Ionic liquid/TiO₂ nanoparticles doped with non-expensive metals: new active catalyst for phenol photodegradation

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TiO₂ nanoparticles were synthesized using 1-n-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF₄) ionic liquid and doped with non-expensive metals Cu²⁺ and Fe³⁺ by the sol–gel method. The new generated photocatalysts had their morphological, textual and structural characteristics analysed by scanning electron microscopy and dispersive X-ray spectroscopy (SEM/EDS), transmission electron microscopy (TEM), Brunauer–Emmett–Teller analysis (BET), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and diffuse reflectance spectroscopy (DRS). The results showed two phases by XRD analysis, anatase (majority) and rutile (minority). The SEM micrographs exposed spherical TiO₂ NPs/BMI-BF₄ IL and compact layers for Cu²⁺ and Fe³⁺-doped TiO₂ NPs in BMI-BF₄ IL, the EDX confirmed only the presence of Ti, O, Fe and Cu. The BET and BJH analyses exhibited high porous TiO₂ NPs/BMI-BF₄ IL. The BET and BJH analyses confirmed that the pore diameter of mesoporous materials was between 12 and 16 nm with similar values for surface area (55–63 m² g⁻¹). The TEM images exhibited spherical shape nanoparticles with mean diameter of 20–22 nm. The DRS analysis and Tauc equation were applied to estimate the optical energy band gap of the photocatalysts. The energy band gap values of 3.1 eV, 3.32 eV, and 2.78 eV were obtained for TiO₂ NPs/BMI-BF₄ IL, 1% Cu²⁺-doped TiO₂ NPs/BMI-BF₄ IL and 1% Fe³⁺-doped TiO₂ NPs/BMI-BF₄ IL, respectively. Phenol photodegradation was realized using Cu²⁺ and Fe³⁺-doped TiO₂ NPs/BMI-BF₄ IL under UV/visible irradiation and quantified by HPLC-FLD. The phenol photodegradation was investigated by different concentrations of metal-doped TiO₂ NPs/BMI-BF₄ IL. The new active photocatalysts 1% Cu²⁺-doped TiO₂ NPs and 1% Fe³⁺-doped TiO₂ NPs/BMI-BF₄ IL exhibited high catalytic activity (99.9% and 96.8%, respectively). The photocatalysts 1% Cu²⁺ and 1% Fe³⁺-doped TiO₂ NPs/BMI-BF₄ IL were also evaluated using industrial wastewater from the tobacco industry. The results showed 56.7% phenol photodegradation, due to the complexity of the tobacco matrix wastewater.

1. Introduction

Phenolic compounds represent an important class of polluting organic molecules present in wastewater.¹ The pesticide, chemical, petrochemical, paint, textile, and biotechnological industries and food processing, generate these compounds.² These compounds are highly toxic and their presence prevents the activity of microorganisms in biological wastewater, reducing the biodegradation of other components.³,⁴ Several technologies exhibit phenol degradation in wastewater.⁵ As an example, we can cite biological treatment, activated carbon adsorption and advanced oxidative processes (AOPs).⁶-¹² Photocatalysis stands out among the advanced oxidative process (AOP) techniques. This consists of the activation of a semiconductor by sunlight or artificial light. One of the main semiconductors used is TiO₂, which demonstrates efficiency in the photodegradation of organic compounds.¹¹,¹³,¹⁴ TiO₂ has been shown to be one of the most suitable catalysts for environmental applications, considering its biological and chemical inertness, strong oxidizing power, non-toxicity, insolubility and stability against chemical corrosion.⁹-¹¹ This semiconductor when at the nanoscale has a pronounced effect on its photocatalytic properties, due to its larger surface area, exhibiting a high percentage of its constitutive atoms on the particle surface.¹³ The metal ion addition to TiO₂ provides good control of the main particle size to produce nanocatalysts.¹⁴ The doping of TiO₂ by transition metal cations is an efficient strategy to reduce the electron–hole pair recombination rate and increase photocatalytic efficiency.⁹ Supported ionic liquid phase (SILP) technology is emerging as an interesting protocol for the immobilization of metal catalysts because it may combine the advantages of ionic
2. Experimental

2.1. Synthesis of Fe\textsuperscript{3+} and Cu\textsuperscript{2+}-doped TiO\textsubscript{2} NPs in BMI-BF\textsubscript{4} IL

The Fe\textsuperscript{3+} and Cu\textsuperscript{2+}-doped TiO\textsubscript{2} NPs in BMI-BF\textsubscript{4} IL occurred by mixing of ethanol (25 mL) and titanium tetraisopropoxide (TTIP) (2.5 mL) under stirring during 10 minutes in a bottle with addition of 1 mL of in BMI-BF\textsubscript{4} IL.\textsuperscript{27} For pH adjusting, sulfuric acid solution (0.125 mL) was added dropwise to the solution, and stirring was continued for 30 minutes. Then, 25 mL double distilled water and 121 mL absolute propanol were stirred and added dropwise to the solution. For doped TiO\textsubscript{2} NPs in BMI-BF\textsubscript{4} IL, Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}-5H\textsubscript{2}O or Cu(SO\textsubscript{4})\textsubscript{2}-5H\textsubscript{2}O were added to this solution in different atomic ratios (Table 1) and the stirring continued for 90 minutes. For the gel formation and exit of the alcohol, the formed sol was stirred at room temperature for 24 h; after that, the gel was dried under vacuum at 90 °C for about 12 h and then calcined at 600 °C for 1 h.\textsuperscript{27} The molecular structure of 1-n-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF\textsubscript{4}) IL is exposed in Scheme 1.

The metal precursors concentrations used in the synthesis of catalysts are shown in Table 1.

2.2. Phenol photodegradation

Phenol photodegradation was performed using a 250 mL photo reactor composed of a stirring system, digital thermometer and a UV light source (consisting of a low-pressure mercury vapor lamp of 150 W, from which the bulb was removed). In the experimental photocatalytic degradation of aforementioned concentrations of phenol (10 mg L\textsuperscript{-1}) at pH 3 and using different atomic ratios (0.5; 1; 5 and 10%), metal-doped TiO\textsubscript{2} NPs under UV irradiation (380 nm) was investigated. The irradiation time was 180 minutes and aliquots of solution were collected from the reactor at 15 minutes intervals. In the experiments, the magnetic stirrer was used to maintain the uniformity of suspensions. The samples were centrifuged (6000 rpm for 5 min) and filtered to separate Fe\textsuperscript{3+} or Cu\textsuperscript{2+}-doped TiO\textsubscript{2} particles. The aliquots were analyzed by HPLC-FLD (Agilent brand, model 1260). The injections of the samples were performed according to the established parameters, with a flow of 1.5 mL min\textsuperscript{-1}, running time of 35 minutes, post-run of 10 minutes, injection volume 20 μL, LiChrospher RP column 18 and 5 μm, 250 × 4 mm and guard column C18, 4 × 3 mm. The results were quantified based on the peak area, using ChemStation software.\textsuperscript{28}

Table 1 Metal precursor and metal-doped TiO\textsubscript{2} NPs/BMI-BF\textsubscript{4} IL percentage

| Metal precursor     | Metal (m/m)   |
|---------------------|---------------|
| —                   | NPs/TiO\textsubscript{2} |
| CuSO\textsubscript{4}-5H\textsubscript{2}O | 0.5% Cu\textsuperscript{2+} |
| CuSO\textsubscript{4}-5H\textsubscript{2}O | 1% Cu\textsuperscript{2+} |
| CuSO\textsubscript{4}-5H\textsubscript{2}O | 5% Cu\textsuperscript{2+} |
| Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}-5H\textsubscript{2}O | 0.5% Fe\textsuperscript{3+} |
| Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}-5H\textsubscript{2}O | 1% Fe\textsuperscript{3+} |
| Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}-5H\textsubscript{2}O | 5% Fe\textsuperscript{3+} |
| Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}-5H\textsubscript{2}O | 10% Fe\textsuperscript{3+} |
3. Characterization

3.1. Fourier transform infrared spectrophotometer (FTIR)

The samples were analyzed in the infrared region with readings from 4000 to 400 cm\(^{-1}\) using a spectrophotometer (Shimadzu brand, model IR PRESTIGE-21). The samples were prepared in solid form in potassium bromide (KBr) tablets and the data generated were treated with the aid of the origin pro 8.0 software.

3.2. Scanning electron microscope (SEM), dispersive energy spectroscopy (EDX)

The SEM and EDX analyses were performed in a Scanning Electron Microscope, in high and low vacuum mode, Jeol, JSM-6610LV, operating at 20 kV. To perform the analysis, the samples were deposited in stubs and metallized with gold using the Denton Vacuum Desk V equipment.

3.3. Transmission electron microscope (TEM)

For the TEM analyses, the samples were prepared by dispersing of the TiO\(_2\) NPs/BMI\(\cdot\)BF\(_4\) IL using isopropanol and deposited on a copper grid, coated with carbon film. The counts were performed with the aid of the Image J software.

3.4. X-ray diffraction (XRD)

X-ray diffraction analyses were performed using an X-ray diffractometer with a cryogenic temperatures chamber, Bruker, D8 Advance with the following parameters: voltage: 40 kV, current: 40 mA, copper tube and wavelength (\(\lambda\)): 1.5418 Å. The generated data were processed with the aid of the origin pro 8.0 software.

3.5. Surface area and porosity analysis (BET and BJH) analysis

The analyses to determine the specific surface area and porosity of the materials were performed through the N\(_2\) adsorption and desorption process with the Micromeritics Gemini VII 2390A. The volume and average size of the pores was obtained by the Barret, Joyner and Halenda method (BJH), using adsorption isotherms.

3.6. Diffuse reflectance spectroscopy (DRS)

The optical band gap of prepared sample has been measured by using DRS measurements. These measurements have been taken in the 200–800 nm wavelength range using Scinco S-4100 UV-vis spectrophotometer.

4. Results and discussion

The combination of non-expensive metals Cu\(^{2+}\) and Fe\(^{3+}\)-doped TiO\(_2\) NPs in BMI-BF\(_4\) IL, formed new photocatalysts with different atomic ratios using the sol–gel method. The sol–gel process involves several steps, hydrolysis/condensation, gelification/polymerization, and aging and drying to form the product. The formation of the colloidal solution, sol stage, was observed through the formation of a whitish and milky solution and the gel stage by a white and viscous precipitate. The gel was subjected to drying to remove the interstitial liquid solvent, and a progressive shrinkage, tension and fragmentation of the material were observed. At the end of the drying and maceration process, a powder of different colors was obtained, which are directly related to the metal precursor/TiO\(_2\) NPs in BMI-BF\(_4\) IL atomic ratio used in the synthesis process (Fig. 1).

The photocatalysts generated were characterized by different techniques. The photocatalysts 1% Cu\(^{2+}\) and 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI-BF\(_4\) IL were first characterized by XRD (Fig. 2). The XRD analysis showed a composition of the anatase (55%) and rutile (45%) phases for the 1% Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI-BF\(_4\) IL photocatalyst and rutile (30%), anatase (70%) phases for the 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI-BF\(_4\) IL photocatalyst. According to reports in the literature, the presence of phase mix tends to favor the photocatalytic activity of TiO\(_2\) NPs/BMI-BF\(_4\) IL, since it minimizes the recombination of photo-generated charges.

The photocatalysts 1% Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI-BF\(_4\) IL and 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI-BF\(_4\) IL calcined and the TiO\(_2\) NPs/BMI-BF\(_4\) IL without calcination process were characterized by XRD. The crystalline phases of the photocatalysts and the effect of calcination on the crystalline structure were analyzed. The analyses of the TiO\(_2\) NPs/BMI-BF\(_4\) IL, 1% Cu\(^{2+}\)-doped TiO\(_2\) NPs/
BMI·BF$_4$ IL and 1% Fe$^{3+}$-doped TiO$_2$ NPs/BMI·BF$_4$ IL photocatalysts calcined showed crystalline planes and intensities according to their crystalline phase, and being characterized by the values of the $2\theta$ angles and the Miller indexes ($hkl$), characteristic of each phase of TiO$_2$.

In Fig. 3, it is possible to observe the planes in 25.35°, 38.16°, 48.06°, 55.03° and 62.22° corresponding to the reflections of the crystalline planes, (101), (112), (200), (211) and (204), respectively, characteristic of the anatase phase. The compounds also showed rutile crystalline phase planes at 27.68°, 36.22°, 41.65° and 54.26°, that correspond to the reflections of the crystalline planes (110), (101), (111) and (211), respectively. In all the photocatalysts analyzed, the anatase and rutile phases were observed, with the presence of the broquira crystalline phase not being observed. The TiO$_2$ NPs without calcination do not show the characteristic planes of the crystalline phases of TiO$_2$, so an amorphous material was obtained. Calcination has a fundamental role in the formation of the crystalline phases of TiO$_2$, with temperature being a determining factor in the composition of the crystalline phases of the material.

The results obtained through XRD analysis are in accordance with the results described in the literature for TiO$_2$. In one study analysis of XRD reported characteristic values of the anatase phase. The values found were 25.24°, 36.98°, 48.02° and 62.74°, corresponding to the diffraction planes (101), (004), (200) and (204). In another study, diffraction planes of the anatase phase (101), (004), (103), (112), (200), (105), (211) and (204) were found, in addition to the planes of the rutile phase (110), (101) and (310). A review of XRD analysis peaks from the database of the International Committee for Powder Diffraction patterns for the crystalline anatase, rutile and broquita phase was presented. For the anatase phase, were described the patterns 25.304° (101), 33.454° (110), 38.566° (112), 48.037° (200) and 55.061° (211). For the rutile phase, the expected diffraction patterns are 27.475° (110), 36.154° (101), 41.326° (111) and 54.442° (211), and for the broquita phase, the plan 31.146° (211) was reported in the TiO$_2$ NPs.

The FTIR spectrum (Fig. 4) obtained for the photocatalysts TiO$_2$ NPs/BMI·BF$_4$ IL, 1% Cu$^{2+}$-doped TiO$_2$ NPs/BMI·BF$_4$ IL and 1% Fe$^{3+}$-doped TiO$_2$ NPs/BMI·BF$_4$ IL, exhibited a band at 1630 cm$^{-1}$ associated with angular deformation due to adsorbed water on photocatalyst surface, HOH, $v_{\text{OH}}$ (BMI·BF$_4$ IL present is hydrophilic). The band obtained in the low energy region between 400 and 900 cm$^{-1}$, more precisely at 750 cm$^{-1}$, is attributed to overlaps of the vibration bands $v_{\text{Ti-O}}$ and $\delta_{\text{Ti-O-Ti}}$ characteristics of TiO$_2$ obtained by the sol-gel method.
The vibration band at 3300 cm\(^{-1}\) is related to Ti–OH, \(\nu_{\text{Ti-OH}}\) (BMI–BF\(_4\) IL present is hydrophilic).\(^{37}\)

For the TiO\(_2\) NPs/BMI–BF\(_4\) IL, 1% Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL and 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL photocatalysts, the same infrared spectrum pattern was observed, confirming that for all cases, water adsorption on the photocatalyst surface. Another band that was observed in the FTIR spectrum is the band in the region of 2335 cm\(^{-1}\) related to Ti–O connection of TiO. This band has already been observed according to the literature.\(^{38,40}\)

The SEM micrographs of the TiO\(_2\) NPs/BMI–BF\(_4\) IL, 1% Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL and 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL photocatalysts are exposed in Fig. 5.

The SEM micrographs obtained for the TiO\(_2\) NPs/BMI–BF\(_4\) IL (Fig. 5A) exhibit spherical particles formation. The photocatalysts 1% Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL (Fig. 5B) and 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL (Fig. 5C) showed layered and compact materials. The layered and compact surface structure presented by photocatalysts was previously described in the literature.\(^{39,40}\) The EDX analyzes were performed together with the SEM analysis for the materials TiO\(_2\) NPs/BMI–BF\(_4\) IL, 1% Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL and 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL. The energy dispersion spectra obtained for the described samples can be exposed in Fig. 6.

Through the bonding energies present, it was possible to prove that only Ti and O elements were detected it the TiO\(_2\) NPs/BMI–BF\(_4\) IL photocatalyst. For the photocatalysts 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL, only Fe, Ti, O elements were detected, and for 1% Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL only Cu, Ti, O elements were observed. The qualitative quantification of the chemical elements present in the described samples is shown in Table 2.

The photocatalysts were prepared using isopropanol dispersion and a drop of the obtained dispersion was deposited in a carbon-covered copper grid for TEM analysis. The micrographs obtained by TEM are exposed in Fig. 7.

Table 3 shows the average diameters obtained for TiO\(_2\) NPs/BMI–BF\(_4\) IL, 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL and 1% Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL obtained by TEM analysis. Through the micrographs (Fig. 7), it is possible to verify that the TiO\(_2\) NPs/BMI–BF\(_4\) IL as well as the 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL and 1% Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL have nanometer diameter (18–22 nm), spherical shape and are preferably agglomerated. The BMI–BF\(_4\) IL ionic liquid acts as an efficient stabilizing agent for synthesis and stabilization for materials on a nanometric scale.\(^{44,45}\)

The average diameters of TiO\(_2\) NPs/BMI–BF\(_4\) IL obtained in this study are very similar to those reported in the literature. As an example, we can mention the synthesis of TiO\(_2\) NPs doped with iron that exhibited diameters in the range of 9–20 nm.\(^{44}\) In another study, the synthesis of TiO\(_2\) NPs formed particles with diameters in the range between 9–23 nm.\(^{43}\) In another example, the synthesis of TiO\(_2\) NPs doped with iron was performed at different calcination temperatures. When the calcination was at 400 °C, particles with an average diameter of 6 to 11 nm were

| Material                        | Element  | %m/m   |
|---------------------------------|----------|--------|
| TiO\(_2\) NPs/BMI–BF\(_4\) IL  | Ti       | 54.9   |
| 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL | O       | 36.31  |
|                                 | Ti       | 46.73  |
|                                 | O        | 38.09  |
|                                 | Fe       | 0.85   |
| 1% Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL | Ti       | 50.48  |
|                                 | O        | 37.87  |
|                                 | Cu       | 0.69   |
obtained, and only the anatase phase were observed. In calcination at 600 °C a change from the anatase to rutile phase was observed, with predominance of the anatase phase, and an average diameter of 22 to 30 nm; it calcination at 800 °C, only the rutile phase was observed, with an average diameter of 50 to 100 nm.45

The Scherrer equation is widely applied to determine the average diameters of the TiO2 NPs on a manometer scale. In Table 4, based on the results, it is possible to verify that the diameters obtained from the TiO2 NPs/BMI-BF4 IL by XRD are smaller than those obtained by TEM. The difference observed between the XRD and TEM analysis indicates that the observed particles (Fig. 7) may not be a single crystalline, but clusters of isolated crystallites with a smaller particle diameter than that observed in the TEM image.

TEM analysis of the 1% Fe3+-doped TiO2 NPs/BMI-BF4 IL and 1% Cu2+-doped TiO2 NPs/BMI-BF4 IL also presented a smaller diameter when compared to XRD analysis. This result shows that the doping of the material with metal ions and the BMI-BF4 IL presence causes a decrease in the diameter of the particles. This fact occurs in relation to the incorporation of metal ions into the crystalline structure of TiO2 and the interaction with the organized structure of the BMI-BF4 ionic liquid, generating a deformation due to the different atomic sizes, such as Fe3+ (0.69 Å) and Ti4+ (0.745 Å) ions. The deformation presented in the crystal line-up results in the restriction of the growth of the Fe3+-TiO2 crystals, decreasing the diameter of the TiO2 crystal.4

Table 5 shows the percentages calculated for the crystalline anatase and rutile phases for the samples: TiO2 NPs/BMI-BF4 IL, 1% Cu2+-doped TiO2 NPs/BMI-BF4 IL and 1% Fe3+-doped TiO2 NPs/BMI-BF4 IL.

After copper doping, the crystalline phase of TiO2 NPs/BMI-BF4 IL presented a higher proportion of the rutile crystalline phase than the other materials studied. This result may be related to the use of doping with cations that present a lower number of valence electrons than the number of valence electrons of the matrix cation, thus generating anion vacancies. In other words, when TiO2 is doped with Cu2+ cations, these tend to diffuse through the structure and replace Ti4+ ions, moving from the O–Ti–O to Cu–O connection, thus leading to the formation of oxygen vacancies.46,47 The presence of oxygen vacancies favors the transition from anatase to rutile phase, because the presence of these vacancies decreases the network deformation energy that must be overcome for the rearrangement of anatase to rutile octahedrons. The unit cell of the anatase phase is composed of 24 Ti–O connections. For the formation of the rutile phase, it is necessary to break 7 bonds of the anatase phase to occur the rearrangement. With the presence of oxygen vacancies in the crystalline network of TiO2, the number of Ti–O connections that need to be broken becomes smaller, thus facilitating the transition from the anatase to rutile phase in materials doped with Cu2+ ions. The surface area and porosity were determined by BET and BJH analysis for the TiO2 NPs/BMI-BF4 IL, 1% Fe3+-doped TiO2 NPs/BMI-BF4 IL and 1% Cu2+-doped TiO2 NPs/BMI-BF4 IL photocatalysts and the results are shown in Fig. 8.

BET analysis provided information about the surface area, the pore volume and the pore diameter values for the different photocatalysts studied. The addition of ionic liquid (IL) in TiO2 result in increase in surface area of the TiO2 nanoparticles prepared with IL.48 For the TiO2 NPs/BMI-BF4 IL sample, the surface area value was 58.9, for 1% Fe3+-doped TiO2 NPs/BMI-BF4 IL it was 63.6 and for 1% Cu2+-doped TiO2 NPs/BMI-BF4 IL it was 55.0,49,50

Table 3 Average diameter and standard deviation of particles obtained for TiO2 NPs/BMI-BF4 IL, 1% Fe3+-doped TiO2 NPs/BMI-BF4 IL and 1% Cu2+-doped TiO2 NPs/BMI-BF4 IL analyzed by TEM.

| Material                        | Average particle diameter (nm) |
|---------------------------------|--------------------------------|
| TiO2 NPs/BMI-BF4 IL             | 21.8 ± 2.9                     |
| 1% Fe3+-doped TiO2 NPs/BMI-BF4 IL | 18.9 ± 2.8                    |
| 1% Cu2+-doped TiO2 NPs/BMI-BF4 IL | 20.2 ± 3.2                    |

Table 4 XRD analysis of the photocatalysts, TiO2 NPs/BMI-BF4 IL, 1% Fe3+-doped TiO2 NPs/BMI-BF4 IL and 1% Cu2+-doped TiO2 NPs/BMI-BF4 IL.

| Photocatalysts                        | XRD diameter (nm) |
|---------------------------------------|-------------------|
| TiO2 NPs/BMI-BF4 IL                   | 14.4              |
| 1% Fe3+-doped TiO2 NPs/BMI-BF4 IL     | 11.2              |
| 1% Cu2+-doped TiO2 NPs/BMI-BF4 IL     | 14.9              |

Table 5 Composition of the crystalline phase of photocatalysts estimated from XRD analysis.

| Photocatalyst                      | Anatase phase (%) | Rutile phase (%) |
|------------------------------------|-------------------|------------------|
| TiO2 NPs/BMI-BF4 IL                | 64                | 35               |
| 1% Cu2+-doped TiO2 NPs/BMI-BF4 IL  | 55                | 45               |
| 1% Fe3+-doped TiO2 NPs/BMI-BF4 IL  | 70                | 30               |
The results described that copper doping caused a minimal reduction in the surface area of the doped TiO$_2$ NPs/BMI$\text{BF}_4$ IL (1% Cu$^{2+}$ when compared to the pure TiO$_2$ NPs/BMI$\text{BF}_4$ IL). The addition of metal ions to TiO$_2$ NPs/BMI$\text{BF}_4$ IL did not significantly change the surface area or the pore volume of the studied materials. This fact is related to the effects of calcination temperature on the surface area and on pore diameter, which causes decreases in the surface area. The synthesized photocatalysts were calcined at constant temperature (600°C), a fact that justifies the approximate values of surface area, volume and pore size. Based on the values obtained, the synthesized materials can be classified as mesoporous, considering that they presented pore size from 12–16 nm (Fig. 8).

Comparing the results obtained by SEM and BET analysis it was possible to observe through the SEM micrographs a different surface structure between TiO$_2$ NPs/BMI$\text{BF}_4$ IL and doped photocatalysts, TiO$_2$ NPs/BMI$\text{BF}_4$ IL showed spherical particles and the 1% Cu$^{2+}$-doped TiO$_2$ NPs/BMI$\text{BF}_4$ IL and 1% Fe$^{3+}$-doped TiO$_2$ NPs/BMI$\text{BF}_4$ IL exhibited a compact layered surface. However, the BET analysis exhibited that the surface area values are similar for the all photocatalysts analyzed, 58.9 m$^2$ g$^{-1}$ (TiO$_2$ NPs/BMI$\text{BF}_4$ IL), 63.6 m$^2$ g$^{-1}$ (1% Fe$^{3+}$-doped TiO$_2$ NPs/BMI$\text{BF}_4$ IL) and 55 m$^2$ g$^{-1}$ (1% Cu$^{2+}$-doped TiO$_2$ NPs/BMI$\text{BF}_4$ IL). These results show that the organization of the surface structure is different, but the properties are similar.

The Cu$^{2+}$ and Fe$^{3+}$-doped TiO$_2$ NPs/BMI$\text{BF}_4$ IL photocatalysts in different atomic metal ratios (0.5%; 1%; 5% and 10%) were first applied in phenol photodegradation to evaluate the catalytic activity. The effects of BMI$\text{BF}_4$ IL, on the photocatalytic performance of TiO$_2$ showed that photogenerated electrons were the main reactive species involved in the catalytic photodegradation of phenol. The addition of BMI$\text{BF}_4$ IL enhanced the catalytic photodegradation of phenol because adsorption of [Bmim]$^+$ ions on the TiO$_2$ surface increased transfer of photogenerated electrons.$^{31}$

### 4.1. Optical energy band-gap determination

The Fig. 9 show the diffuse reflectance (DR) spectra of powder of the photocatalysts (TiO$_2$ NPs/BMI$\text{BF}_4$ IL, 1% Fe$^{3+}$-doped TiO$_2$ NPs/BMI$\text{BF}_4$ IL and 1% Cu$^{2+}$-doped TiO$_2$ NPs/BMI$\text{BF}_4$ IL) along with the Tauc representations. The DR spectra exhibited a large decrease in the reflectance below 400 nm that is associated to the optical absorption edge of the photocatalysts. The Tauc representations for the photocatalysts display the commonly reported linear dependence of the Kubelka–Munk function with $hv$, with a smooth function with a low curvature below and above the absorption edge. This allows an easy evaluation of the band gap as the extrapolation of the linear least squares fit of $[F(R_{\infty})hv]^{1/n}$ to zero. For materials with a well-defined absorption edge of the material, the analysis by using a double linear fitting range yields similar extrapolation values thus the main difficulty relies in the choice of the electronic transitions, as it defines the value of the $n$ exponent. Indeed, the energy band gap values are quite sensitive to the selection of the fitting range and the type of electronic transitions (Fig. 9).

The band gap energy of the photocatalysts was estimated using Tauc’s formula.$^{32}$

\[
(ahv)^n = A(hv - E_g),
\]  

Fig. 8 Surface area and porosity by BET and BJH analysis of the TiO$_2$ NPs/BMI$\text{BF}_4$ IL, 1% Fe$^{3+}$-doped TiO$_2$ NPs/BMI$\text{BF}_4$ IL and 1% Cu$^{2+}$-doped TiO$_2$ NPs/BMI$\text{BF}_4$ IL photocatalysts.

Fig. 9 (Above) UV-vis diffuse reflectance spectra of TiO$_2$ NPs/BMI$\text{BF}_4$ IL, 1% Fe$^{3+}$-doped TiO$_2$ NPs/BMI$\text{BF}_4$ IL and 1% Cu$^{2+}$-doped TiO$_2$ NPs/BMI$\text{BF}_4$ IL; (down) Tauc’s plot.
where \( a \) is the absorbance, and \( h\nu \) is the photon energy. The band gap energy was obtained by extrapolating the linear region of the plot \((a\nu)^2\) vs. \((h\nu)\) to intersect the photon energy axis (Fig. 9b). For the calculations, we have considered indirect transitions for TiO\(_2\) (\( a_n = 2 \)) and the energy band gap values of 3.1 eV, 3.3 eV, 2.8 eV was obtained for the samples of TiO\(_2\) NPs/BMI–BF\(_4\) IL, 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL and 1% Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL, respectively. These results observed indicate that 1% Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL reduced the distance between the conduction band and valence band of TiO\(_2\) NPs, which could be favorable for photocatalytic reactions.\(^{32}\) The 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL band gap energy was 3.3 eV, similar results were observed by researchers for iron.\(^{26}\)

The results obtained in phenol photodegradation showed that the most active photocatalysts were 1% Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL (99.9%) and 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL (96.6%) (Fig. 10). This result is due to the oxidation potential of Fe\(^{3+}\) species being (−0.77 V) and Cu\(^{2+}\) species (−0.15 V). Thus, the Cu\(^{2+}\) species has a greater tendency to be oxidized by dissolved oxygen, thus initiating the photocatalysis cycle and with a greater recombination between the photogenerated electron and Cu\(^{2+}\) ions, leaving hole in the valence band more time available for the generation of OH radicals.\(^{25}\) The other photocatalysts studied; 0.5% Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL: 5% Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL, 0.5% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL, 5% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL and 10% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL did not show phenol photodegradation greater than 60%.

In catalytic processes, an important factor is the catalyst/substrate ratio. The Fig. 10 shows the influence of the catalyst concentration on phenol photodegradation. The experiments exhibited that with the increase in the concentration of the catalyst from 0.5 to 1% (m/m), the photodegradation of phenol increases (43% to 96%). This result is because the increase in the number of Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL or Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL increases the number of photons absorbed, the active sites and the number of adsorbed phenol molecules. However, there was no considerable increase in the phenol photodegradation when catalyst concentration was increased from 1% to 5% or 10%. This is attributed to catalyst agglomeration when in high concentration. The opacity and screening effect of excess Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL or Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL act as a surface layer on the surface, reducing light penetration, decreasing the active surface area, reducing photon absorption and, consequently, decreasing the catalytic activity. Therefore, the best concentration of Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL or Cu\(^{2+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL was determined as 1% (m/m).

The 1% Cu\(^{2+}\) and 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL synthesized using the sol–gel method at 90 °C and calcined at 600 °C during 1 h generated the photocatalytic materials. The phenol photodegradation as a function of time (0–180 min) was investigated by applying the following photocatalysts; UV light, TiO\(_2\) NPs/BMI–BF\(_4\) IL, 1%, 5% and 10% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL. The displayed curves clearly exhibit the higher catalytic efficiency obtained by the 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL photocatalyst, compared to the other given photocatalysts (Fig. 11).

The results of phenol photodegradation showed a degradation of around 42.3% when only UV light was used. In comparison, the use of photocatalyst TiO\(_2\) NPs/BMI–BF\(_4\) IL exhibited higher photocatalytic activity (52.2%) than that obtained using only UV light. This fact is related to TiO\(_2\) NPs/BMI–BF\(_4\) IL present valence bands (VB) and conduction bands (CB) separated by a well defined energy. In the presence of visible light, the photocatalyst has its VB electrons excited and promoted to CB, generating the electron/hole pair (h\(^+\)). The hole formed is extremely oxidative, presenting a potential to generate HO\(^{-}\) radicals (which is even greater due to the presence of BMI–BF\(_4\) IL), from water molecules adsorbed on the surface of TiO\(_2\), thus degrading phenol to CO\(_2\) and H\(_2\)O.\(^{34}\)

The application of the 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL photocatalyst exhibited high phenol degradation rates (96.8%), with the high degradation potential of the 1% Fe\(^{3+}\)-doped TiO\(_2\) NPs/BMI–BF\(_4\) IL photocatalyst due to rapid regeneration of the electron–hole pair. TiO\(_2\) NPs/BMI–BF\(_4\) IL doped with iron ions forms a cycle where dissolved oxygen oxidizes iron, forming the O\(_2\)- species, which with the help of H\(^+\) present in the solution,
form the HO• radical. In this process, the photogenerated electrons reduce the iron, not quickly returning to the BV of the photocatalysts and leaving the hole generated in the BC available for a longer time.\textsuperscript{34} The 5% Fe$^{3+}$-doped TiO$_2$ NPs and 10% Fe$^{3+}$-doped TiO$_2$ NPs photocatalysts exhibited low photocatalytic activity, with values similar to those obtained with the percentage of degradation when only UV light was applied (40–45%). This fact indicates that doping with 5% and 10% of iron made the photocatalyst inactivated. According to literature data, the solubility of iron in TiO$_2$ is 1% m/m, thus the higher concentration of iron ions makes diffusion in the TiO$_2$ structure impossible (even with the presence of BMI-BF$_4$ IL, which improves porosity of TiO$_2$), leading to agglomeration on the TiO$_2$ surface and formation of Fe$_2$O$_3$. The formation of agglomerates of Fe$_2$O$_3$ cause a reduction of the active catalytic centers decreasing the photocatalytic activity.\textsuperscript{35}

The use of 0.5% Fe$^{3+}$-doped TiO$_2$ NPs/BMI-BF$_4$ IL photocatalysts showed an increase in photocatalytic activity initially, but after this period (15 min) the photocatalyst activity was statistically equivalent (t test, 95% confidence) to TiO$_2$ NPs/BMI-BF$_4$ IL photocatalyst activity (45%).\textsuperscript{27} In the literature, results similar to those obtained in this work were observed. When comparing the different concentrations of TiO$_2$ NPs doped with iron ions, the material with 1% Fe$^{3+}$ showed the best photocatalytic activity. The effect of 1% Cu$^{2+}$-doped TiO$_2$ NPs/BMI-BF$_4$ IL photocatalyst was also investigated in this work. Table 6 shows the degradation percentages obtained for phenol.

The curves shown in Fig. 12 exhibit the results of phenol degradation using the photocatalysts: UV light, TiO$_2$ NPs/BMI-BF$_4$ IL, 1% Fe$^{3+}$-doped TiO$_2$ NPs/BMI-BF$_4$ IL, and 1% Cu$^{2+}$-doped TiO$_2$ NPs/BMI-BF$_4$ IL.

### 4.2. Kinetic studies of phenol photodegradation

Kinetic studies of the investigated photocatalysts were also carried out (Fig. 13–15). From the results obtained in the kinetic studies of phenol photodegradation, it was possible to observe the obtainment of first-order kinetics for the photocatalysts: UV light, TiO$_2$, 1% Fe$^{3+}$-doped TiO$_2$ NPs/BMI-BF$_4$ IL and TiO$_2$ NPs/BMI-BF$_4$ IL. Fig. 13 shows the graphs obtained for the first-order kinetic equations for the phenol compound. The 1% Fe$^{3+}$-doped TiO$_2$ NPs/BMI-BF$_4$ IL photocatalyst showed a first-order rate law was observed (Fig. 14) and the 1% Cu$^{2+}$-doped TiO$_2$ NPs/BMI-BF$_4$ IL photocatalyst, exhibited a zero-order rate law was observed (Fig. 15).

As shown in Fig. 15, it is possible to verify that for the 1% Cu$^{2+}$-doped TiO$_2$ NPs/BMI-BF$_4$ IL catalyst, the photodegradation followed a zero-order velocity law. The kinetic degradation curves obtained for the phenol compound using catalysts were those in which the $R^2$ correlation coefficient was closer to one (1), according to eqn (2).\textsuperscript{36}

This parameter was chosen to evaluate the degradation kinetic curves, because the correlation coefficient measures the fraction of the variation observed in $y$, that is, the closer the points are to the line predicted by least squares analysis, the smaller are the residues observed for the experimental model.\textsuperscript{37}

$$ R^2 = 1 - \frac{(\text{Sum of squares of residuals})}{(\text{Sum of total squares})} \tag{2} $$

Table 7 shows the correlation coefficients for phenol with zero-order and first-order reaction kinetics for the photocatalysts: UV light, TiO$_2$ NPs/BMI-BF$_4$ IL, 1% Fe$^{3+}$-doped TiO$_2$ NPs/BMI-BF$_4$ IL, 1% Cu$^{2+}$-doped TiO$_2$ NPs/BMI-BF$_4$ IL.

Through the data shown in Table 7, it is possible to observe that the best correlation coefficients for phenol were with the 1% Cu$^{2+}$-doped TiO$_2$ NPs/BMI-BF$_4$ IL photocatalyst, which

### Table 6 Effect of photocatalysts (UV light; TiO$_2$ IL; 0.5%, 1%, 5%, and 10% Fe$^{3+}$/IL; and 1% Cu$^{2+}$/IL) on the percentage of phenol degradation as a function of time

| Time (min) | UV light | TiO$_2$ IL | 0.5% Fe$^{3+}$ | 5% Fe$^{3+}$ | 10% Fe$^{3+}$ | 1% Fe$^{3+}$ | 1% Cu$^{2+}$ |
|-----------|----------|-----------|---------------|-------------|--------------|--------------|-------------|
| 0         | 100      | 100       | 100           | 100         | 100          | 100          | 100         |
| 15        | 93.5     | 92.6      | 79.4          | 77.5        | 98.5         | 70.0         | 87.5        |
| 60        | 81.4     | 79.8      | 70.0          | 57.2        | 83.9         | 45.4         | 78.7        |
| 120       | 63.2     | 55.2      | 58.9          | 56.9        | 67.8         | 38.0         | 10.3        |
| 180       | 57.7     | 47.8      | 56.1          | 55.0        | 59.8         | 32.5         | 0.1         |

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exhibited a zero-order equation and an $R^2$ of 0.93, values greater than those obtained by the first-order equation, which showed $R^2$ values around 0.85. The other photocatalysts applied to phenol presented $R^2$ close to one (1) for the first order equation. Literature data reported the photocatalytic decomposition of phenol following pseudo zero-order reaction kinetics for TiO$_2$ doped with copper ions. In addition, Khraisheh also found that TiO$_2$ doped with copper ions has a higher percentage of degradation when compared to TiO$_2$ doped with Fe and Mn 1% m/m. In another study, it was described that degradation of phenol followed the first order kinetics with the use of TiO$_2$ photocatalyst doped with Fe$^{3+}$ ions. In this same work, it was highlighted that the doping of TiO$_2$ with Fe$^{3+}$ ions promotes an increase in the photocatalytic activity in the degradation of phenol when compared to pure TiO$_2$, and that this result is due to the recombination of Fe$^{3+}$ charges and the TiO$_2$ e$^-$/h$^+$ pair.

4.3. Phenol photodegradation studies in wastewater from the tobacco industry

The phenol photodegradation was also carried out in an wastewater from the tobacco industry, the wastewater contains, in addition to phenol, other compounds such as alkaloids, specific nitrosamines (TSNAs), metals, metalloids, acetones, pesticide residues, humectants, benzo[a]pyrene (B[a]P), radionuclides and alphatoxins, benzene, naphthalene, pyridine, among other compounds.

The studied industrial wastewater was exposed to the photocatalysis process without any pre-treatment. The two photocatalysts that showed the best photocatalytic activity in the standard phenol sample, 1% Cu$^{2+}$-doped TiO$_2$ NPs/BMI-BF$_4$ IL and 1% Fe$^{3+}$-doped TiO$_2$ NPs/BMI-BF$_4$ IL, were investigated in phenol degradation in industrial wastewater. The results obtained are shown in Table 8. Through the exposed data, it is observed that the photocatalyst 1% Fe$^{3+}$-doped TiO$_2$ NPs/BMI-BF$_4$ IL exhibited the best photocatalytic activity, with degradation values of 60.2% for the phenol compound in tobacco industry wastewater and the 1% Cu$^{2+}$-doped TiO$_2$ NPs/BMI-BF$_4$ IL exhibited slightly lower phenol photodegradation with value of 56.7%.

The lower values of phenol degradation present in industrial effluent, when compared to values obtained for standard samples, can be related to the high complexity of the tobacco
matrix, which is composed of more than 4700 organic and inorganic compounds. The complexity of the tobacco matrix and the fact that an effluent without pretreatment was used may have generated competition by the HO’ radicals present in the medium, which probably acted as oxidizing agents for other organic species existing in the matrix.41

5. Conclusions

The synthesis of the photocatalysts under UV/vis irradiation by the sol–gel method, using non-expensive metals Fe3+ and Cu2+-doped TiO2 NPs/BMI-BF4 IL, proved to be simple and effective in generating highly active catalysts in phenol photodegradation (99.9%).

The active TiO2 NPs, 1% Cu2+ and 1% Fe3+-doped TiO2/BMI-BF4 IL NPs photocatalysts were characterized by different techniques. The FTIR analysis showed the presence of characteristic bands for the formation of the connections $\text{Fe}^{3+}$-O-Ti and $\delta_{\text{Ti}-\text{O}-\text{Ti}}$ in the analyzed photocatalysts, confirming the formation of the TiO2 NPs. BET and BJH analysis showed a similar surface area (55–63 m² g⁻¹) and pore diameter 12–16 nm. XRD analysis confirmed the presence of two crystalline phases of TiO2, anatase (majority) and rutile, with particle diameter of 11–14 nm. SEM micrographs showed spherical particles formation for TiO2 NPs and compact layers for 1% Cu2+ and 1% Fe3+-doped TiO2 NPs. EDX analysis confirmed only the presence of Ti, O, Fe and Cu in the analyzed photocatalysts. The TEM images exhibited spherical shape, for all photocatalysts with an average diameter of 18–22 nm. The smaller particle diameter observed by XRD occurs in relation to the incorporation of metal ions into the crystalline structure of TiO2, causing a decrease in the diameter. DRS analysis and Tauc equation exhibited energy band gap values of 3.1 eV, 3.32 eV, 2.78 eV by TiO2 NPs/BMI-BF4 IL, 1% Fe3+-doped TiO2 NPs/BMI-BF4 IL and 1% Cu2+-doped TiO2 NPs/BMI-BF4 IL, respectively. The various concentration of photocatalysts were tested, but 1% Cu2+-doped TiO2 NPs/BMI-BF4 IL and 1% Fe3+-doped TiO2 NPs/BMI-BF4 IL exhibited high catalytic activity (99.9% and 96.8%, respectively) in phenol photodegradation. The best photocatalysts 1% Cu2+ and 1% Fe3+-doped TiO2 NPs/BMI-BF4 IL were also investigated in an industrial wastewater from a tobacco industry, the results showed 56.7% and 60.2% respectively, of phenol degradation due to the complexity of the tobacco matrix wastewater.

Author’s contribution

Daiane Kessler Fischer (Master’s student): synthesis, characterization and application of photocatalysts. Karina Rodrigues de Fraga (Graduation student): characterization and application of photocatalysts. Carla Weber Scheeren (PhD): guidance in the development of work and writing and work organization.

Conflicts of interest

There are no conflicts to declare.

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