**INTRODUCTION**

Calcium stannate, CaSnO$_3$, is a distorted orthorhombic perovskite with space group $Pbnm$, which belongs to the family of alkaline earth stannates. The degree of distortion of these perovskites may be described by tilting of the SnO$_6$ octahedra [1]. CaSnO$_3$ has been received increasing attention due to applications as capacitor component [2], gas sensor [3], anode materials for lithium ion batteries [4], catalyst [5], and photocatalyst [6]. Heterogeneous photocatalysis is an effective method for wastewater treatment, especially when organic pollutants are present in aqueous media [7-9]. In the photocatalytic process, a semiconductor is used as a light absorber to promote the breakage of pollutant molecules. Photodegradation may occur by a direct mechanism, i.e., by oxidation or reduction of pollutant molecules on the photocatalyst surface due to photogenerated electrons ($e^-$) or holes (h$^+$), or by an indirect mechanism when •OH radicals are formed from reaction of pollutant species with H$_2$O, OH$^-$ or O$_2$ adsorbed on the surface of the photocatalyst. These •OH radicals react with organic compounds to form CO$_2$ and H$_2$O [10].

A high activity in the degradation of organic pollutants has been reported for alkaline earth stannates as a consequence of their dielectric semiconductor properties [9, 11, 12]. Some of these works reported the use of alkaline earth stannates in water splitting [5, 13, 14], whereas others applied these materials for dye photodegradation.
especially using BaSnO₃ or SrSnO₃ [9, 12]. For instance, Sales et al. [15] synthesized SrBaSnO₄ powders and observed that the photodegradation of remazol golden yellow is strongly influenced by the composition of the photocatalyst. In a recent study, Moshtaghi et al. [16] investigated the photodegradation of acid blue 92 and acid black 1 using SrSnO₃ as the photocatalyst and obtained discoloration percentages larger than 93%. Wang et al. [17] evaluated the use CaSnO₃ with microcube morphology for the photodegradation of rhodamine B, methyl orange and 4-hydroxyazobenzene dyes and observed high photocatalytic efficiency. According to authors, a network of corner-shared octahedra can improve the charge carrier mobility, which indicates that CaSnO₃ may be an interesting photocatalyst. However, there are few reports on its photocatalytic properties. Several studies have reported the synthesis of perovskite-type stannates by the conventional method, but this methodology may be less flexible and less convenient for large-scale production. A modified Pechini method, as described in previous work [22, 23], was used as photocatalyst for the degradation of remazol golden yellow dye (RNL). The photocatalytic tests were performed in a homemade reactor with dimensions of 10 cm x 10 cm x 100 cm using UVC lamps (λ=254 nm). The experiments were carried out in triplicate using 10 mg of the photocatalyst and 15 mL of the dye solution with a concentration of 10 mg.L⁻¹ at pH= 3 and 6. The solution pH was kept constant by the use of a CH₃COOH/CH₃COONa solution (2 mol.L⁻¹) as buffer. Petri dishes containing the dye solution and the photocatalysts were photoirradiated for 5 h. After photocatalysis, the mixtures were centrifuged and filtered. The percentage of discoloration and degradation of the dye solutions were quantified using a UV-vis spectrophotometer (UV-2550, Shimadzu) in absorbance mode by measuring the absorbance of the solution at 410 and 240 nm, respectively [25]. The photocatalytic efficiencies of the photocatalysts were calculated by calibration curves; the initial absorption of the untreated dye solution and the respective concentrations before and after photocatalytic treatment were considered. In addition, tests at pH= 3 and 6 were performed in the dark, using the same conditions of the photocatalytic tests, to evaluate the discoloration solely due to the adsorption of the dye on the surface of the material.

RESULTS AND DISCUSSION

Characterization of the material

The XRD pattern of the CaSnO₃ photocatalyst calcined at 800 °C is presented in Fig. 1. According to the XRD pattern, the sample crystallized with an orthorhombic perovskite structure with space group Pbnm (62) and all of the diffraction peaks were indexed according to the ICDD powder diffraction file n. 77-1797. According to the ICDD
76-0606, the peak at 27º indicated the presence of CaCO$_3$ as a secondary phase. The presence of CaCO$_3$ in CaSnO$_3$ and Ca$_{1-x}$Sr$_x$SnO$_3$ samples was also confirmed in [26, 27].

where: $h$ – Planck’s constant, $v$ - frequency, $\alpha$ - absorption coefficient, $E_g$ - band gap energy, $A$ - constant. The value of the exponent $n$ denotes the nature of the sample transition. In the present work, $n=1/2$ was used, which corresponds to a direct transition.

The IR spectrum of the CaSnO$_3$ is shown in Fig. 3. The bands located at 870, 1051, and 1454 cm$^{-1}$ were assigned to carbonate vibrations [31], and the band at 1643 cm$^{-1}$ was associated with water angular deformation. The vibrations assigned to stannates (SnO$_3^{2-}$) generally produce high-intensity bands in the infrared region at 300-400 cm$^{-1}$ and 600-700 cm$^{-1}$ with a band broadening typical of orthorhombic perovskite structures [27, 32]. The mid-IR spectrum of CaSnO$_3$ showed a band at 641 cm$^{-1}$ assigned to the stretching mode of Sn-O [33, 34]. For the spectrum obtained in the far-IR range (inset of Fig. 3), the bands at 362 and 390 cm$^{-1}$ corresponded to the bending mode of O-Sn-O [34], while modes at 459 and 503 cm$^{-1}$ were assigned to SnO$_6$ vibrations [32], and bands at 559 and 642 cm$^{-1}$ referred to the stretching modes of Sn-O bonds [32, 34].

The Raman spectrum of the CaSnO$_3$ sample is displayed in Fig. 4. The bands located at 161, 181, 276 and 354 cm$^{-1}$ were assigned to Ca-SnO$_3$ and O-Sn-O vibrations [30]. The bands at 441, 583 and 701 cm$^{-1}$ were related to the torsional and stretching modes of SnO$_2$ and Sn-O, respectively [30, 32, 35]. The modes at 1079 and 1092 cm$^{-1}$ were assigned to calcium carbonate vibrations [36]. Maul et al. [37] performed a harmonic analysis of CaSnO$_3$ and presented the phonon density of states (PDOS) to correlate the contribution of Ca$^{2+}$, Sn$^{4+}$ and O$^{2-}$ movements (apical and equatorial) with the dislocation frequency ($\nu$). According to the authors, the bands between 100 and 300 cm$^{-1}$ have higher contribution of Ca$^{2+}$ and Sn$^{4+}$ atoms and small contribution of apical O$^{2-}$; for frequencies higher than 300 cm$^{-1}$, the highest contribution is from oxygen ions.

\[
(h\nu)^{1/n} = A(h\nu - E_g) \tag{A}
\]
The influence of the pH on the surface properties was evaluated by calculating the point of zero charge (PZC) of the perovskite, as presented in Fig. 5. In aqueous media, the surface of the oxides is hydroxylated. Surface dissociation occurs because most metal oxides are amphoteric, as shown by Equations B and C [38-40].

\[
\text{MOH} + \text{H}^+ (\text{aq}) \rightarrow \text{MOH}_2^+ (s) \quad (B)
\]

\[
\text{MOH} + \text{OH}^- (\text{aq}) \rightarrow \text{MO}^- (s) + \text{H}_2\text{O}(l) \quad (C)
\]

Therefore, when \(\text{pH}<\text{pH}_{\text{PZC}}\), the material surface becomes positively charged, which favors the adsorption of anions. When \(\text{pH}>\text{pH}_{\text{PZC}}\), the material surface becomes negatively charged, which favors the adsorption of cations [41]. The result presented in Fig. 5 showed that \(\text{CaSnO}_3\) has \(\text{pH}_{\text{PZC}}=7.26\).

**Photocatalytic efficiency**

The UV-vis spectra and the discoloration percentages of the dye solution after adsorption and photocatalytic tests at pH 6 and 3 are presented in Fig. 6a and 6b, respectively. For the adsorption tests, as measurements were done in the dark, the decrease in the intensity of the band at 411 nm was solely attributed to the reduction of the dye amount in the solution due to its adsorption on the material surface. For the solutions at pH 6, a very small adsorption occurred (8%), while the adsorption at pH 3 was much larger (16%). This behavior may be understood by considering the Coulombic attraction and repulsion forces between the azo dye and the perovskite. According to the evaluation of the PZC, a positive surface charge density is obtained at pH 3, while a slightly positive charge density is attained at pH 6. On the other hand, according to literature data the RNL azo dye has three pKₐ.
values: 3, 3.5 and 6 - the sulphonic group is deprotonated at pH 3, the sulphate group is deprotonated at pH 3.5 and the amido group is deprotonated at pH 6, which results in a large negative charge, as displayed in Fig. 7 [42, 43]. Therefore, an attractive force between the positive surface charge of the perovskite and the negative charge of the azo dye occurs at pH 3 favoring the dye adsorption and the highest solution discoloration. At pH 6, few molecules are adsorbed on the CaSnO$_3$ surface due to the slight positive surface charge, leading to a small discoloration of the solution. These results are in agreement with literature data [38, 40].

UV irradiation had an important influence on the amount of discoloration, which indicated that a photocatalytic reaction had occurred. XRD pattern (Fig. 1) and Raman spectrum (Fig. 4) obtained in the present work confirmed the formation of CaSnO$_3$ with orthorhombic structure, which consists of tilted and distorted SnO$_6$ octahedra [30]. According to [44], structures consisting of p-block metal oxides containing alkaline earth metals with large distortion of octahedral and tetrahedral units have interesting properties as photocatalysts, due to local internal fields caused by dipole moments in the distorted octahedra, which avoid electron-hole recombination upon photoexcitation. This behavior was confirmed in [45] for alkaline earth stannates. Another important characteristic observed in the present work was the high short- and long-range order, indicated by the well defined peaks in the XRD pattern (Fig. 1) and in the Raman spectrum (Fig. 4). Moreover, UV-vis spectrum (Fig. 2) displayed an intense absorption band with a steep edge, without Urbach tail. According to [17], this behavior indicates that a band-band transition takes place instead of transitions from impurity levels. This behavior, associated with the CaSnO$_3$ large band gap, may decrease the possibility of electron-hole recombination reactions.

An interpretation of the influence of pH on photocatalytic degradation must be performed considering the semiconductor surface charge, substrate nature and •OH production, which also changes at different pH values [40, 41, 46, 47]. According to literature data, two different photocatalysis mechanisms may occur for basic and acidic solutions. At low pH, some organic substances are adsorbed on the material surface and oxidized by holes, as formation of hydroxyl radicals due to H$_2$O or OH$^-$ oxidation by holes may be thermodynamically unfavorable. For neutral and alkaline solutions, •OH is formed more easily due to the presence of OH$^-$ on the material surface, which is readily oxidized by holes [38, 47, 48]. In the present case, the photodegradation of the RNL azo dye was smaller at pH 6 (Fig. 6a). In spite of this, a comparison with the results of the adsorption test indicated that a noticeable improvement in the activity occurred after UV irradiation, with a discoloration increase of 320%. As dye adsorption onto this perovskite was not favored at pH 6, it is believed that an indirect mechanism for the photocatalytic reaction prevailed, with the formation of hydroxyl radicals due to reaction of electrons with O$_2$, and/or holes with OH$^-$ and/or H$_2$O. For the solution at pH 3 (Fig. 6b), a comparison with the results of the adsorption test also showed that UV irradiation increased the photocatalytic activity for all of the materials, but the activity was increased by a smaller amount than that of the solutions at pH 6 (219%). This result indicated that a direct mechanism had also an important effect on photodegradation, due to oxidation of adsorbed azo dye molecules by holes in the valence band or cleavage of the azo bonds by electrons in the conduction band [38, 47]. A similar effect was observed in [38], which evaluated the photodegradation of an azo dye by TiO$_2$ and concluded that dye adsorption onto TiO$_2$ at low pH favors the photocatalytic reaction.

CONCLUSIONS

CaSnO$_3$ perovskite was successfully obtained by the modified Pechini method, leading to a material with high short and long-range order. This high crystallinity, the large band gap value associated with distorted octahedra characteristic of the CaSnO$_3$ orthorhombic structure enhanced the photocatalytic activity. UV radiation favored the discoloration of the solution, but the results were relatively different when the photocatalytic tests were conducted.
under different conditions. At pH 3, a higher electrostatic attraction between the positive surface and negatively charged dye molecule favored the direct mechanism of photocatalysis, as indicated by the adsorption results. At pH 6, the smallest positive surface charge led to a smaller adsorption of the dye molecules. At this condition, photocatalysis seemingly occurred by an indirect mechanism.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support by the INCT/CNPq/MCTI and CT-INFRA/FINEP/MCTI.

REFERENCES


(Rec. 14/11/2016, Rev. 07/02/2017, Ac. 01/03/2017)