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Al/Fe-, Al/Cu- and Al/(Fe-Cu)-pillared clays: effect of the atomic metal ratio on the catalytic wet peroxide oxidation of methyl orange aqueous solutions

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Introduction

The environmental laws are getting everyday more restrictive about biorefractory substances present in wastewater streams. For that, it is necessary to develop new, cleaner and cheaper technologies of treatment. Although Al/Fe- and Al/Cu-pillared clays have been repeatedly claimed as very active materials for the catalytic wet peroxide oxidation (CWPO) of toxic organic compounds polluting aqueous solutions, at present, there is not total accord about whether the isomorphic substitution of the active metals within the structural sites of the Keggin-like Al based intercalating polycations is taking place, nor even enough clarity about the nature of the metallic species responsible for the very high catalytic activity exhibited by these materials. In the present work, the efficiency to incorporate Fe and Cu to the structure of a montmorillonite clay by means of species active and stable to the chemical leaching, and the effect of the atomic metal ratio (AMR) on the oxidation of the azo dye Orange III were studied.

Experimental

A Colombian bentonite (BVC) from the *Valle del Cauca* region, previously particle size separated (<2µm) and Na-homoionized, was employed as starting material. The clay was modified with intercalating solutions with various AMR values ranging between 2 and 10% for the corresponding active metals: percent AMR = (((M/(Al+M))·100), with M = Fe, Cu, or Fe + Cu. In the trimetallic system a 1:1 ratio for Fe:Cu was kept constant. The intercalating solutions were prepared from the metal chlorides (Sigma-Aldrich), and added to 2.0 wt.% clay suspensions in amount enough to provide 20 meq. (positive charge)/g clay [1]. The materials were characterized by elemental chemical analysis in a Perkin Elmer 2380 atomic absorption spectrometer and cationic exchange capacity (CEC) by micro-Kjeldahl analysis. The chemical oxidation of an aqueous solution of the azo dye Orange III (Sodium 4-(4-dimethylaminophenylazo) benzenesulphonate), also known as acid orange 52 (100 mg/L), used in this work as model of toxic organic molecule, was conducted in a stirred glass batch reactor at 18 °C and 0.7 atm. As oxidant, hydrogen peroxide solution (0.15 M) was used.

Results and discussion

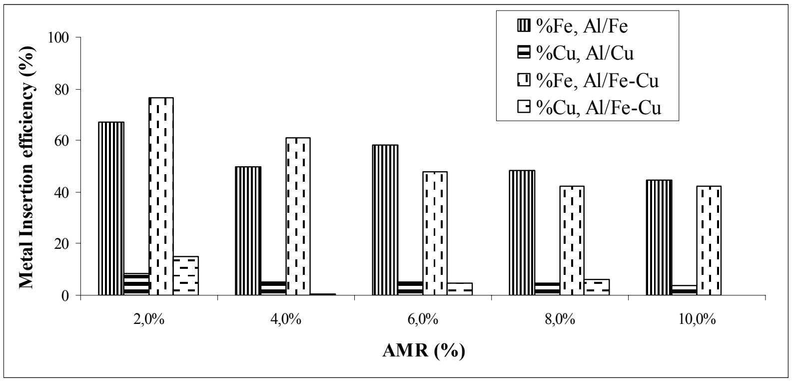

Figure 1. Metal insertion efficiency at different AMR

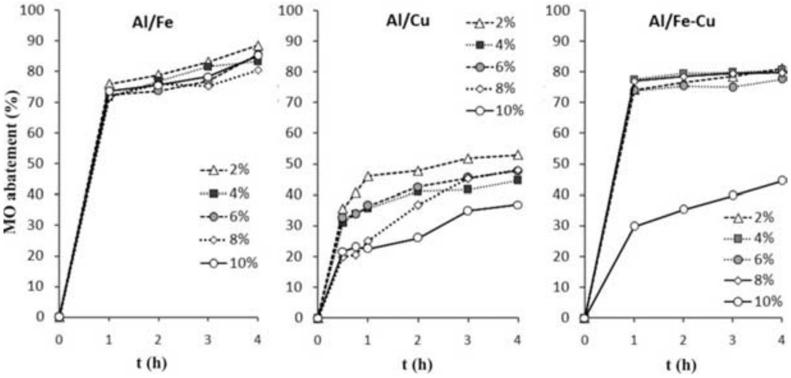

Figure 2. Catalytic performance of PILCs in the CWPO reaction.

A higher insertion of the active metals into the final materials is observed as the AMR of active metals in the pillaring solution decreases, and iron is stabilized in the clay framework with significant higher efficiency than copper (Fig. 1). In addition, the solids based in the system Al/Fe showed higher performances in the catalytic abatement of the model molecule (Fig. 2). These results suggest that the species responsible for the catalytic activity and chemical stability of the bimetallic systems would be related to isomorphic substitution of iron or copper into structural sites of the Keggin-like oligocations, being this variable even more important than the absolute amount of metal incorporated into the clay structure.

Acknowledgements

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