**Nb-doped Hematite: highly active catalyst for the oxidation of organic dyes in water**

Henrique S. Oliveira¹, Flávia C. C. Moura¹, Luiz C. A. Oliveira¹,*, Patterson Souza² and Marcio C Pereira¹

¹Universidade de Minas Gerais, Belo Horizonte, Departamento de Química, Centro Federal de Educação Tecnológica de Minas Gerais, 30480-000 Belo Horizonte, Minas Gerais, Brazil. ²Universidade Federal dos Vales do Jequitinhonha e Mucuri, 39100-000 Diamantina, Minas Gerais, Brazil.

**luizoliveira@qui.ufmg.br**

**Introduction**

The preparation of niobium containing materials has been developed by different methods and has been used in a great variety of reactions such as oxidation, for example in oxidation of alkenes by metal niobium oxide assisted by H₂O₂ [1], epoxidation of cyclohexene using Metal Organic Frameworks(MOFs) with Nb, which has differentiated structure and porosity [2], oxidation of textile dye type molecules using synthetic and natural iron oxide doped with Nb [3]. The doping of iron oxides by elements such as Al⁺⁺, Mn⁺⁺, Cr⁺⁺, V⁺⁺, Ni⁺⁺, Co⁺⁺, Zn⁺⁺, Cd⁺⁺, Cu⁺⁺, Mg⁺⁺, Nb⁺⁺ has been studied due to the similar ionic radius of these elements with iron particles of Fe⁰ and Fe³⁺ with 0.76 and 0.64Å respectively [4]. The substitution of Fe in the crystal lattice, whose detection can be confirmed by Mössbauer spectroscopy, X-ray diffraction and tested in oxidation reactions such as the heterogeneous Fenton [3], causes changes in the oxide phases, conditioning different morphological, kinetic, magnetic and thermodynamic stability profiles for the material.

**Materials and Methods**

The synthesis of iron oxide, α-Fe₂O₃, was performed using the emulsion method Fe(NO₃)₃·9H₂O (3.9 × 10⁻¹ mol L⁻¹) and a mixture of 15% distilled water, 16% of 1-butanol, 45% 1-hexanol and C₂H₅BrN(6.1x10⁻¹ mol L⁻¹). The system was heated at 90°C under stirring, and precipitated with addition of KOH(1.0 mol L⁻¹) and NaHCO₃(1.0 mol L⁻¹) solutions and named as A. The Nb-doped iron oxide were prepared using two emulsions as described above, butone was made with vanadium salt NbCl₅ (4.3 × 10⁻² mol L⁻¹). The resulting solid was washed with distilled water, centrifuged, dried in an oven at 70°C for 48 hours and thermally treated at 550°C for 4 hours, and named as ANb. The Nb-doped iron oxide was submitted to hydrogen peroxide treatment in order to generate more active surface sites. This treatment was prepared by adding 1.0 g of ANb, 14mL of H₂O₂ (34% w/w) and 270mL of water and mixing them for 30min. The material was vacuum-filtered, washed and oven-dried for 12 h at 90 °C and named ANb-H.

The oxidation of methylene blue (MB) dye, used as a model molecule (10 mg L⁻¹) with H₂O₂ (8 mol L⁻¹) at pH 5 (natural pH of MB solution with the composite) was carried out with a total volume of 10 mL, using 10 mg of composite. The reactions were monitored by UV–Vis spectroscopy (Shimadzu UV 2550) at 665 nm.

**Results and Discussion**

Nb-doped iron oxides were used as heterogeneous catalyst to oxidize organic compounds in aqueous medium containing hydrogen peroxide. XRD and Mössbauer spectroscopy reveal that niobium is incorporated into the iron oxide structure. The H₂O₂ pretreatment of the solid catalyst promotes important surface and structural changes of the iron oxides mainly by peroxo-niobium complex formations [3], which expressionly enhance the catalytic properties of the material. Transmission electron microscope images show that the incorporation of Nb into structure of iron oxide tends to decrease the mean particle size of the material grains (Figure 1). Nb-doped iron oxides were found to impart an important role to the solid catalyst towards H₂O₂ reactions. The developed niobium containing iron oxide was confirmed to have remarkable catalytic activity on the oxidation of organic substrates and can be applied for degrading organic pollutants in water as showed in Figure 1. In fact, the ESI-MS spectrum obtained for the methylene blue after reaction with Nb-doped oxide shows a hydroxylation by hydroxyl radicals in solution forming species m/z =130 and m/z=110.

**Significance**

In this paper, we present the use of niobium to improve the catalytic properties of iron oxide. The catalyst containing niobium incorporated showed high capacity for organic removal of methylene blue dye in the presence of H₂O₂. Environmental processes low cost are of great interest from industry, which makes the process described here quite promising.