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

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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]. Methyl orange (MO) is a very toxic azo dye well known as a common reagent in basic labs of chemistry. CWPO decolourization of MO catalyzed by Al/Fe-pillared clays (Al/Fe-PILCs) has recently demonstrated to be very efficient.

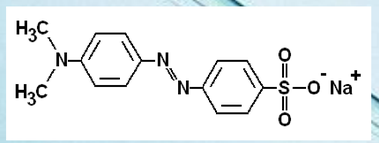

Figure 1. *Methyl orange (MO)*

Table 1. *Methyl orange by-products by some AOPs*

AOP	Technique	By-products
Photo-Fenton [2]	GC/MS	4-dimethylamino aniline
Radiation-induced[3]	GC/MS	N-Methylbenzenamine; 4-(dimethylamino)phenol; Aniline 4-Hydrazinyl N,N – dimethylbenzenamine

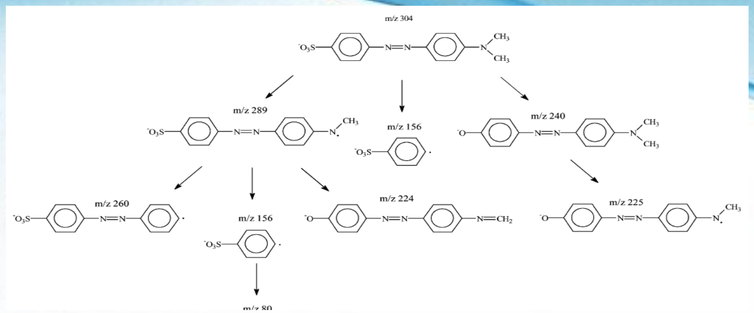

Figure 2. *Proposed fragmentation for methyl orange [4]*

Experimental

Figure 3. *Catalytic experiments*

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 = 2.0 %.
Catalytic experiments:
pH= 3.5
[NM] = 50
[cat] = 0.5 g/L y 5.0 g/L
$[H_2O_2]_0$ = 0.0685 y 1.0964 mol/L

Table 2. *Analytic conditions by chromatographic techniques*

HPLC: Waters Brezze	**GC/MS:** Shimadzu QP2010S
Detector: PDA at 210 nm y 480 nm	Detector MS Interphase 300 °C, full scan mode.
Column C18 (X-Terra Waters, 100 mm x 4.6 mm)	Capillar Column SHRXI-5MS (Shimadzu 30 m x 0,25 x 0,25 mm)
Mobile phase: Phosphoric acid pH 3.0	Injector: split/splitless 280 °C
Flow: 0.8 mL/min	Carrier gas: He UAP 1.0 mL/min.
Analysis time per run: 15 min	Analysis time per run: 35 min.

HPLC Compounds analyzed: Carboxylic acid: oxalic, malonic, succinic, butyric, propionic, acetic, formic y sulfanilic.

Results and Discussion

Figure 4. *HPLC chromatograms in MO by-product identification at (a) 15 min of reaction (b) 4 hours of reaction. Conditions: pH=3.5; [MO]=50 mg/L; [cat]=0.5 g/L; $[H_2O_2]_0$=1.0964 mol/L.*

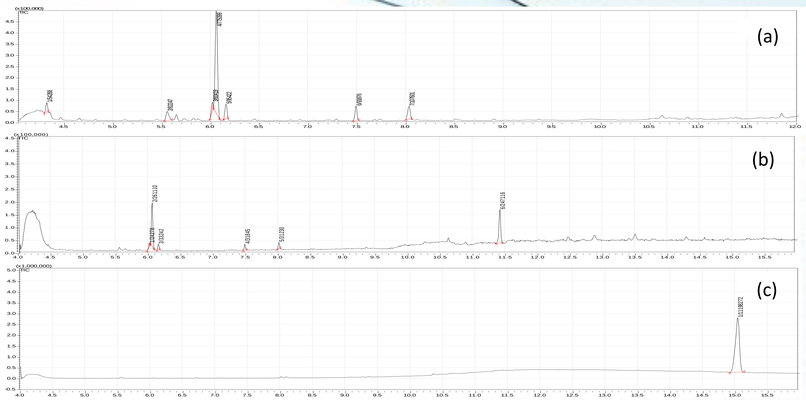

Figure 5. *GC/MS chromatograms in MO by-product identification at (a) 4 hours of reaction (b) 15 min of reaction (c) 0 min of reaction. Conditions: pH= 3.5; [MO]=50 mg/L; [cat]=5.0 g/L; $[H_2O_2]_0$=0.0685 mol/L.*

CWPO treatment starts mineralization of the azo-dye very fast (15 min). From samples taken throughout the catalytic tests at different reaction times (0, 15, 30, 60, 120, 180 and 240 min) the carboxylic acids shown in Table 3 were identified.

Table 3. *MO oxidation by-products identified by HPLC*

Signal	Compound	t_r (min)
2	Acetic Acid	1.448
3	Oxalic Acid	2.059
4	Sulfanilic Acid	2.397

Table 4. *MO oxidation by-products identified by GC/MS*

Compound	t_r (min)	m/z
1,2,3-trimethyl benzene	6.014	120
2-ethyl-2-hexenal	6.155	127
Ethyl, 2-ethyl hexanoate	7.485	127

Significance

HPLC-DAD and GC/MS monitoring of the intermediates generated during the CWPO decomposition of methyl orange showed that acetic acid is formed even at very short times of reaction. Some targeted aromatic amines, the most dangerous potential by-products expected from the already known fragmentation pathways, have not been identified at all. It suggest CWPO as interesting AOP in the treatment of colored wastewaters from the textile industry, giving rise to products less toxic and hazardous for the environment.

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