 6 h are listed in Table 1.

The results revealed that the increasing of the degree of chlorine substitution on the phenol ring increased the adsorption rate and adsorption efficiency of the CPs on the activated carbon. The adsorption of the CPs increased in the order monochlorophenols < dichlorophenols < trichlorophenol, which was correlated with the respective increase in the molecular mass, hydrophobicity and the decrease in the solubility. Similar results were reported by other authors [29–32]. The differences in the k_2 and q_e values between the mono-, di- and TCP were statistically significant. However, the differences between the individual monochlorophenols (2-CP, 3-CP and 4-CP) as well as the dichlorophenols (2,3-DCP, 2,4-DCP, 2,5-DCP and 2,6-DCP) were not significantly different (ANOVA-Tukey test).

The combination of the activated carbon and hydrogen peroxide increased the removal of the chlorophenols in comparison with the single AC adsorption. The degradation order of the CPs by AC/H$_2$O$_2$ was 3-CP > 4-CP > 2-CP > 2,3-DCP ≥ 2,5-DCP ≥ 2,6-DCP ≥ 2,4-DCP > 2,4,6-TCP. For comparison, Tang and Huang [33] reported that the oxidation rates decreased in the order 3-CP > 2-CP > 4-CP > 2,5-DCP > 3,5-DCP > 2,3-DCP > 2,6-DCP > 2,4-DCP > 2,4,6-TCP for Fenton's reagent. The oxidation kinetics of the chlorophenols in the aqueous solution with the potassium permanganate followed the sequence 2-CP > 2,6-DCP > 4-CP > 2,4-DCP > 3-CP [34]. For the single photodecomposition produced by the polychromatic UV irradiation and oxidation by the combined UV/H$_2$O$_2$ system, Benitez et al. [35] found that the oxidation rates decrease in the order 4-CP > 2,4-DCP > 2,4,6-TCP. On the other hand, Hugül et al. [36] reported that the degradation order of CPs was 2,4,6-TCP ≥ 2,4-DCP > 2-CP for the UV-catalyzed oxidation with the H$_2$O$_2$. Zhou et al. [37] described the oxidation of the chlorophenols with the H$_2$O$_2$ catalyzed by the Cu–Al hydrotalcite/clay composite. They found that the content and position of the chlorine on the aromatic ring had

◄**Fig. 5** Degradation rate of chlorophenols by adsorption on activated carbon (AC) and adsorption/ oxidation using activated carbon in the presence of hydrogen peroxide (AC/H_2O_2). Experimental conditions: [CP] = 0.5 mmol L^{-1}, [H_2O_2] = 5.0 mmol L^{-1}, AC = 0.015 g, pH = 3.0, temperature: 25 °C

significantly different effects on the oxidation rate of the CPs, with the rate sequence of   3-CP > 2-CP > 4-CP > 3,5-DCP > 3,4-DCP > 2,5-DCP > 2,4-DCP > 2,6-DCP > 2,4,5-TCP. Simon et al. [38] investigated the effect of chlorine substituents on the oxidation of all 19 chlorophenols by cerium(IV). The oxidation rate constants of the chlorophenols (used in this paper only) decreased in the order 4-CP > 3-CP > 2,4,6-TCP > 2,5-DCP > 2,3-DCP ≥ 2-CP > 2,4-DCP > 2,6-DCP.   2,4,6-Trichlorophenol was removed faster than all of the dichlorophenols and 2-CP, but the authors found that 2,4,6-TCP showed a substantially different behavior than other chlorophenols. In general, the *ortho*- substitution decreased the reactivity, the *meta*- substitution had no significant effect on the reactivity while the *para*-substitution increased the reactivity in the cerium(IV) oxidation [38].

These examples suggest that the chlorine substitution on the aromatic ring could cause many different effects on the reactivity of the chlorophenols for the different oxidation methods.

Based on the results obtained in this work, it can be concluded that the reactivity of the chorophenols decreases with the increasing substitution of the chlorine on the aromatic ring. The oxidation of the monochlorophenols was faster than that of the dichlorophenols, which were oxidized more easily than the trichlorophenol. The differences between the mono- and di-, between mono- and tri- as well as between monochlorophenols and trichlorophenol were statistically significant (ANOVA-Tukey test). Increasing the degree of the Cl content decreases the solubility of the chlorophenols. As suggested by Tang and Huang [39], the increase in the hydrophobicity of the chlorophenols decreases the probability of the molecules encountered by the hydroxyl radical attack due to the non-dissolved CPs, resulting in an increase in the recombination rate of the hydroxyl radicals and, in consequence, a reduction in the oxidation rate of the organic compounds. Moreover, the increase of the chlorine atoms number in the molecules can block some favorable positions susceptible to the hydroxyl radical attack and, as a consequence, decrease the effectiveness of the chlorophenols oxidation [38].

The results showed also that the chlorine position of the chlorophenols has a significant effect on the degradation rate. The values of k_2 for 2-CP, 3-CP and 4-CP were 2.744, 3.294 and 2.982 g mmol^{-1} h^{-1}, respectively. At the 0.05 level, the differences of the k_2 values were significantly different. The removal of the 3-CP was faster than that of the 4-CP, which was degraded more easily than the 2-CP. The oxidation rate may be influenced by the interaction of the electron-withdrawing chlorine and the hydroxyl groups, the resonance of the phenolic anion and the steric effect of the chlorine. The attack of the free radicals is more favorable at the *ortho*- and *para*- positions of the benzene ring structure. The chlorine atom at the *ortho*-position strongly inhibits the oxidation of the C–OH to C=O by the steric hindrance effect; while the Cl atom at the *para*- position might inhibit the oxidation of the C–Cl to C=O by both the σ-electron withdrawing conductive effect and

Table 1 The kinetic (k_2) and equilibrium (q_e) constants of chlorophenols removal using activated carbon (AC) and activated carbon integrated with hydrogen peroxide (AC/H$_2$O$_2$)

CP	AC			AC/H$_2$O$_2$			
	k_2 g mmol^{-1} h^{-1}	q_e mmol g^{-1}	Removed (%)[a]	k_2 g mmol^{-1} h^{-1}	q_e mmol g^{-1}	Removed (%)[b]	Oxidized (%)[c]
2-CP	1.200 ± 0.043	1.161 ± 0.033	62.3	2.744 ± 0.065	1.576 ± 0.027	91.1	28.8
3-CP	1.189 ± 0.046	1.147 ± 0.028	60.2	3.294 ± 0.082	1.572 ± 0.019	90.5	30.3
4-CP	1.161 ± 0.008	1.138 ± 0.032	61.3	2.982 ± 0.080	1.561 ± 0.030	90.8	29.5
2,3-DCP	1.368 ± 0.032	1.213 ± 0.037	73.2	2.412 ± 0.111	1.382 ± 0.049	90.0	16.8
2,4-DCP	1.468 ± 0.055	1.233 ± 0.049	73.7	2.296 ± 0.071	1.386 ± 0.043	89.6	15.9
2,5-DCP	1.406 ± 0.056	1.239 ± 0.050	74.4	2.315 ± 0.092	1.404 ± 0.056	89.7	15.3
2,6-DCP	1.370 ± 0.028	1.247 ± 0.028	74.5	2.305 ± 0.104	1.391 ± 0.071	89.5	15.0
2,4,6-TCP	1.700 ± 0.048	1.281 ± 0.028	80.5	1.972 ± 0.076	1.340 ± 0.053	86.2	5.7

Experimental conditions: [CP] = 0.5 mmol L^{-1}, [H$_2$O$_2$] = 5.0 mmol L^{-1}, temperature 25 °C, pH = 3.0, AC = 0.015 g

[a] Amount of CP adsorbed after 6 h

[b] Amount of CP adsorbed/oxidized after 6 h

[c] Calculated from the difference: a − b

dechlorination [37]. Therefore, the higher degradation rate of the 3-CP is due to the fact that the benzene ring structure of the 3-CP provides one more site than those of 2-CP and 4-CP available for the free radical attack. A similar observation was reported by Tang and Huang [33] and by Zhou et al. [37]. Ku et al. [28] also reported that the decomposition rates of 3-CP by sonolysis were higher than those for the 2- and 4-chlorophenol. As shown in Table 1, 4-CP was removed faster than 2-CP by the AC/H_2O_2. 2-Chlorophenol was more resistant than 4-CP because 2-CP have some steric hindrance effect due to the closer location between the –OH and the –Cl groups on the aromatic ring than that on 4-CP [33].

The oxidation rate of the dichlorophenols depends on the directory effect of the –OH and the –Cl groups and the steric hindrance of the chlorine atoms [33]. The chlorine blocked at the *ortho-* position will decrease the dechlorination rate constants more than the chlorine atom blocked at the *meta-* position. The more Cl atoms existing on the aromatic ring especially at the *ortho-* and *para-* position makes the molecule more stable and more difficult for the oxidation [33]. The removal rate of the DCPs by the activated carbon in the presence of the H_2O_2 followed the sequence 2,3-DCP ≥ 2,5-DCP ≥ 2,6-DCP ≥ 2,4-DCP. The differences between all of the dichlorophenols were small and were not statistically significant.

It is found that 2,4,6-TCP was the most resistant to oxidation. This is due to the fact that the chlorine atoms in the molecule prevent the hydroxyl radical attack on the unoccupied sites of the aromatic ring.

The removal of the CPs by the AC/H_2O_2 was a combination of oxidation and adsorption. In general, the degradation of the chlorophenols by the activated carbon integrated with the hydrogen peroxide was more effective and faster in comparison with the single AC adsorption. The differences in the k_2 and q_e values between the same chlorophenols obtained during their removal on the activated carbon and on the activated carbon in the presence of H_2O_2 were statistically significant ($p < 0.05$). Only the q_e values obtained for the 2,4,6-TCP adsorption (1.281 ± 0.028 mmol g^{-1}) and the adsorption integrated with H_2O_2 (1.340 ± 0.053 mmol g^{-1}) were not statistically significant ($p = 0.166$).

The percentage removal of 3-CP, after 6 h, in the AC/H_2O_2 was 90.5 % (60.2 % of the 3-CP was adsorbed and 30.3 % was oxidized). Under the same experimental conditions, the removal of 2,4,6-TCP was found to be 86.2 % (80.5 % was adsorbed and 5.7 % was oxidized). This suggests that in the process, the adsorption played a dominant role.

The important part of the oxidative studies is identification of the oxidation products and intermediates. This is important because these compounds could also be toxic and moreover, their presence could affect the chlorophenols degradation rate and efficiency. A variety of reaction by-products were observed to form during the oxidation of chlorophenols (e.g. phenols, quinones, catechols) and the degradation pathways and mechanisms for many of the oxidation processes have been proposed [37, 40–44]. Unfortunately, in this work, during the oxidation experiments, the additional peaks on the chromatograms were not observed, suggesting that the oxidation intermediates were rapidly adsorbed on the activated carbon. The adsorption of the by-products formed during the oxidation of

chlorophenols in AC/H$_2$O$_2$ system was demonstrated by Huang et al. [19] who studied the relationship between the total reduction of 4-CP and dissolved organic carbon in suspension. They found that the decrease of dissolved organic carbon was similar to the total reduction of 4-CP, indicating that the chlorophenol and its oxidation by-products were almost adsorbed further onto activated carbon surface [19].

Conclusions

The removal of eight chlorophenols by the adsorption on the activated carbon and using activated carbon in the presence of H$_2$O$_2$ was investigated. The effects of the operational parameters including the pH, activated carbon dosage and hydrogen peroxide concentration were studied. The influence of the chlorine position and the chlorine content in the chlorophenol molecules on their degradation were also studied. The results showed that the increasing of the degree of the chlorine substitution on the phenol ring increased the adsorption kinetics and the adsorption efficiency of the CPs on the activated carbon with the rate sequence of monochlorophenols < dichlorophenols < trichlorophenol. The integration of the activated carbon and the H$_2$O$_2$ treatment was more effective for the removal of the CPs than using the activated carbon alone. The chlorine content and the position on the aromatic ring had a significant effect on the chlorophenols removal. 3-CP was removed faster and more effectively than 4-CP, which was oxidized more easily than 2-CP. The CP degradation rate and degradation efficiency decreased with the increasing substitution of the chorine on the aromatic ring (mono- > di- > trichlorophenol). The combination of both the adsorption and the heterogeneous catalysis (AC/H$_2$O$_2$) could be used as an eco-friendly process for wastewater treatment.

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