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Degradation of Methylene Blue by Catalytic Wet Air Oxidation with Fe and Cu Catalyst Supported on Multiwalled Carbon Nanotubes

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Oxidation catalysts, based on Fe and Cu on multi-walled carbon nanotubes were synthesized by incipient wetness impregnation. The metal content in the catalyst was 3 %. MWNT used was synthesized by chemical vapour deposition in our laboratories. The catalytic activity of the above mentioned formulations were tested in the oxidation reaction of 50 mg.L^{-1} of Methylene Blue (MB) aqueous solutions, with 4, 5 and 6 g.L^{-1} of catalyst and at 120-140 ºC temperature range. Reaction tests were carried out in a batch reactor at 8.8 bar of partial pressure, and the non converted fractions were measured in UV-vis equipment. The parameters TOC, color and toxicity (EC_{50}) were measured. In the tested temperature interval, no diminution in the MB concentration due to the non-catalyzed oxidation reaction was observed, practically. The catalyzed oxidation at 120 ºC was low for two synthesized catalysts, however a significant activity at 140 ºC. TOC and color removal was significantly affected by temperature. The catalyst concentration did not significantly affect to color and TOC removal. The Cu based catalyst showed the highest catalytic activity at 130 ºC in color and TOC removal. At 150 min of reaction time, Cu/MWNT shows a decrease of EC_{50} to 68 %. A reaction mechanism has been proposed, based on experimental data obtained from GC-MS analysis.

1. Introduction

For medium-high concentration wastewaters, as often encountered in industrial streams, wet air oxidation (WAO) has proved to be an effective technique in the largest number of practical cases (Bhargava et al., 2006; Levec and Pintar, 2007). Because of utilizing molecular oxygen or air as an oxidant, the most economically attractive and environmentally friendly oxidizing agent, WAO has been the subject of considerable studies (Bhargava et al., 2006; Ovejero et al., 2006). However, the conventional WAO is usually conducted at high temperature (200-320 ºC) and high pressure (2-20 MPa) (Levec and Pintar, 2007), which results in high capital and operating costs. To ease reaction conditions consequently to reduce costs, appropriate catalysts can be used; thus, the process becomes catalytic CWAO (Ovejero et al., 2006).

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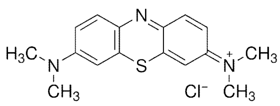
The objective of the present study was to clarify whether the degradation of organic pollutants, as exemplified by the methylene blue dye, might occur when iron or copper supported catalysts are employed in CWAO.

2. Esperimental

2.1 Materials

The MWCNT used as support in the preparation of the iron or copper catalysts were produced by chemical vapour deposition (CVD) of acetylene/nitrogen, using Fe/Al_2O_3 as catalyst. The as-obtained material, consisting of nanotubes, iron and alumina, was then purified by a sulphuric acid treatment, aiming at the total dissolution of alumina and partial elimination of iron contained in the tubes. The final material has a purity of 97%. The surface chemistry of the carbon nanotubes was modified by introducing carboxylic acid (–COOH) groups by means of an acidic treatment (HNO_3, 5 M) for 3 h under reflux. Then, the support was washed with water under reflux (6 h) until neutrality of the washing waters, and finally dried overnight at 110 ºC. Methylene Blue (MB), copper or iron metal precursors ($Cu(NO_3)_2 \cdot 3H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$.and all other reagents used for analysis were analytical reagent grade and were purchased from Sigma-Aldrich, USA. Air from a cylinder with a minimum stated purity of 99.5% provided by Air Liquid S.A., Spain was used for oxidation. Table I shows the structural formula of MB and their main characteristics.

Table I. Structural formula of MB compound and main characteristics

Structure	Formula and molecular weigth	Boiling Point	Melting point	Vapor density (Air=1)
	$C_{16}H_{18}ClN_3S$ 373.91 g.mol^{-1}	Decomposes	100-110 ºC	13

2.2 Preparation and characterization of catalysts

Copper and iron precursors were used and dissolved in water with a concentration calculated as to give a theoretical value of 3 wt.% Cu/MWCNT or Fe/MWNT catalysts after impregnation. The catalysts were prepared using incipient wetness impregnation to incorporate the metal. The wet solid was dried overnight at 110 °C and then reduced under N_2/H_2 (3:1) flowing at 350 °C for 3 h in a furnace, in order to reduce the metal precursor to its corresponding ground state.

The morphology of the sample was observed by transmission electron microscopy analysis using a JEOL JEL2010 electron microscope at 200 kV. XRD patterns were recorded by a difractometer SIEMENS D-501. The specific areas of the catalysts were measured using N_2 adsorption-desorption at 77 K with a Micromeritics ASAP 2010.

2.3 Catalytic experiments

All experiments were conducted in a Hastelloy high-pressure microreactor C-276 autoclave Engineers with a volume of 100 mL. The reactor (i.d. 50 mm) was equipped with an electrically heated jacket, a turbine agitator and a variable speed magnetic drive. The temperature and the stirring speed were controlled by means of a PID controller. The gas inlet, gas release valve, cooling water feed line, pressure gauge and rupture disk were situated on the top of the reaction vessel. The liquid sample line and the thermocouple well were immersed in the reaction mixture.

The reactor was first charged with 75 mL of the MB solution and the catalyst and initially pressurize with nitrogen to ensure inert atmosphere. Afterwards, the system was heated to the desired temperature and a sample was withdrawn. This was considered zero time for the reaction, and TOC conversion during this time can be neglected while calculating initial rates. Oxygen from the cylinder was then sparged into the liquid phase and samples were withdrawn periodically after sufficient flushing of the sample line. Pressure drop was monitored and additional oxygen was charged in order to maintain a constant total pressure.

2.4 Product analysis

At present reaction times, aliquots of the solution were collected and analyzed for total organic carbon (TOC) using a combustion/non-dispersive infrared gas analyzer (Shimadzu TOC analyzer). The residual methylene blue concentration was determined by UV-vis spectrophotometer using a Shimadzu spectrophotometer at 631 nm. Toxicity was determined by means of a Microtox analyzer (model 500). Finally, the intermediates were identified by GC-MS (Agilent 5973 N MSD).

3. Results and Discussion

3.1 Characterization of catalyst Metal supported on multiwalled carbon nanotubes

The N_2 isotherm of Cu on MWNT is shown as example in Fig. 1a. It is known that many porous materials with meso and macropores display hysteresis loop normally at low relative pressure (0.4) in a full adsorption–desorption isotherm, due to the fact that the gas desorbs from inside the pores in a different way than it was originally adsorbed into them. The shape of the hysteresis loop suggests the presence of wedge-shaped pores with open ends and the sharp rise in the isotherm at relative pressure close to unity can be due to the existence of macropores (Yang et al., 2002). The BET surface areas (S_{BET}) were 141 and 135 $m^2.g^{-1}$ for Cu/MWNT and Fe/MWNT, respectively.

On the other hand, the TEM images of MWNT showed many defects on their structure and wide distribution of size. These images suggest that most of the copper or iron particles were dispersed on the outer surface of the MWNT. Figure 1b shows TEM images of the copper supported on MWNT as example.

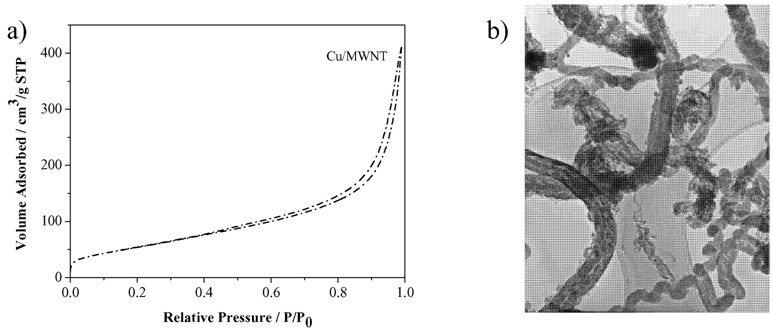


Figure 1 a) Nitrogen adsorption-desorption isotherm of copper and iron supported on MWNT, b) TEM image of copper supported on MWNT.

Figure 2 displays the XRD pattern of the Cu and Fe supported on MWNT. Characteristic peaks (002) and (100), of the graphite structure are visible (Gommes et al., 2004), corresponding to the periodicity between the graphene layers and within the graphene layer respectively. The characteristic XRD peaks of each metal, copper (2θ= 43.3) and iron (2θ= 45.3) were visible clearly.

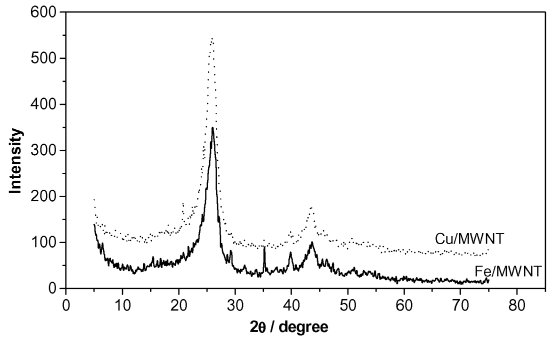


Figure 2 X-ray diffractogram of copper/MWNT and iron/MWNT.

3.2 Catalytic activity: Catalytic wet air oxidation process

The influence of temperature on the MB removal using Cu and Fe catalysts was studied by varying the temperature from 120 to 140 ºC. The reductions in TOC and color (concentration dye) for the different temperatures are shown in Figure 3. It can be seen that the copper catalyst, gave higher removal of TOC and color at different temperatures than iron catalyst. In general, when the temperature increases from 120-140 ºC, increase TOC and color removal in both catalysts.

Also, a positive effect (medium) was observed when catalyst concentration was increased (4-6 $g.L^{-1}$), the catalytic results show that the activity for oxidation was increased (Figure 4). TOC and color removal increase in both catalysts.

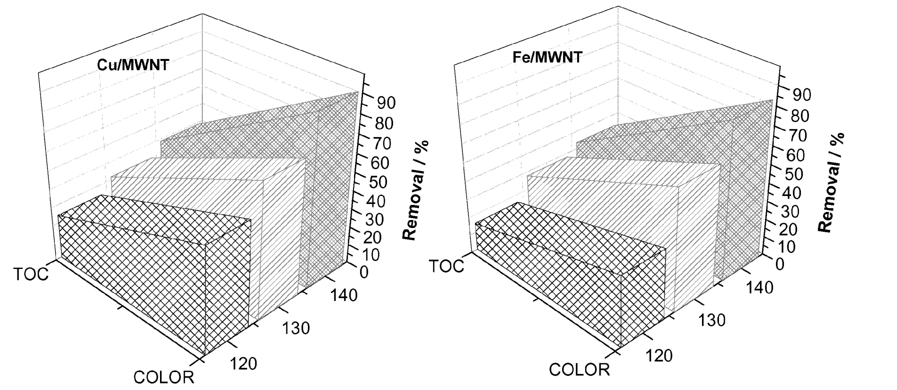


Figure 3 Influence of Temperature: Color and TOC removal with Cu and Fe catalysts in CWAO.

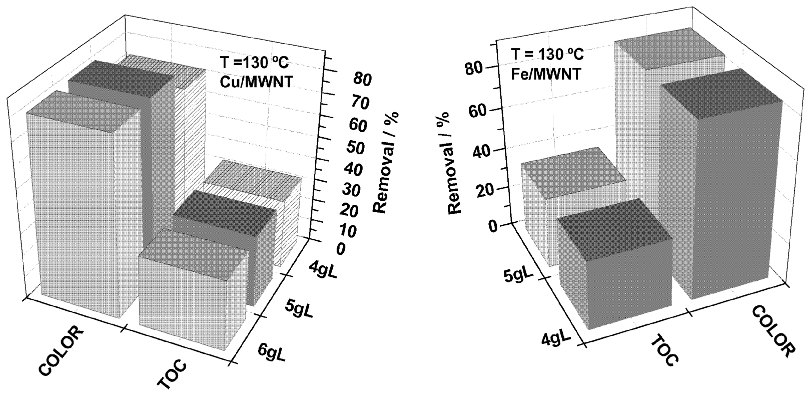


Figure 4 Influence of catalyst concentration: Color and TOC removal with Cu and Fe catalysts in CWAO.

To measure intermediates formed during the oxidation, a concentration of 50 $mg.L^{-1}$ was used for reaction at 130 ºC and 8.8 bar partial pressure over Cu/MWNT catalysts. The oxidized solution was taken for GC-MS analysis. Five intermediates were identified in the oxidized solution: butan-2-amine, acridinone, benzylidene, benzeneacetic acid and Benzonitrile m-phenethyl. Also, it is known that the main product of MB mineralization is SO_4^{2-} (Tang et al., 2004). Some studies on oxidative degradation of organic dyes have been reported previously (Garcia et al., 2005; Thompson et el., 1994). Several species are believed to be responsible for the decoloration, which include free radical species (Thompson et al., 1994). However, the exact mechanism for dye destruction is still in question. Most probably, the degradation proceeds by an adsorption-oxidation-desorption mechanism. Firstly, the MB molecules are adsorbed on the surface of the MWNT. Secondly, the nascent free radical species have high oxidizing ability and cause destructive oxidation of the organic dye. Thirdly, the small molecules from dye degradation are desorbed off the MWNT surface and the catalyst is, thus, recovered. For the last, the measured MB EC_{50} based on the Microtox procedure was better in toxicity reduction for the Cu catalyst (68%).

4. Conclusions

Copper or iron supported on multiwalled carbon nanotubes can be used as catalysts for selective oxidation of methylene blue in aqueous media. The catalytic activity of these catalysts when the reaction is carried out in temperature range 120-140 ºC and catalyst concentration 4-6 $g.L^{-1}$ is moderate in TOC removal, but high in color elimination, Cu/MWNT being the catalysts that showed the highest catalytic performance at 130 °C. In addition, the catalyst can be recycled without any loss in its capacity and efficiency (dates not shown). The high external surface areas heighten the potential capabilities of MWNT as support material.

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