Electrochemical Dechlorination of 2-Chlorophenol on Pd/Ti, Ni/Ti and Pd-Ni Alloy/Ti Electrodes

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The 2-chlorophenol has been treated by advanced oxidation processes (AOPs) and by electrochemical oxidation, but these methods show several disadvantages, such as: high-energy costs, hazardous substances production and electrode deactivation. To avoid the problems caused by oxidation, electrochemical reduction (dechlorination) was proposed as an alternative and promising method. Pd/Ti, Ni/Ti and Pd-Ni alloy/Ti cathodes were used for electrochemical dechlorination of 2-chlorophenol. The cathodes were prepared by electrodeposition under experimental conditions determined from both a thermodynamic study by using predominance existence and distribution species diagrams and a voltammetric study. The electrodes were characterized by SEM, XRD, and XPS. SEM images showed that Pd-Ni/Ti electrode has a different morphology from that of Pd/Ti and Ni/Ti electrodes and the alloy composition is 45% Pd and 49% Ni mol. XRD analyses showed that Pd-Ni alloy/Ti exhibits a network parameter different from those of Pd/Ti and Ni/Ti electrodes. The XPS formation of the formation of Pd-Ni alloy. The efficient dechlorination of 2-chlorophenol to phenol was achieved under electrochemical conditions where proton reduction and atomic hydrogen adsorption took place. The Pd-Ni alloy/Ti electrode had the highest dechlorination efficiency (100% removal) and phenol formation (100% formation) at a potential of −0.40 V vs Ag/AgCl/KCl sat.

2-Chlorophenol (2-CP) is a toxic, recalcitrant compound that has been classified as a priority pollutant by the United States Environmental Protection Agency (USEPA).1,2 Nowadays, the accumulation of this chlorinated aromatic compound in the environment is an urgent problem that needs solving. 2-CP is very slowly consumed by microorganisms and is difficult to treat with conventional microbiological technologies.1 One alternative is incineration that involves high costs and causes chemical transformations that produces hazardous substances such as dioxins and polychloro biphenyls. Advanced oxidation processes (AOPs), such as Fenton’s reagent, ozone, UV, UV/H2O2, and UV/Fenton have been studied for the purpose of degrading chlorinated organic compounds; however, the efficiency of these processes requires choosing adequate, but high-cost, catalytic materials.3,4 Another method explored for chlorinated organic compound degradation is electrochemical oxidation; however, the production of a polymer film at the electrode surface causes electrode deactivation.5 In electrochemical oxidation, organic compounds can be oxidized up to carbon dioxide using a Boron Doped Diamond (BDD) electrode, but the electrode preparation is quite costly.6 In order to avoid the problems caused by oxidation, electrochemical reductive dechlorination has been suggested as an alternative and promising method, because of several advantages, such as: rapid reaction, low-cost equipment, operating at room temperature and atmospheric pressure, and no production of secondary pollutants more toxic than the original.7,8 Electrochemical dechlorination is an indirect reaction known as electrocatalytic hydrogenolysis (ECH).9 In a ECH mechanism, the chemisorbed hydrogen atoms (Hads) generated on the electrode surface by water electrolysis provide the driving force for chemical reduction causing the C-Cl bond cleavage from 2-CP. ECH involves several steps as described in reactions 1 through 610,11,12:

\[2H_2O + 2e^- + M \rightarrow 2H_{ads}M + 2OH^-\]  
\[R - Cl + M \rightarrow (R - Cl)_{ads}M\]  
\[(R - Cl)_{ads}M + 2H_{ads}M \rightarrow (R - H)_{ads}M + (H - Cl)_{ads}M\]  
\[(R - H)_{ads}M \rightarrow R - H + M\]  
\[(H)_{ads}M + H_2O + e^- \rightarrow H_2 + O^- + M\]  
\[(H)_{ads}M + (H)_{ads}M \rightarrow H_2 + M\]  

where M represents the electrocatalytic metal or alloy.

The key steps of the ECH process are proton reduction (H⁺) and hydrogen adsorption (Hads) (reaction 1). The adsorbed hydrogen reacts in two different ways: the 2-CP reduction to phenol (reactions 3 and 4) and the electrochemical/chemical H₂ formation (reactions 5 and 6). H₂ generates a layer on the electrode surface inhibiting mass transfer of 2-chlorophenol to the catalysts, decreasing the activity of the ECH.13 Thus, nature and surface characteristics of the electrode material and potential at which the reduction takes place are of paramount importance in electrochemical dechlorination efficiency.14 Palladium (Pd) is considered the ideal for electrochemical dechlorination due to its capacity in hydrogen adsorption, but the preparation of pure palladium electrodes are high costs.15 An alternative that has been proposed is the use of alloys capable of reducing the proton (H⁺) and adsorbing hydrogen (Hads) on the surface. Sun et al. (2012)12 observed that a Pd-Ni/Ti electrode could perform electrochemical dechlorination of 2,4-dichlorophenol, generating phenol and cyclic non aromatic hydrocarbons as final products. However, these authors neither described the experimental conditions for electrodeposition of Pd-Ni alloy nor the influence of reduction potential on dechlorination efficiency. Therefore, it is of special interest to investigate more on the electrochemically dechlorination capacity of alloy electrodes for degrading chlorinated organic compounds at high process efficiency.

In the present work, a thermodynamic study was included to establish experimental conditions, such as pH and NH₄Cl concentration at which ammonia complexes of Pd and Ni are present in electrodeposition baths, and to prevent the formation of insoluble toxins that hinder the electrodeposition. The potentials to prepare Pd/Ti, Ni/Ti, and Pd-Ni/Ti electrodes were established as well. These electrodes were characterized by cyclic voltammetry, SEM, XRD and XPS, and
their performance in 2-CP dechlorination was analyzed in a comparative study that allowed establishing the influence of nature surface electrode and reduction potential on the process efficiency.

**Experimental**

**Chemical products and experimental materials.** — Chemical products and materials included ethanol (CH₃CH₂OH) (98%, J.T. Baker), dihydrated palladium sulfate (PdSO₄·2H₂O) (99.999%, Alfa Aesar), hexahydrated nickel sulfate (NiSO₄·6H₂O) (99.9%, J.T. Baker), ammonium chloride (NH₄Cl) (99.9%, J.T. Baker), hydrochloric acid (HCl) (36%, J.T. Baker), sulfuric acid (H₂SO₄) (99%, J.T. Baker), sodium hydroxide (NaOH) (J.T. Baker), sodium sulfate (Na₂SO₄) (J.T. Baker), oxalic acid (99.6%, J.T. Baker), Millipore-Q water and titanium (Ti) plates.

**Preparation and characterization of Pd, Ni and Pd-Ni electrodes.** — Titanium plates were subjected to surface pretreatment by sandblasting (steel balls); afterwards, they were rinsed with Millipore-Q water in an ultrasound bath, washed with oxalic acid 10% w/w at 70 °C to remove oxides from the surface, rinsed again in an ultrasound bath with Millipore-Q water, and stored in ethanol for later use.

Three electrodeposition baths were prepared: palladium bath, nickel bath and palladium-nickel alloy bath. Palladium and nickel electrodeposition baths were prepared by dissolving separately PdSO₄·2H₂O and NiSO₄·6H₂O in 1.2 M HCl solution and by adding NH₄Cl salt under constant stirring. For palladium-nickel alloy bath, PdSO₄·2H₂O was dissolved together with NiSO₄·6H₂O in 1.2 M HCl solution and NH₄Cl under constant stirring. In all cases, the concentrations of Pd(II) and Ni(II) were 38 mM and 120 mM, respectively, and the baths’ pH was adjusted at 8.5 with sodium hydroxide.

The deposits were prepared on titanium plates of 2.4 cm² geometric area in a glass cell under constant potential conditions: −0.95 V vs. Ag/AgCl/KCl(sat) for palladium bath, −1.30 V for nickel bath and −1.25 V for bimetallic Pd-Ni bath. In all cases, the deposition time was 20 minutes and the deposition bath was stirred with a magnetic stirrer at 50 rpm. Then, the electrodes were rinsed with Millipore-Q water to eliminate the remaining electrolyte.

Voltammetric studies were carried out using PAR 273 A type potentiostat/galvanostat with a conventional three-electrode system to determine electrodeposition parameters and characterize the formed electrodes as well as for potentiostatic formation of the electrodes. A graphite bar was used as counter electrode and an Ag/AgCl/KCl(sat) electrode as reference. Working electrodes for electrochemical studies were the previously prepared Pd/Ti, Ni/Ti and Pd-Ni/Ti electrodes.

The H⁺ reduction and hydrogen adsorption were performed using 0.1 M H₂SO₄ solution. The electrodes were characterized in terms of morphology, composition and crystal structure. Surface morphology and elemental composition were observed and analyzed through scanning electron microscopy (SEM) in a JEOL ultrahigh resolution field emission electron microscope JSM-7800 F, with 15 kV accelerating voltage and 10.1 mm WD. The qualitative elemental analysis of electrodes’ surface was performed with an integrated system for energy dispersive X-ray spectroscopy (EDX), EDA/AMETEK Apollo X with a 30 mm² silicon drift detector (SDD). Crystal structure of electrodeposition was analyzed by X-ray diffraction (XRD) using a Siemens D-500 Kristalloflex apparatus. In addition, X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer provided with a monochromatized AlKα X-ray source (1.487 V). XPS wide and narrow spectra were collected using an X-ray spot size of 400 μm² at 160 and 60 eV pass energy, respectively. The surface of the samples was ion beam etching (IBE) cleaned with Ar at ion acceleration potential of 3.0 keV for 3 min in order to remove the major part of the oxide layer before XPS testing.

**Electrochemical dechlorination of 2-chlorophenol.** — Electrocatalytic activities of the prepared electrodes were evaluated for 2-CP degradation. The experiments were carried out in a cell array split in two half-cells by a salt bridge (Figure 1) that was utilized to prevent chloride ion (Cl⁻), generated on the cathode during dechlorination process, from being transported to the anode surface to form Cl₂ or to prevent 2-CP oxidation. The 2-CP electrolysis at a controlled potential was performed at room temperature using Pd/Ti, Ni/Ti and Pd-Ni/Ti electrodes as cathode and a graphite rod as anode. During dechlorination, the electrolyte was stirred with a magnetic bar at 200 rpm. The electrolyte volume in the cathodic compartment was 60 mL in aqueous solution containing 0.1 M H₂SO₄ and 50 mM Na₂SO₄, whereas the 2-CP concentration was 50 mg L⁻¹ (0.388 mM). 2-CP and phenol were analyzed by high performance liquid chromatography (HPLC) (Perkin Elmer 200 UV series), with a C-18 column (Phenomenex), acetonitrile-water (60:40 v/v) as mobile phase and a flow rate of 1.5 mL min⁻¹. Phenolic compounds were detected at 274 nm.

**Results and Discussion**

**Thermodynamic study.** — For the purpose of determining the pH and NH₄Cl concentration necessary for the formation of Ni(II) and Pd(II) complexes with ammonium that prevent formation of insoluble species in electrodeposition baths, a thermodynamic study was carried out using species predominance-zone diagrams (PZDs) and distribution diagrams. PZDs were built with The Chemical Equilibrium Software (MEDUSA), in ammoniacal medium, in the presence of Cl⁻ and SO₄²⁻ considering the following concentrations: Pd(II) = 0.038 M, Ni(II) = 0.12 M, Cl⁻ = 4 M, SO₄²⁻ = 0.035 M (Figure 2), where Pd(II) and Ni(II) concentrations are eight times higher than those proposed by Sun et al. (2012) meanwhile Pd(II)/Ni(II) concentration ratio is similar. In the case of Ni(II), the Ni(II)-NH₃ complexes form at pH above 8 and at higher concentrations of 2M NH₄Cl (Figure 2a); whereas the Pd(II)-NH₃ complexes form at pH above 6 and at the entire range of NH₄Cl concentrations considered herein (Figure 2b). PZDs only show predominant chemical species (more important fraction) in a given concentration zone; however, it is also necessary to know the fraction of other species in the solution that may affect the processes to be studied. Diagrams of the fraction of Ni(II) and Pd(II) chemical species were plotted at pH 8.5. The nickel fraction diagram (Figure 2c) shows that for a total Ni(II) concentration of 120 mM, the NH₄Cl concentration must be above 2.4 M to prevent the formation of Ni(OH)₂ solid and at such concentrations, the ammonia complexes Ni(NH₃)₄²⁺ and Ni(NH₃)₆⁺ present the greatest fractions, 50% and 30% respectively, followed by lower fractions of Ni(NH₃)₄²⁺ and Ni(NH₃)₆⁺ complexes. For palladium (Figure 2d), the diagram shows that at concentrations above 0.25 M NH₄Cl, the Pd(NH₃)₄²⁺ complex with 100% fraction predominates. Taking into account that ammonia complexes of Pd(II) and Ni(II) ions allow controlling the process of electrodeposition, the conditions established for electrodeposition baths of Ni(II), Pd(II) and Ni-Pd
alloy in this study were: 120 mM Ni(II) and 38 mM Pd(II) in solutions with NH₄Cl concentration of 2.5 M and pH 8.5.

**Electrodeposition potential selection.**—The selection of the potential for electrodeposition and formation of catalytic deposits was carried out using a voltammetric study in different electrodeposition baths containing Pd(II), Ni(II) and Pd(II)-Ni(II) under the following conditions: 38 mM Pd(II), 120 mM Ni(II) and 38 mM-120 mM Pd(II)-Ni(II), pH 8.5 and 2.5 M NH₄Cl, on a titanium rotating disc electrode (A = 1.2 cm²) with constant 100 rpm stirring. When the potential scan for Pd(II) and Ni(II) baths (Figures 3a and 3b) is initially conducted in the cathodic direction, reduction peaks c₁ and c₂ appear at potentials (Epc) of −0.95 V and −1.30 V, respectively, which are attributed to the reduction process of Pd(II) and Ni(II) species, respectively. However, when the potential is reversed, oxidation peaks a₁ and a₂ appear at potentials of −0.20 V (Epa₁) and −0.40 V (Epa₂) that are attributed to the oxidation process of reduced species deposited on titanium surface.

Figure 3c shows the voltammogram corresponding to the Pd(II)-Ni(II) alloy bath. When the potential scan is started in the cathodic direction, just one reduction peak c₃ appears at Epc₃ = −1.25 V, and this potential is close to that obtained in Ni(II) bath (−1.30 V); however, no reduction peak of Pd(II) arises. Upon reversing the potential scan in the anodic direction, only one oxidation peak, a₃, arises at Epa₃ = −0.35 V. Such behavior may indicate the formation of Pd-Ni alloy, ruling out the independent deposition of Ni and Pd. In order to prove this hypothesis, deposits of each metal were prepared using reduction potentials at which the process is controlled by diffusion in the corresponding electrolytes (Figure 3). Once the deposits were formed on titanium plates (electrodes), they were characterized by different spectroscopic and electrochemical techniques.

**Electrodeposition and characterization of Pd, Ni and Pd-Ni alloy on titanium plates.**—The deposits of Pd/Ti, Ni/Ti and Pd-Ni alloy/Ti were prepared potentiostatically on titanium plates of 2.4 cm², at potential of −0.95, −1.30 and −1.25 V, respectively, and under constant solution stirring of 50 rpm with a magnetic bar for 20 min. During the time of electrodeposition, the current remained constant, indicating that the concentration of electroactive species was not significantly modified during the electrolysis.

An important aspect of electrochemical dechlorination is the electrode surface because of its influence on H⁺ reduction and H adsorption. Figure 4 shows SEM images of the different prepared electrodes. The Pd/Ti electrode (Figure 4a) shows a densely dendritic coating composed of large continuous agglomerates, whereas the Ni/Ti electrode (Figure 4b) has a uniform deposit all over the surface. Lastly, the morphology of the electrode formed in the bath containing Ni(II) and Pd(II) (Figure 4c) is similar to that of Pd/Ti electrode and its coating composed of large continuous agglomerates, but in this case the agglomerates are much larger than in Pd/Ti. After elemental analysis by EDS made on Pd/Ti and Ni/Ti electrodes (Figures 4d and 4e), ZAF method was used to determine their composition consisting of 87% Pd and 85% Ni mol, respectively. The presence of oxygen was detected on both electrodes, 12% and 15% mol in the Pd/Ti and Ni/Ti electrodes respectively, because of the layer of palladium and nickel oxides formed on the surface of electrodeposits, corroborated by XPS analysis (see below). The electrode formed in the bath containing both Ni(II) and Pd(II) (Figure 4f) was estimated to have the composition of
Figure 3. Polarization curves ($v = 20 \text{ mV/s}$) obtained on a Ti rotating disc (1.2 cm$^2$) (100 rpm) in electrodeposition baths: a) Pd(II), b) Ni(II) and c) Pd(II)-Ni(II)). The potential scan is started in the negative direction from OCP (−0.35 V, 0.14 V and −0.4 V, respectively).

45% Pd and 49% Ni mol of palladium and nickel, respectively. This proved that deposition of both metals was accomplished in the Pd(II)-Ni(II) bath at a potential of −1.25 V. Likewise, as in the previous case, the presence of the oxygen peak in EDS spectrum gave proof of the presence of a layer of oxides with 6.2% mol oxygen content.

Then, images obtained by back-scattered electron detector (SEM-BSE) were used to determine the distribution of oxygen, nickel and palladium in the different aggregates that make up the surface of the electrodes. Figure 5a shows the SEM-BSE image of Pd-Ni/Ti alloy exhibiting white and gray zones that were associated with the presence

Figure 4. SEM-EDS analysis of cathodes prepared by electrodeposition; upper images show wide view micrographs obtained at 15 kV and WD: 10.1 mm: a) Pd/Ti, b) Ni/Ti and c) Pd-Ni/Ti. Lower images display EDS spectra with all major peaks identified; d) Pd/Ti, e) Ni/Ti and f) Pd-Ni/Ti.
Figure 5. a) SEM-BSE image of Pd-Ni/Ti electrode, two different zones are indentified where EDS spectra were obtained; b) and c) EDS spectra and elemental composition of zones 1 and 2, respectively.

of higher and lower average atomic numbers (Z), respectively. Thus, white-colored aggregates are mainly made up of a metallic phase (zone 1) whereas darker aggregates are richer in oxygen (zone 2). The above findings were corroborated by punctual EDS analyses carried out in each of these zones (Figures 5b and 5c).

Crystal structure.— Crystal structure of the electrodes was established by obtaining X-ray diffraction patterns (Figure 6). The diffraction of crystal faces taking place on the electrodes (Pd-Ni/Ti, Pd/Ti, Pd-Ni/Ti) coincides with the orientation of (111) and (200) planes that are associated with a body-centered cubic structure (BCC). Diffractograms were used to calculate d-spacing for (111) plane of each electrode (Table I). Network parameter of Pd-Ni alloy is between the values of Pd and Ni, higher than that of Ni and lower than Pd’s which demonstrates that a change in the crystal lattice occurs during formation of Pd-Ni/Ti electrode.

X-ray photoelectron spectroscopy.— In order to corroborate the formation and homogeneity of Pd-Ni alloy on Ti electrode, three measurements at different spots on the electrode surface were taken and employed to obtain XPS wide and narrow spectra. To remove the major part of metallic oxide formed by exposure of electrodes to air, the sample underwent an IBE in a vacuum chamber for 3 minutes. XPS wide spectra of Pd-Ni/Ti electrode before and after IBE are shown in Figure 7a, where besides different signal features, C1s, Pd3d, O1s and Ni2p main peaks are distinguishable and identifiable. Figure 7b shows the evolution of Ni2p region after different IBE stages (level 0, without IBE) and how an appreciable decrease in oxide and satellite signals is observed while the metal peak increases in intensity.

For a more detailed determination of oxidation states and composition of Pd-Ni chemical species formed on the alloy electrode, analysis was performed by decomposition-based modeling of the high-resolution XPS narrow scans for Pd3d. To detect and compensate the charge shift of the core level peaks, O1s peak position at 531.0 eV was used as an internal standard instead of C1s. The foregoing was done because carbon is neither the main component nor it forms continuous and homogeneous layers over the electrode surfaces.

Table I. Determination of d-spacing by XRD.

| Electrodes   | d-spacing value of (111) | d-spacing value of (111) |
|--------------|-------------------------|-------------------------|
|              | plane (experimental)     | plane (reported)<sup>a</sup> |
| Pd/Ti        | 2.2321                  | 2.2460                  |
| Ni/Ti        | 2.0285                  | 2.0340                  |
| Pd-Ni/Ti     | 2.1350                  | -                       |

<sup>a</sup>From JCPDS<sup>17</sup> file 5-681 (Pd) and 4-850 (Ni).
Figure 7. a) XPS wide spectra, before and after IBE, of Pd-Ni alloy film previously deposited on Ti electrode, where main regions for C1s, Pd3d, O1s and Ni2p are indicated; b) Ni2p XPS core-level spectrum evolution during IBE processes (level 0, without IBE).

doublet spectra were fitted using a Gaussian–Lorentzian mix function and Shirley background subtraction.

XPS narrow scan of Pd3d doublet spectrum (Figure 8) shows that 3d_{5/2} and 3d_{3/2} were fitted with three double contributions. One is metallic palladium at 336.7 ± 0.2 eV and 341.0 ± 0.2 eV for Pd3d_{5/2} and 286 Pd3d_{3/2} peaks, respectively. The second contribution corresponds to palladium oxide where Pd3d_{5/2} is located at 335.1 ± 0.2 eV and Pd3d_{3/2} at 340.4 ± 0.2 eV. The third contribution is for Pd3d_{5/2} and Pd3d_{3/2} related to Pd-Ni alloy, which are located at 335.7 ± 0.2 eV and 341.0 ± 0.2 eV, respectively. These latter peaks show the major contribution of the total peaks (Figure 8), which confirms the formation of the Pd-Ni alloy formation.

Hydrogen adsorption.— The study of H⁺ reduction and H adsorption on Ni/Ti, Pd/Ti and Pd-Ni alloy/Ti electrodes (2.4 cm² area) was carried out by cyclic voltammetry in 0.1M H₂SO₄ solution stirred at 200 rpm (Figure 9). The potential scan started in the negative direction. Pd/Ti and Ni/Ti electrodes showed that the current increases as the potentials are more negative, and this increase corresponds to the process of proton reduction. Upon reversing the potential scan in the positive direction, peaks a₄ and a₅ arise at potentials Eₚₐ₄ and Eₚₐ₅ of 0.25 V and 0.38 V, respectively (Figures 9a and 9b); these peaks, absent in the case of the scan initially done in the positive direction, correspond to the oxidation of hydrogen (Hads) that was adsorbed (Hads) on the surface of the electrodes in the direct scan.²¹

In the case of Pd-Ni/Ti alloy (Figure 9c), hydrogen reduction-oxidation process is totally different from that occurred on separate metals, since independent deposition of Pd and Ni is ruled out, and interaction between the metals (alloy) is confirmed. In this case, two well-defined reduction peaks, c₄ and c₅, appear at potentials Eₚₐ₄ and Eₚₐ₅ of −0.15 V and −0.30 V, respectively. These peaks are attributed to H⁺ reduction to form H₂ in two different crystal planes; whereas at a potential scanned to more negative values, the current continues to increase due to reduction of the medium and the evolution of H₂. When the potential is reversed in the anodic direction, two oxidation peaks, a₆ and a₇, appear at potentials Eₚₐ₆ and Eₚₐ₇ of −0.1 V and −0.028 V, respectively, which are attributed to the oxidation of adsorbed hydrogen (Hads). According to the results obtained by XRD characterization, the Pd-Ni alloy exhibits two (111) and (200) planes in which the process of Hads adsorption is more important (higher reduction peaks) than in the same planes of pure metals. Thus, at −0.15 V and −0.30 V potentials or those more negative than −0.30 V, the presence of adsorbed hydrogen is ensured in order to carry out the dechlorination of 2-CP.

Electrochemical dechlorination of 2-chlorophenol.— To establish the electrode nature and potential influence on the efficiency of electrochemical dechlorination, electroreduction of 2-CP was carried out in a cell array split into two half-cells by a salt bridge (Figure 1), the following conditions were set: potentials that ensure the presence of Hads (−0.30 V, −0.40 V and −0.60 V, marked in Figure 9), 180-minute electrolysis and 200 rpm constant stirring. Equations 7 and 8 show the reactions carried out for indirect dechlorination of 2-CP. According to Equation 8, one mol of 2-CP is transformed into one mol of phenol, i.e.,, for every 50 mg of 2-CP, 36.6 mg of phenol are produced.

\[
H_3O^+ + e^- + M \rightleftharpoons H_{ads/mol} + H_2 \tag{7}
\]
Figure 9. Cyclic voltammograms (v = 20 mV/s) obtained for a) Pd/Ti, b) Ni/Ti and c) Pd-Ni/Ti electrodes (A = 2.4 cm²) in 0.1 M H₂SO₄ solution. The potential scan is started from corresponding OCP (0.4 V, −0.2 V and −0.22 V, respectively, vs. Ag/AgCl(s)/KCl(sat)) in the negative (continuous line) and positive (dotted line, inset) directions. Potentials at which 2-CP dechlorination is carried out (−0.3, −0.4 and −0.6 V vs. Ag/AgCl(s)/KCl(sat)) are indicated in each voltammogram.

\[ 2H_{ads} + 2 - \text{chlorophenol} \leftrightarrow \text{phenol} + 2M + HCl \]  

The efficiency of dechlorination and phenol formation is obtained in the following manner:

\[
\text{2-CP removal (\%)} = \frac{2CP_0 - 2CP_f}{2CP_0} \\
\text{phenol formation (\%)} = \frac{P_f}{P_0} \times 100
\]

Where:

\(2CP_0\) = initial 2-chlorophenol concentration
\(2CP_f\) = final 2-chlorophenol concentration
\(P_0\) = stoichiometric formed phenol concentration (theoretical)
\(P_f\) = final formed phenol

Table II shows the results of dechlorination with the three electrodes at different electrolysis potentials. In the case of Ni/Ti electrode, the 2-CP removal, phenol formation was practically independent of the imposed potential. The 2-CP removal was 51% at the three potentials imposed, whereas phenol formation efficiency kept lower than 18% with respect to stoichiometry, Equation 8, so nickel was not a good catalyst to carry out electrochemical dechlorination of 2-CP. For Pd/Ti and Pd-Ni/Ti electrodes, the potential had an effect on the efficiency of 2-CP removal, being higher at more negative potentials. On the Pd/Ti electrode, 2-CP removal reached 60%, which could be associated with the fact that H_{ads} is absorbed in the bulk of palladium decreasing the amount of H_{ads} available on the surface to carry out the complete dechlorination of 2-CP. In the case of Pd-Ni alloy/Ti electrode, the 2-CP removal reached 100% because the imposed potentials ensure the existence of H_{ads} on the surface (as shown in Figure 9c), and the amount of H_{ads} absorbed in the bulk of Pd-Ni alloy is lower as compared to Pd/Ti electrode, remaining available on the surface for further dechlorination of 2-CP. The phenol formation appeared to follow the same behavior, but upon imposing a more negative potential (−0.60 V), the efficiency decreased on both electrodes reaching even 0% in the case of Pd-Ni/Ti alloy and 40% on Pd/Ti electrode. This was due to the fact that at this potential, the process of H₂ evolution becomes present affecting the mechanism of electrochemical dechlorination, transforming 2-CP to other not identified intermediates in HPLC. The Pd-Ni/Ti electrode turned out to be the best option.
to carry out the process of electrochemical dechlorination since an efficiency of 100% was obtained for both 2-CP removal and phenol formation at a potential of $-0.40 \text{ V}$.

Phenol is a less toxic, inhibitory, and recalcitrant compound than 2-CP for microorganisms and it is more easily degradable in biological systems. The electrochemical process obtained in the present study might be coupled to a low-cost biological process where phenol could be totally mineralized. Under the experimental conditions established in this study, the stoichiometric transformation of 2-CP into phenol was obtained, limiting the accumulation of other intermediates that could be toxic or inhibitory for the subsequent biological treatment. It has been reported that the limiting step in 2-CP mineralization by microbial processes is the reductive dechlorination of 2-CP to phenol, making very slow the overall process. In the present study, 50 mg/L of 2-CP was reduced into phenol after only 3 h of electrolysis. Results from the present study showed that the electrochemical dechlorination of 2-CP might constitute an alternative of pretreatment for the biological treatment of industrial wastewater polluted with chlorinated phenols.

**Conclusions**

2-chlorophenol is a compound difficult to degrade by biological methods; in chemical and electrochemical oxidation processes it presents several problems that need solving. Therefore, reduction by electrochemical dechlorination has been carried out in this study as an alternative process to provide a less toxic and more easily degradable compound for biological systems. Electrolytic bath conditions have been set for the preparation of three electrodes containing Pd/Ti, Ni/Ti and Pd-Ni alloy, which were later characterized by XRD, SEM, EDS and XPS. The voltammetric study helped to detect potential conditions for both 2-CP dechlorination and Pd-Ni alloy, which were later characterized by XRD, SEM, EDS and XPS. The voltammetric study helped to detect potential conditions for both 2-CP dechlorination and Pd-Ni/Ti alloy electrode, where the dechlorination process was selective for phenol. The obtained dechlorination conditions will be used to operate an (ECCOCEL-type) electrochemical reactor and carry out 2-CP dechlorination at a larger scale as pretreatment to feed a biological reactor (denitrifying process) for its complete mineralization.

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