Preparation and characterization of bimetallic Fe–Cu allophane nanoclays and their activity in the phenol oxidation by heterogeneous electro-Fenton reaction

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ABSTRACT

Bimetallic (Fe–Cu) allophane nanoclays were synthesized using a two-step wet impregnation method with different Fe/Cu ratios. The catalytic activities of bimetallic (Fe–Cu) allophane were studied for phenol oxidation by heterogeneous electro-Fenton reaction (HEF) at different initial pHs (3.0 and 5.5), and were compared with Fe-allophane and Cu-allophane catalysts. A glassy carbon electrode modified with the bimetallic allophane nanoclays was used as working electrode. FTIR, SEM, X-ray diffraction, XPS, Mossbauer spectroscopy and 
N2 adsorption–desorption were used to characterize the catalysts, and indicated the formation of small copper oxide particles stabilized by iron oxide species. Phenol conversion by HEF process at initial pH 3.0 was near 100% for all bimetallic (Fe–Cu) allophane nanoclays in less than 2 h of reaction, following an exponential decay. The chemical oxygen demand (COD) removal was less than 47% for Cu-allophane and 65% for Fe-allophane, whereas for the bimetallic (Fe–Cu) allophane nanoclays the COD removal decreased with the amount of copper oxide in the catalyst, achieving an 80% COD removal with Fe5.4Cu0.6 catalyst. These results showed the synergetic effect between the Fe3+ and Cu2+ ions present in the bimetallic (Fe–Cu) allophane nanoclays. Similarly, when the reactions were performed at initial pH 5.5 the phenol conversion was near 100% after 4 h for Fe-allophane and bimetallic (Fe–Cu) allophane with lower copper content. In the bimetallic (Fe–Cu) allophane clays the leaching of iron and copper into the solution was less than 1.25 mg/L and 0.638 mg/L, respectively, indicative of the high stability of the bimetallic (Fe–Cu) allophane catalysts.

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1. Introduction

Heterogeneous Fenton reaction and electro-Fenton process have been shown to be interesting alternatives for the degrading of recalcitrant organic pollutants from wastewater and industrial effluents. Heterogeneous Fenton reaction (HFR) involves the use of a solid catalyst, in which, iron or copper species are "immobilized" in the structure of the catalyst. Thus, the reaction can be performed in a wide pH range, avoiding the iron hydroxide precipitation [1]. On the other side, the electro-Fenton process is based on the continuous electro-generation of hydrogen peroxide by oxygen reduction on the cathode whereas the regeneration rate of Fe2+ is increased by a direct cathodic reaction [2].

By combining the efficiency of electro-Fenton with the advantages of heterogeneous catalysts, a new process has been developed, called heterogeneous electro-Fenton (HEF). In this process, a higher catalytic efficiency is expected, while the reaction can be performed in a wide range of pH, with low concentration of soluble iron and therefore, with minimal oxyhydroxide precipitation [3,4].
In a previous work [4] the atrazine oxidation by heterogeneous Fenton and heterogeneous electro-Fenton processes using iron oxide-supported allophane clay (AlSi2Fe6) as catalyst was studied. The reactions were performed at different initial pHs. In the case of HEF, AlSi2Fe6 was incorporated on glassy carbon electrodes. The results showed that both processes were efficient in oxidizing atrazine under acidic conditions (pH ~3). Besides, it was possible to carry out the reaction at more neutral pH (~6), achieving 68% atrazine oxidation in HFR after 48 h and 76% in HEF after 8 h. In this work it was concluded that HEF is more efficient than HFR, mainly due to the continuous electro-regeneration of iron species (Fe3+/Fe2+). However, incomplete atrazine mineralization was observed with desethyl-atrazine and desethyl-desisopropyl-atrazine reported as the main degradation products.

Therefore, some efforts can be made in order to improve the catalytic efficiency of the heterogeneous electro-Fenton to obtain a complete mineralization of recalcitrant organic pollutants. In this way, it has been suggested that the performance of iron catalysts is often improved by adding certain metals, such as Cu2+ species, which can contribute to the production of additional hydroxyl radicals according to Fenton-like reactions [5–7]. Recently the use of iron–copper bimetallic catalyst has attracted great attention [6–12]. For instance, Guimarães et al. [7] showed higher hydrogen peroxide decomposition rate over surface containing Cu2+ in the goethite structure when compared to the surface containing only Fe3+ species. Frank et al. [8] reported that iron–copper bimetallic catalyst supported on MCM-41 had the highest catalytic activity compared with the monometallic catalysts (FeM41 and CuM41). In addition, this catalyst was able to maintain its high catalytic activity after 10 consecutive runs and operate in a wide pH range. Han et al. [6] reported that Cu–Fe-bimetal amidoximated-polyacrylonitrile (PAN) fiber complexes were better catalysts for aqueous dye degradation in water than the respective Fe complexes. Similar results were reported for CuFe-mesoporous carbon [9], CuFeZSM-5 zeolite [10,11] and Fe–Cu bimetallic oxide-supported aluminium-containing MCM-41 [12].

The synergetic effects could also be a consequence of highly dispersed Fe and Cu oxides entrapped in the matrix of ordered mesoporous structure, increasing the numbers of active sites leading to efficient catalytic activity for the activation of H2O2 [9].

Therefore, the aim of this work is to improve wastewater treatment based on the heterogeneous electro-Fenton process, in order to achieve an effective degradation of recalcitrant organic pollutants using bimetallic (Fe–Cu) allophane nanoclays as Fenton reagent. Allophane is a nanoclay size mineral, which is abundant in volcanic ash soils and is the most important constituent of clays-fraction of Chilean southern soils (mostly Andisols). Due to the allophane properties, such as, large surface area, unique structure and high porosity, they have been proposed as highly adsorbing compounds [13], enzyme support [14] and solid catalysts [1]. Iron oxide-supported allophane clays with a hydrous feldspathoids structure were reported to be highly active and stable in the phenol oxidation by catalytic wet peroxide oxidation [15].

For that purpose, we have synthesized for the first time bimetallic (Fe–Cu) allophane clays with different Fe/Cu proportions using a two-step wet impregnation method. The solid catalysts were characterized by various techniques, such as nitrogen adsorption–desorption isotherm, scanning electronic microscopy, FTIR, XRD, XPS and 57Fe Mössbauer spectroscopy. The catalytic performance of the heterogeneous electro-Fenton process was studied in the phenol oxidation. Phenol has been used as a model of recalcitrant chemical compound because it is one of the most common organic in wastewater discharged from petrochemical, chemical and pharmaceutical industries [16].

2. Materials and methods

2.1. Chemicals

All chemicals were used as received. Phenol and Nafion® per-fluorinated ion-exchange resin were purchased from Sigma–Aldrich, whereas, Na2SO4, H2SO4 (analytical grade) and methanol (HPLC grade) were supplied by Merck. Graphite powder, Riedel-de Haën, was washed in dilute nitric acid, filtered, washed thoroughly with twice-distilled water until neutral pH was achieved, dried in an oven under argon atmosphere at 120 °C for 4 h, and cooled and stored under nitrogen.

2.2. Catalysis preparation

Allophane nanoclays with a theoretical Si/Al ratio of 3.0 and with a similar structure as hydrous feldspathoids were synthesized by co-precipitation method [17]. Part of the allophane nanoclays were impregnated with 6 wt.% iron oxide (Fe-allophane) and the other with 6 wt.% copper oxide (Cu-allophane) using a wet impregnation method, as previously reported [15]. The bimetallic Fe–Cu allophane nanoclays were prepared by a two-step wet impregnation method. In the first step, different amounts of iron oxide were deposited into 60 mL of a dispersion containing 1 g of allophane. The dispersion was evaporated at 25 °C and at a pH near 3.0, in a rotary evaporator, to obtain 1/3 of the initial volume. The dispersion finally was washed three times with 1 M KCl; afterwards, it was washed with distilled water by centrifugation in order to remove the chloride anions. In the second step, different amounts of copper oxide were deposited into 60 mL of a dispersion containing 1 g Fe-allophane at 25 °C and at a pH near 5.0, following the same methodology described above.

2.3. Catalyst characterization

Textural properties of the allophane, Fe-allophane, Cu-allophane and bimetallic (Fe–Cu) allophane were evaluated by N2 adsorption–desorption at 77 K on a Tristar II micromeritics instrument. Prior to N2 adsorption, the samples were degassed under vacuum at 250 °C for at least 6 h. The specific surface area (SBET) was determined from the linear part of the BET plot [18]. The micropore volume (V0) was calculated with DR (Dubidin Radushkevish) equation and the total pore volume (Vtotal) was calculated by subtracting the total pore volume and the micropore volume. The BJH method [19] was used to determine the average pore diameter. Fourier transform infrared spectra (FTIR) were recorded on a Spectrum Two IR Spectrometer over a wavenumber range of 400–4000 cm⁻¹. Samples were pressed into KBr discs (0.5 mg in 100 mg KBr). Powder X-ray diffraction (XRD) patterns were obtained in the 2θ values range 10°–70° using a Bruker D8 Advance equipped with a CuKα radiation at 40 kV, 30 mA and. The surface and morphology of the allophane samples were examined by transmission electron microscopy (TEM) using a Jeol-1200 EXII instrument operating at 120 kV, as well as by scanning electron microscopy (SEM) using a Jeol JSM-S410 apparatus. For SEM analysis, the samples were suspended in analytical grade methanol, sonicated for 5 min before being coated with gold-palladium. Images were obtained at 20 keV and a magnification of 5000×. Energy dispersive X-ray spectroscopy (EDX) was also used for Si, Al, Fe and Cu spot detection over the sample surface. The EDX analyses were performed at 20 keV, an angle of 28.8° and a magnification of 500×. XPS data were recorded using a Leybold LHS-10 spectrometer with Mg Kα radiation, under a vacuum lower than 5 × 10⁻9 Torr and constant pass energy of...
50 eV. The energy scale was calibrated using the C 1s binding energy of the adventitious carbon contamination layer, which was set at 284.6 eV. The background of the spectra was subtracted using the Shirley method [20] and the data were fitted using mixed Gaussian–Lorentzian functions. 57Fe Mössbauer data were recorded at 16 K in the transmission mode using a constant acceleration spectrometer, a 57Co (Rh) source and a He closed-cycle cryorefrigerator. The velocity scale was calibrated using a 6 μm thick iron foil and the isomer shifts are referred to the centroid of the spectrum of metallic iron at room temperature.

Allophane, Fe-allophane, Cu-allophane and bimetallic (Fe–Cu) allophane were also characterized by cyclic voltammetry (CV) using a 6 mg of allophane, Cu-allophane, Fe-allophane or bimetallic (Fe–Cu) allophane were mixed and ultrasonically homogenized for 2 h. The solvent was evaporated in air, in a stove at controlled temperature (60 °C) for 2 h. As a blank electrode, the same GC electrode was painted with drops of a dispersion prepared according to Ureta-Zaartu et al. [21]. Briefly, 50 mg of graphite, 0.5 mL of Nafion® perfluorinated ion-exchange resin and 4 mL of an aqueous dispersion containing 30 mg of allophane. Cu-allophane, Fe-allophane or bimetallic (Fe–Cu) allophane were prepared according to Ureta-Zaartu et al. [21]. Briefly, 50 mg of graphite, 0.5 mL of Nafion® perfluorinated ion-exchange resin and 4 mL of an aqueous dispersion containing 30 mg of allophane. Cu-allophane, Fe-allophane or bimetallic (Fe–Cu) allophane were mixed and ultrasonically homogenized for 2 h. The solvent was evaporated in air, in a stove at controlled temperature (60 °C) for 2 h. As a blank electrode, the same GC electrode was painted with drops of a dispersion prepared according to the precedent but without the addition of solid catalyst.

2.5 Phenol oxidation by heterogeneous electro-Fenton reaction

Phenol oxidation by HEF process was studied using the modified glassy carbon as working electrode, platinum wire as counter electrode and Ag/AgCl/saturated KCl as reference electrode. A single compartment electrochemical glass cell was employed using a typical three-electrode arrangement in order to hold both anode and cathode as close as possible. Oxygen was bubbled during 30 min before starting the electrolysis and then it was kept bubbling for the entire duration of the reaction in order to keep the solution saturated in this gas. The solution was mechanically stirred in order to improve mass transfer and decrease the thickness of the Nernst diffusion layer. The initial phenol concentration was 5 × 10–4 M (100 mL), prepared in 0.05 M Na2SO4. Electrolysis was carried out at different initial pHs (3.0 and 5.5), adjusted by adding drops of 0.1 M H2SO4 or 0.1 M NaOH at room temperature. Every 1 h 1 mL of sample was withdrawn and immediately filtered (0.2 μm) and analysed by HPLC. The electrolysis experiments were performed at the oxygen reduction potential (−0.6 V), which was previously determined by CV.

2.6 Analytical methodology

Decay in phenol concentration was determined by HPLC equipped with an array diode detector L-2455 (Elite LaChrom Hitachi) at 213 and 271 nm, using a reverse phase column RP18e (5 μm). Phenol determination was performed using 50% methanol and 50% water as mobile phase at 1 mL min–1 and 30 °C. The hydrogen peroxide concentration was determined by the potassium titanium(IV) oxalate method at 400 nm [22]. The chemical oxygen demand (COD) was measured by COD analyser (HANNA HI83099) instrument. Total iron and copper were determined by inductively plasma atomic emission spectrometry (ICP).

3. Results and discussions

3.1 Catalyst characterization

Chemical composition and textural properties of allophane, Fe-allophane, Cu-allophane and bimetallic (Fe-Cu) allophane are presented in Tables 1 and 2. The chemical and textural properties of allophane clays were modified during impregnation with iron and/or copper oxide. An increase of Si/Al ratio was observed in all catalysts (Table 1), which was highest for the allophane clays with the highest content of iron oxide. This could be a consequence of aluminium dissolution occurring under pH near 3.0, used to impregnate the allophane with iron oxide, or also due to isomorphous substitution of aluminium by iron on the octahedral network [23]. The EDX analysis is consistent with the expected presence of Fe and/or Cu in the different catalysts (Table 1). FTIR spectrum of allophane clays (Fig. 1) shows the typical bands of hydrous feldspaths allophane. The bands centred at 3444 cm–1 and 1635 cm–1 are assigned to OH stretching of structural hydroxyls and OH bending of adsorbed waters, respectively. The bands at 1043 cm–1, 722 cm–1 and 452 cm–1 are associated to the tetrahedral aluminosilicate framework. The band at 593 cm–1 is due to octahedral aluminium and the shoulder at 905 cm–1 can be associated to Si–OH groups [24,25]. Changes in the FTIR spectra were also observed after impregnation with iron and/or copper oxide. The bands associated to tetrahedral aluminium were weakened or shifted to higher wavenumber in the presence of iron and/or copper oxide. These changes in the FTIR spectra may be associated to the formation of new bonds as a consequence of the interaction between Si–O groups and Fe(OH)+, Fe(OH)2+, Fe3+(OH)2+, Cu2+ or Cu(OH)+ species, all present in solution as it has been previously reported [15,17,23,26]. It is important to mention that the impregnation method used does not affect the framework of the allophane as was observed by FTIR (Fig. 1). BET surface area of parental allophane clays was increased when the allophane was impregnated with iron oxide (Fe-allophane). This increase could be associated to iron oxyhydroxide formation [23], which was confirmed by Mössbauer analysis (see discussion below). BET surface area of the parental allophane clays decreases after the impregnation with copper oxide (Table 2), possibly due to the formation of copper oxide nanoparticles covering the external surface and clogging the micropore of the allophane support [27]. A uniform pore size and volume pore is observed for all the catalysts (Table 2). Fe-allophane, Cu-allophane and bimetallic (Fe–Cu) allophane exhibit N2 adsorption–desorption type IV isotherms (data not shown) typical of mesoporous materials. This result is similar to that of the parental allophane, in total accordance with the FTIR data which showed that the impregnation method did not change
the structural properties of the allophane clays. Similarly, SEM micrographs of the catalysts (Fig. 2) show highly porous aggregated particles, in agreement with the unitary structure of allophane clays.

X-ray diffraction patterns of allophane (Fig. 3) shows broad lines centred at 3.3 and 2.2 Å d spacing, indicating the presence of allophane [25,28,29]. No diffraction of iron or copper oxide is presented in the patterns of Fe-allophane, Cu-allophane and bimetallic (Fe–Cu) allophane nanoclays, suggesting that these species are finely dispersed on the allophane surface or that the iron and copper oxides particles are very small particles [27].

The XPS and the Fe 2p XPS spectra recorded from the various samples (Fig. 4a and b) showed very broad lines and were fitted to a combination of spin–orbit doublets, multiplet splitting peaks and shake-up satellite components. The different contributions and their respective assignments are listed in Table 3. The data indicate the presence of both Fe$^{2+}$ and Fe$^{3+}$ in all the samples. Inspection of Fig. 4b clearly shows that the Fe$^{2+}$ contributions increase with increasing Cu content in the nanoclays. In contrast, the Mössbauer data at 16 K of the sample with the highest Fe content (Fe-allophane) do not show the presence of Fe$^{2+}$ (Fig. 5a). This spectrum is dominated by an intense quadrupole doublet absorption, which was deconvoluted into two different quadrupole doublets. The Mössbauer parameters of these doublets (IS = 0.44 mm s$^{-1}$; QS = 1.10 mm s$^{-1}$, area 13%; IS = 0.44 mm s$^{-1}$; QS = 0.63 mm s$^{-1}$, area 44%) are characteristic of Fe$^{3+}$ in octahedral oxygen coordination and could correspond to Fe$^{3+}$ substituting Al$^{3+}$ ions in the allophane framework. The spectrum also shows broadened magnetic components, which were fitted using a discrete magnetic sextet and a broad single line. The parameters of the sextet (IS = 0.44 mm s$^{-1}$; QS = −0.14 mm s$^{-1}$; H = 44.6 T; area 9%) do not allow its assignment to any specific Fe$^{3+}$ oxide or oxyhydroxide. Its quadrupole shift is intermediate between that of goethite (−0.20 mm s$^{-1}$) and that of ferrihydrite or lepidocrocite (−0.05 mm s$^{-1}$) while its hyperfine magnetic field is more similar to that of lepidocrocite (ca. 46 T) than to those of goethite or ferrihydrite (ca. 49–50 T). As pointed out by Murad and Schwertmann

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$V_p$ (cm$^3$ g$^{-1}$)</th>
<th>$V_0$ (cm$^3$ g$^{-1}$)</th>
<th>$V_m$ (cm$^3$ g$^{-1}$)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allophane</td>
<td>144</td>
<td>0.26</td>
<td>0.07</td>
<td>0.19</td>
<td>3.69</td>
</tr>
<tr>
<td>Cu-allophane</td>
<td>118</td>
<td>0.20</td>
<td>0.06</td>
<td>0.14</td>
<td>3.85</td>
</tr>
<tr>
<td>Fe$_3$Cu$_3$</td>
<td>152</td>
<td>0.26</td>
<td>0.07</td>
<td>0.19</td>
<td>3.85</td>
</tr>
<tr>
<td>Fe$_4$Cu$_1.5$</td>
<td>166</td>
<td>0.27</td>
<td>0.08</td>
<td>0.19</td>
<td>3.84</td>
</tr>
<tr>
<td>Fe$_5$Cu$_0.6$</td>
<td>161</td>
<td>0.24</td>
<td>0.16</td>
<td>0.15</td>
<td>3.81</td>
</tr>
<tr>
<td>Fe-allophane</td>
<td>161</td>
<td>0.23</td>
<td>0.08</td>
<td>0.15</td>
<td>3.81</td>
</tr>
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![Fig. 1. FTIR spectrum of allophane, Fe-allophane, Cu-allophane and bimetallic (Fe–Cu) allophane nanoclays.](image1.png)

![Fig. 2. Scanning electron microscopy of the allophane nanoclays, Fe-allophane, Cu-allophane and bimetallic (Fe–Cu) allophane nanoclays.](image2.png)
it is difficult to differentiate among the various Fe$^{3+}$ oxyhydroxides in the microcrystalline domain. This difficulty is more pronounced when the materials contain Al or Si substitutions within its structure, resulting in a dilution of the magnetic super-exchange interactions and, hence, in a reduction of the hyperfine magnetic field. The broad singlet component (area = 34%) tries to simulate the fraction of the oxyhydroxide particles, which remain in superparamagnetic state at this low temperature. In any case, the results indicate that for this particular sample a considerable proportion of the present Fe$^{3+}$ pertains to an oxyhydroxide and does not substitute Al$^{3+}$ in the allophane framework.

The spectrum using two paramagnetic Fe$^{3+}$ doublets having parameters close to those obtained from the fit of the Fe-allophane sample plus a tiny Fe$^{2+}$ doublet, in a similar fashion to what we did in a previous publication [4]. Given the low iron concentration in the sample its signal-to-noise ratio is quite poor but, nevertheless, the quality of the fit increases significantly upon the introduction of the Fe$^{2+}$ doublet (IS = 1.11 mm s$^{-1}$; QS = 2.83 mm s$^{-1}$, area 4%). Given the low relative area of the Fe$^{2+}$ contribution it might have gone undetected in the spectrum of the previous sample due to the presence of the broad magnetic components observed there. In any case, the results endorse the XPS observations and, taken together, they strongly suggest that the Fe$^{2+}$ component is mainly due to a surface species since its contribution to the XPS spectra is certainly important.

A remarkable fact is that in the samples that contain both Fe and Cu, Cu is not observed in the wide-scan XPS spectra, which indicates that, at least within the thickness which can be explored by XPS (ca. 3 nm), Fe is segregated preferentially to Cu in the allophane surface. Note that, however, Cu is detected in these samples by EDX showing that Cu is present in the bulk of the material.

The Cu 2p spectrum recorded from the Cu-allophane sample shows a spin–orbit doublet compatible with the presence of Cu$^+$ (Fig. 6). However, there is strong evidence that Cu is initially present as Cu$^{2+}$ and that it is reduced to Cu$^+$ upon irradiation under the X-rays of the XPS spectrometer as previously reported by Chusuei et al. [31]. Although with poor energy resolution, the wide scan spectrum recorded from the Cu-allophane shows that the Cu 2p region contains strong shake-up satellites close to the main photoemission lines (Fig. 7). This is indicative of the presence of Cu$^{2+}$. However, during the long periods of time needed to record a Cu 2p spectrum with reasonable statistics and better energy resolution the shake-up satellites disappear indicating the reduction of the initial Cu$^{2+}$ to Cu$^+$ as a consequence of the irradiation of the XPS X-rays. This would indicate that Cu is present initially as very small CuO nanoparticles in the allophane surface. As Chusuei et al. [31] reported, this effect is much more marked when the particle size decreases below 3 nm.

The presence of iron and copper oxide in the allophane was also confirmed by cyclic voltammetry (CV). CV for Fe-allophane (Fig. 8a) presents a well-defined quasi-reversible couple (peaks 1C/1A) attributed to Fe$^{3+}$/Fe$^{2+}$ process at 0.0 V and 0.33 V, for the cathodic
and anodic process, respectively. In the case of Cu-allophane clays (Fig. 8b) a main couple with the reduction process at /C0 0.205 V and the associated oxidation process at 0.05 V are observed (peaks 1C/1A). Both main peaks shows a potential shoulder with higher overpotential (2C/2A), which could be considered as an evidence of coexistence of two species with Cu atoms, two phases or well, species based on Cu with different states of oxidation (CuO and Cu2O) [32 e34]. The bimetallic Fe4.5Cu1.5 and Fe5.4Cu0.6 allophane clays (line number 3 and 2, respectively, Fig. 8c) present a width reduction peak (1C), which could have two contributions (both peaks well defined in the sample Fe3Cu3). The more negative peak is attributed at Cu2+/Cu one-electron process, whereas the less negative is assigned to Fe3+/Fe2+, in accordance with the processes described above. In the reverse scan to positive potentials, the two oxidation peaks at 0.024 V and 0.34 V are better defined. In the case of Fe atoms, clearly the process in both sense of the potential scan can be associated with the Fe3+/Fe2+ redox couple, in agreement with Fig. 8a. However, for Cu atoms, it is possible to think that in the oxidation process the copper atoms pass for species with relatively stable Cu+. From Fig. 8a and b, it is evident that the oxidation process for Fe2+ occurs in the same potential window as the copper oxidation and with markedly lower current. This, together with the fact that the charge associated to both anodic process in Fig. 8c are very similar, and that the cathodic process charge is double of each anodic peak, could be considered as evidence that copper passes from Cu to Cu2+ in two steps. The stability of glassy carbon electrodes modified with Fe-allophane, Cu-allophane and bimetallic (Fe–Cu) allophane clays was determined at pH 5.5 by repetitive cyclic voltammetry. The results (data not shown) indicate that all the peaks remain invariant after 20 potential cycles at 0.1 V s−1.

### Table 3
Fe 2p binding energies obtained from the fit of the Fe 2p spectra.

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<tr>
<td>Fe2+</td>
<td>708.3</td>
<td>–</td>
<td>714.3</td>
<td>722.6</td>
<td>725.9</td>
</tr>
<tr>
<td>Fe3+</td>
<td>710.4</td>
<td>712.3</td>
<td>718.8</td>
<td>724.1</td>
<td>–</td>
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3.2. Catalytic activity

3.2.1. Phenol oxidation over bimetallic Fe–Cu allophane nanoclays

Catalytic activities of Fe-allophane, Cu-allophane and bimetallic (Fe–Cu) allophane nanoclays were determined in the phenol
oxidation by heterogeneous electro-Fenton process. The results are shown in Figs. 9 and 10.

Phenol conversion of near 100% at initial pH 3.0 was observed for all bimetallic Fe–Cu catalysts in less than 2 h of reaction, following an exponential decay (Fig. 9a and Table 4). In the case of Fe-allophane and Cu-allophane the phenol conversion was 71% and 62%, respectively, after 2 h, whereas in the absence of catalyst (blank) low phenol conversion was observed. The chemical oxygen demand (COD) removal after 4 h was less than 47% for Cu-allophane and 65% for Fe-allophane, whereas for the bimetallic Fe–Cu allophane the COD removal decreased with the amount of copper oxide in the catalyst (Table 5). Therefore, the best mineralization grade was achieved for the Fe5.4Cu0.1 catalyst (80% COD decay).

It is known that the catalytic activity of bimetallic Fe–Cu catalyst is influenced by the availability of active sites (iron or copper oxide) on the surface of the catalyst, which react with the hydrogen peroxide in order to generate the hydroxyl radicals [9]. As was pointed by Frank et al. [8] when copper based compounds are deposited after iron based compounds on the solid catalyst, it is possible that at acid pH the deposited iron may be dominant for COD degradation while a neutral pH the copper may be responsible for the reaction. Therefore, when the Fe/Cu ratio decreases it is possible that the copper deposited on the allophane surface may cover the catalyst surface limiting the activity of iron on the phenol degradation, especially under acidic conditions.

The hydrogen peroxide concentration achieved a plateau after 3 h reaction for all the catalysts (Fig. 9b), except for the Cu-allophane catalyst, implying different hydrogen peroxide decompositions for the Fe and Cu based catalysts. The catalytic decomposition of H2O2 by Cu2+ is slower at acidic conditions and is accelerated with increase of pH since the deprotonated form of H2O2 (HO^−/C02, pK_a of H2O2 is 11.6) is the major electro-donor responsible for the reduction of Cu(II), whereas, acidic conditions favour the production of OH^− in the Fe3+/H2O2 system [35].

When the heterogeneous electro-Fenton reactions were performed at initial pH 5.5 (Fig. 10a), phenol conversion was nearly complete after 4 h for both Fe-allophane and the bimetallic (Fe–Cu) allophane nanoclays with lower copper oxide content (Fe5.4Cu1.5 and Fe4.5Cu1.5). However, the COD removal was highest for the bimetallic catalysts, achieving a DOC removal of 69% and 68% for Fe5.4Cu0.6 and Fe4.5Cu0.6, respectively, whereas for Fe-allophane a 48% of COD removal was obtained. In the case of Cu-allophane and blank experiment (in the absence of catalyst) a COD removal of 21% and 6%, respectively, were observed (Table 5).

In order to correlate the decrease in phenol concentration with the hydrogen peroxide availability during the electrolysis time at

![Fig. 8. Cyclic voltamgrams of Fe-allophane (a), Cu-allophane (b) and bimetallic (Fe–Cu) allophane nanoclays (c). Blank in dash line, Fe5Cu3 (line number 1), Fe4.5Cu1.5 (line number 3) and Fe5.4Cu0.6 (line number 2).](image)

![Fig. 9. Phenol conversion (a) and hydrogen peroxide generation during phenol degradation (b) by heterogeneous Fenton reaction over Fe-allophane, Cu-allophane and bimetallic (Fe–Cu) allophane nanoclays at initial pH 3.0.](image)
At higher content, copper oxide nanoparticles hydroxyl generation from oxygen peroxide only if the copper is in a stable oxidation state. This indicates that native copper oxide is not active in synergetic catalysis. The plausible mechanism could be explained because the electro-generated \( \text{H}_2\text{O}_2 \) molecules adsorbed on the allophane surface (Fe–Cu) can reduce \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \) and \( \text{Cu}^{2+} \) to \( \text{Cu}^{+} \) ions through a Fenton-like process (Eqs. (1) and (3)), and the generated \( \text{Fe}^{2+} \) and \( \text{Cu}^{+} \) ions on the bimetallic allophane catalyst are then oxidized immediately by \( \text{H}_2\text{O}_2 \) to complete \( \text{Fe}^{3+} / \text{Fe}^{2+} \) and \( \text{Cu}^{2+}/\text{Cu}^{+} \) redox processes and produce \( \text{OH}^- \) radicals (Eqs. (2) and (4)). Meanwhile, the formed \( \text{Fe}^{3+} \) ions can also react with the \( \text{Cu}^{+} \) ions to form \( \text{Fe}^{2+} \) and \( \text{Cu}^{2+} \) to accelerate the transformation of \( \text{Fe}^{3+} / \text{Fe}^{2+} \) and \( \text{Cu}^{2+}/\text{Cu}^{+} \), giving rise to additional \( \text{OH}^- \) radical during the degradation (Eq. (5)).

\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{2+} + \cdot \text{O}_2\text{H} + \text{H}^+ \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^- \\
\text{Cu}^{2+} + \text{H}_2\text{O}_2 &\rightarrow \text{Cu}^{+} + \cdot \text{O}_2\text{H} + \text{OH}^- 
\end{align*}
\]

As has been previously reported, the phenol degradation is optimal at acidic pH for the iron catalytic systems, whereas the optimal pH for Cu-based systems is about pH 5.5 [4,35]. In this work, we have been shown that simultaneous incorporation of \( \text{Cu}^{2+} \) and \( \text{Fe}^{3+} \) ions on the allophane surface significantly increased the catalytic activity for the phenol oxidation at both pHs (3.0 and 5.5) due to synergetic effect in the bimetallic (Fe–Cu) allophane catalyst.

This synergetic effect could be a consequence of an increase of the numbers of active sites (iron and copper oxide) on the surface of allophane, leading to efficient catalytic activity for the activation of \( \text{H}_2\text{O}_2 \). The plausible mechanism could be explained because the electro-generated \( \text{H}_2\text{O}_2 \) molecules adsorbed on the allophane bimetallic surface (Fe–Cu) can reduce \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \) and \( \text{Cu}^{2+} \) to \( \text{Cu}^{+} \) ions through a Fenton-like process (Eqs. (1) and (3)), and the generated \( \text{Fe}^{2+} \) and \( \text{Cu}^{+} \) ions on the bimetallic allophane catalyst are then oxidized immediately by \( \text{H}_2\text{O}_2 \) to complete \( \text{Fe}^{3+} / \text{Fe}^{2+} \) and \( \text{Cu}^{2+}/\text{Cu}^{+} \) redox processes and produce \( \text{OH}^- \) radicals (Eqs. (2) and (4)). Meanwhile, the formed \( \text{Fe}^{3+} \) ions can also react with the \( \text{Cu}^{+} \) ions to form \( \text{Fe}^{2+} \) and \( \text{Cu}^{2+} \) to accelerate the transformation of \( \text{Fe}^{3+} / \text{Fe}^{2+} \) and \( \text{Cu}^{2+}/\text{Cu}^{+} \), giving rise to additional \( \text{OH}^- \) radical during the degradation (Eq. (5)).

\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{2+} + \cdot \text{O}_2\text{H} + \text{H}^+ \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^- \\
\text{Cu}^{2+} + \text{H}_2\text{O}_2 &\rightarrow \text{Cu}^{+} + \cdot \text{O}_2\text{H} + \text{OH}^- 
\end{align*}
\]

Table 4

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( k_{app}/\text{min}^{-1} ) pH 3.0</th>
<th>( R^2 )</th>
<th>( k_{app}/\text{min}^{-1} ) pH 5.5</th>
<th>( R^2 )</th>
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</thead>
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<tr>
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<td>0.987</td>
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<td>Cu-allophane</td>
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<td>0.988</td>
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<td>0.987</td>
<td>0.00349</td>
<td>0.991</td>
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<td>0.00822</td>
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<td>0.962</td>
<td>0.00890</td>
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<td>0.00576</td>
<td>0.999</td>
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Table 5

<table>
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<tr>
<th>Sample</th>
<th>pH</th>
<th>Phenol conversion (%)</th>
<th>DOC decay</th>
<th>Dissolved iron in solution (mg L(^{-1}))</th>
<th>Dissolved copper in solution (mg L(^{-1}))</th>
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<tr>
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<td>47</td>
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<td>66</td>
<td>0.9</td>
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<tr>
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<td>68</td>
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<td>Fe5.4Cu0.6</td>
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<td>0.81</td>
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<tr>
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<td>71</td>
<td>48</td>
<td>0.28</td>
<td>–</td>
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</tbody>
</table>

\( a \) After 2 h reaction  
\( b \) After 4 h reaction
\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{OH} + \text{OH}^- \quad (4) \]

\[ \text{Fe}^{2+} + \text{Cu}^{+} \rightarrow \text{Fe}^{2+} + \text{Cu}^{2+} \quad (5) \]

The stability of iron- or copper-rich minerals (as heterogeneous catalysts) is strongly dependent on pH of the solution. It is known that the leading of iron increase at low pH, whereas in the case of copper oxide a significant leaching of copper could occur at pH 5–5.5. In a previous work [15] the catalytic wet peroxide oxidation of phenol was studied using iron oxide-supported allophane and copper oxide-supported allophane at pH 3.7 and 5.0, respectively. It was noticed that copper oxide-supported allophane catalysts are far less stable in the CWPO of phenol than their iron-based counterparts. The presence of soluble copper species in the reaction medium could account for the significant homogeneous catalytic contribution. This behaviour could stem from an insufficient stabilization of the impregnated copper oxide on the surface of allophane support or could be caused by the presence of intermediate reaction products leading to the complexation of Cu²⁺ ions, thus forming soluble moieties [15]. In this sense, we have studied the stability of glassy carbon electrodes modified with Fe-allophane, Cu-allophane and bimetallic Fe–Cu allophane at pH 5.5 by repetitive cyclic voltammetry. The results (data not shown) indicate that bimetallic (Fe–Cu) allophane nanoclays were more stable than Cu-allophane after 20 potential cycles at 0.1 V s⁻¹. However, when the heterogeneous electro-Fenton for phenol oxidation was performed the leaching of iron and copper species at pH 3.0 and 5.5 was highest for the bimetallic Fe–Cu allophane (Fe₃₅Cu₆₅). In the case of initial pH 3.0 the leaching of iron and copper oxide could be a consequence of minerals leaching into solution due to acidic conditions. Whereas, at pH 5.5 we hypothesized that the iron and copper solubilisations are due to the complexation of Cu²⁺ and Fe³⁺ species by the presence of intermediate reaction forming soluble moieties. However, in all bimetallic catalysts the iron concentration was less than 1.25 mg/L and 0.638 mg/L after 4 h reaction, much lower than 5 mg/L and 1 mg/L, which is the legal limit imposed by the Chilean Normative D.S. 90/2000 [36] for effluent disposition in superficial watercourse for iron and copper, respectively. Therefore, the bimetallic (Fe–Cu) allophane with lower copper contents could be used as highly active and stable heterogeneous catalysts for the heterogeneous electro-Fenton process in a wide pH range without a significant drop in their catalytic efficiency and with minimal iron and copper solubilisation.

4. Conclusions

In this work we have prepared, for the first time, bimetallic (Fe–Cu) allophane nanoclays and characterized them by diverse methods. The results showed that the bimetallic allophane nanoclays are composed of small copper oxide particles stabilized by iron oxide. The simultaneous incorporation of iron and copper ions on the allophane nanoclays improves the catalytic efficiency of the phenol oxidation by heterogeneous electro-Fenton reaction compared with Fe-allophane and Cu-allophane nanoclays due to synergetic effect. This synergetic effect could be explained by cooperation between iron and copper metals in the bimetallic (Fe–Cu)/H₂O₂ systems by Fenton-like reaction mechanism. The catalytic activity of bimetallic (Fe–Cu) allophane nanoclays decreased with the copper content, suggesting that a higher amount of copper in the catalyst could cover the active sites decreasing the catalytic efficiency. In the bimetallic (Fe–Cu) allophane clays, the leaching of iron and copper into the solution was low which is indicative of the high stability of bimetallic (Fe–Cu) allophane catalysts. Therefore we proposed that bimetallic (Fe–Cu) clays with low iron content allophane could be used as highly active and stable heterogeneous catalyst in HEP process for recalcitrant organic pollutant under environmental friendly conditions.

Acknowledgements

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References