Monitoring of Chemical Intermediates through the Methyl Orange's Catalytic Wet Peroxide Oxidation (CWPO) by HPLC-DAD and GC/FID

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Introduction

The Catalytic Wet Peroxide Oxidation (CWPO) is one Advanced Oxidation Process (AOP) that allows highly efficient generation of hydroxyl radicals (HO•) even under pretty mild conditions of ambient temperature and pressure [1].
On the other hand, colored effluents of the textile industry are current problems of environmental concern. Methyl orange (MO) is a very toxic azo dye well known as a common reagent in basic labs of chemistry; besides, its degradation can be easily followed by single-wavelength visible spectroscopy. Hence, it is an excellent low-cost model molecule to assess AOP's performance in decolourization studies. CWPO decolourization of MO catalyzed by Al/Fe-pillared clays (Al/Fe-PILCs) has recently demonstrated to be very efficient [1]. However, once the color disappears of course it cannot be deduced that all hazard organic content has been completely degraded to innocuous products of mineralized to CO_2 and inorganic ions. In fact, the oxidizing break-down of this kind of dyes might lead to intermediate by-products still more toxic than the starting molecule, like some aromatic amines. Thus, a proper monitoring of the compounds produced during oxidizing decolourization by a variety of AOPs is an issue still mandatory to enable real-scale application of AOPs in detoxification of colored industrial wastewaters [2].
In this regard, this work is devoted to the follow up of the main intermediate by-products formed along the Al/Fe-PILC catalyzed CWPO degradation of methyl orange by both liquid and gas chromatography.

Materials and Methods

The preparation of the catalyst was carried out by the procedure described in [1]. The catalyst was prepared from a bentonite modified with Al/Fe, AMR = 2 %. The catalytic experiments were made in a glass 500 mL semi-batch reactor under average ambient temperature of 18 ºC and atmospheric pressure (0.71 atm). The reactor was charged with 250 mL of MO solution and the corresponding amount of catalyst; air bubbling (~2 L/h) and constant magnetic stirring also provided. H_2O_2 solution was drop-wise added at 3 mL/h, starting 15 minutes later (zero time of reaction). Drops of NaOH or H_2SO_4 0.1 mol/L solutions were used to control constant pH along the entire test. Samples of 2.5 mL were delivered and micro-filtered (0.45µm) at different times of reaction (0, 15, 30, 60, 120, 180 and 240 min). Three catalytic experiments were carried out, by using the following set of conditions: (1) Peroxide concentration $[H_2O_2]$ = 0.0685 mol/L, MO concentration [MO] = 50 mg/L, pH = 7.0 and catalyst loading [cat] = 0.5 g/L; (2) $[H_2O_2]$ = 0.0685 mol/L, [MO] = 200 mg/L, pH = 7.0 and [cat] = 5.0 g/L; and (3) $[H_2O_2]$ = 1.064 mol/L, [MO] = 50 mg/L, pH = 3.5 and [cat] = 5.0 g/L. Then, a set of 21 samples were reserved to chromatographic analyses at 4 °C immediately once delivered and the peroxide excess inactivated by addition of a tiny amount of $MnO_{2(s)}$.
The evolution of the intermediates was recorded based on reported methodology [2,3] by using chromatographic techniques (HPLC-DAD and GC-FID). Oxalic, malonic, succinic, butyric, propionic, acetic, formic and sulfanilic carboxylic acids were analyzed by HPLC-DAD under the following conditions: high performance liquid chromatograph (HPLC) Waters Brezze, PDA detector at 210 nm and 480 nm, C18 column (X-Terra, Waters, 100 mm x 4.6mm), flow 0.8 mL/min, mobile phase H_2O/phosphate buffer:MeOH at pH= 3; total time of analysis was 15 min. Meanwhile, presence of 4,N-N dimethylaniline, methylanilin, aniline and benzenesulfonic acid were analyzed by GC-FID under following conditions: gas-chromatograph Shimadzu GC-17, FID detector at 300 °C, DB-5 column (J&W Scientific), split/splitless injection (280 °C), gas carrier He UHP 1.0 mL/min. Identification of by-products was performed by comparison of retention times with the corresponding standard amines and carboxylic acids (Sigma-Aldrich) found along the catalytic experiments.

Results and Discussion

Acetic, oxalic, succinic and sulfanilic acids were detected by HPLC-DAD in samples from the catalytic experiments. Among them, acetic acid was the only one detected even at short reaction times as low as 15 min. It indicates that the CWPO treatment starts mineralization of the azo-dye very fast. Meanwhile, oxalic, sulfanilic and succinic acids became detectable at longer times of reaction over 180 min. Light carboxylic acids are well known by-products of AOPs because of their character strong refractory against chemical treatment. The GC-FID analyses showed four major signals that do not correspond to the retention times of the compounds initially proposed as potential by-products. Additional experiments by GC/MS are currently being performed in order to identify such a set of side products. However, in the current state of the study it can be said that apparently the hazardous aromatic amines proposed are not formed during the CWPO decomposition of methyl orange, and probably the same behavior could be inferred for other structural related azo-dyes.

Significance

HPLC-DAD and GC/FID monitoring of the intermediates generated during the CWPO decomposition of methyl orange have shown that acetic acid is formed even at very short times of reaction, while some targeted aromatic amines have not been identified at all, although other four side products were detected and will be shortly identified by GC/MS.

References

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