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WET PEROXIDE OXIDATION OF PARACETAMOL USING Fe/Co-PILLARED CLAY CATALYSTS PREPARED FROM NATURAL CLAYS

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ABSTRACT

This work deals with the catalytic wet peroxide oxidation of paracetamol, considered as model emerging pollutant, using as catalysts low-cost materials based on pillared clays prepared from natural clays. Pillared clays were prepared successfully through a pillaring solution containing cobalt and iron. The prepared clays allow to remove completely the pollutant after 8 h of reaction at 80 ºC, initial pH 3.5, $C_{catalyst}$ = 2.5 g L^{-1}, $C_{pollutant}$ = 100 mg L^{-1} and C_{H2O2} = 472 mg L^{-1}, whereas in the non-catalytic run only 20% removal of pollutant was obtained after 24 h at the same operating conditions.

Keywords: advanced oxidation process, wastewater treatment, emerging pollutants, pharmaceuticals, catalysis.

INTRODUCTION

In recent years, and especially after the advancement of sophisticated analytical techniques, many pharmaceutical compounds have been identified worldwide at trace levels (ng L^{-1} ~ mg L^{-1}) in the aquatic environment [1]. Despite the low concentration, the continuous input of these compounds constitutes an important environmental threat, given their persistence and hazardous nature [2]. Advanced Oxidation Processes are a set of chemical treatment procedures designed to remove organic matter present in wastewater effluents by oxidation through reactions with hydroxyl radicals (HO•). The Catalytic Wet Peroxide Oxidation (CWPO) is an AOP based on the use of a catalyst to promote the decomposition of H_2O_2 into hydroxyl radicals that oxidize organic matter under mild operating conditions (up to 130 ºC and 10 bar) [3]. Heterogeneous catalysts based on pillared clays have been shown in the last decades as active low-cost materials for the treatment of wastewater effluents by AOP. For this purpose, several mixtures of polyoxocation pillaring solutions, mainly based on Al, Zr and Fe, have been tested in the pillarization of the clays. This work aims to explore

natural clays in the preparation of pillared clays to be used as catalysts in the CWPO of paracetamol, considered as model emerging pollutant.

METHODOLOGY

Preparation and characterization of pillared clays

Natural clays were supplied from four different deposits of Kazakhstan, *viz.* Akzhar, Asa, Karatau and Kokshetau (AKN, ASN, KAN and KON samples, respectively). The pillaring solution was prepared by dropwise addition of 0.5 M NaOH at room temperature to an aqueous solution of 0.5 M $FeCl_3$ and 0.25 M $CoCl_2$ to obtain a final solution with a molar ratio OH/(Fe+Co) = 2:1. Then, the pillaring solution was added into a 2 wt% natural clay suspension (natural clays were washed previously with a sodium acetate buffer solution). The resultant suspension was stirred at room temperature during 3 h, aged during 72 h and the clay was recovered by filtration. The material was washed with water until the rinsing waters reach the natural pH, dried overnight at 60 ºC and calcined at 600 ºC during 5 h, resulting in AKPILC, ASPILC, KAPILC, KOPILC materials, obtained respectively from AKN, ASN, KAN and KON samples. N_2 adsorption-desorption isotherms at 77 K were determined with a Quantachrome instrument NOVA TOUCH LX^4. Fourier Transform Infrared (FT-IR) spectroscopy was performed with a Perkin Elmer FT-IR spectrophotometer UATR Two. X-ray diffraction (XRD) analysis was performed on a diffractometer DRON-3. A semiquantitative analysis was carried out using ICDD data: a base of powder diffractometric data PDF2 (Powder Diffraction File) and diffractograms of mineral-free impurities with the EVA program version 7.0.

CWPO of paracetamol

Batch oxidation runs were carried out in a 250 mL well stirred round flask reactor, equipped with a condenser and a temperature measurement thermocouple at the following operating conditions: 80 ºC, initial pH 3.5, adjusted by means of H_2SO_4 (runs not buffered), catalyst concentration of 2.5 g L^{-1}, initial concentration of paracetamol of 100 mg L^{-1} and the stoichiometric amount of H_2O_2 needed for mineralization of paracetamol. Adsorption runs were performed at similar operating conditions in the absence of H_2O_2 to compare with the pollutant removal obtained in CWPO experiments.

RESULTS AND DISCUSSION

Characterization of clays

Fig. 1A) shows the nitrogen adsorption-desorption isotherms at 77 K of each pillared clay.

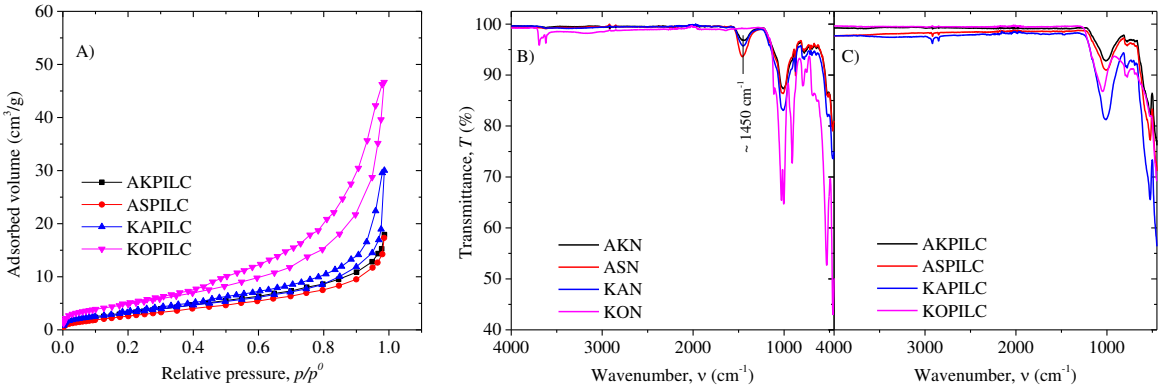

Fig. 1. A) N_2 adsorption-desorption isotherms at 77 K of the pillared clays, B) FT-IR spectra of the natural clays and C) FT-IR spectra of the pillared clays.

As can be observed, all materials present an isotherm of Type-IV according with the IUPAC classification, as typically found in mesoporous adsorbents. BET surface values around 11-19 m^2 g^{-1} were obtained for pillared clays, which were found to be close to the values of natural clays. This

was ascribed to the high content of quartz in the natural clays that was determine by the semiquantitative analysis of XRD spectra. The FT-IR spectra of the natural and pillared clays are depicted in Fig. 1B-C). As can be observed, AKN, ASN and KAN show a band at 1450 cm^{-1} that disappeared after the pillaring process. This band was ascribed to the presence of calcite in the raw materials [4]. The disappearance is a consequence of the exchange between calcium and the pillaring ions, putting in evidence the success of the pillarization procedure.

Screening of catalysts

The removal of pollutant and the consumption of hydrogen peroxide in the CWPO experiments are represented in Fig. 2. All pillared materials show catalytic activity, enabling the decomposition of hydrogen peroxide (Fig. 2A) and conversions of paracetamol higher than 65% after 8 h, whereas close to only 10% was obtained without catalyst at the same time (Fig. 2B). Maximum removals of paracetamol by pure adsorption experiments were found from 6 to 18% in equilibrium conditions (after 72 h). Thus, the adsorption contribution in CWPO experiments can be considered negligible. The highest active catalysts in the CWPO of paracetamol were KAPILC and KOPILC, being able to remove completely the pollutant after 8 h.

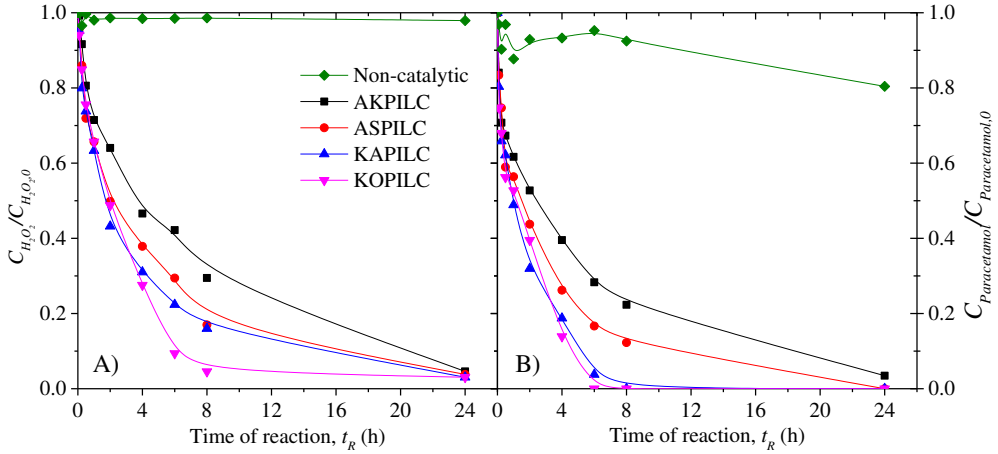

Fig. 2. Relative concentration of (A) hydrogen peroxide and (B) paracetamol upon reaction time during CWPO runs with pillared clays.

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