Platinum catalysts supported on MWNT for catalytic wet air oxidation of nitrogen containing compounds

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Available online 25 March 2005

Abstract

Multi-walled carbon nanotubes (MWNT) activated by nitric acid oxidation were used to prepare supported platinum (1% Pt) catalysts by the excess solution impregnation method. Three different platinum precursors were used to prepare the impregnation solutions, namely diiodo dicarbonyl platinum(II) $[PtI_2(CO)_2]$, dimethyl (1,5-cyclooctadiene) platinum(II) $[Pt(CH_3)_2(C_8H_{12})]$ and hydrogen hexachloroplatinate(IV) hexahydrate $H_2PtCl_6 \cdot 6H_2O$. The catalysts were characterized by transmission electron microscopy (TEM) analysis and H_2 chemisorption. They were tested in the catalytic wet air oxidation (CWAO) of aniline aqueous solutions (200 °C and 6.9 bar of oxygen partial pressure). The Pt/MWNT catalyst prepared from $H_2PtCl_6 \cdot 6H_2O$ showed the best performance with respect to combined activity and selectivity for aniline conversion to non-organic compounds. This catalyst was used in CWAO (150 °C and 6.9 bar of oxygen partial pressure) of aqueous solutions of various textile dyes such as the monoazo dye chromotrop 2R (C2R), the diazo dye erionyl red B (ERB) and the triazo dye solophenyl green BLE (SG) 155%. It was found that the selectivity for dye removal decreased in the order diazo > monoazo > triazo. The CWAO of a textile wastewater was also performed using the same catalyst and identical reaction conditions. Complete color removal and 51.2% TOC abatement was obtained under these conditions.
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Keywords: Catalytic wet air oxidation; Platinum; Multi-walled carbon nanotubes; Wastewaters; Azo dyes

1. Introduction

Since their discovery [1] carbon nanotubes (CNT) have attracted great interest from both fundamental and applied standpoints. Following this interest, large-scale syntheses facilities are currently being established by several research laboratories [2,3]. Carbon nanotubes are examples of materials with a broad range of potential applications owing to their high mechanical and unique electrical properties [4]. These properties are also interesting when considering CNT as a support for preparing heterogeneous catalysts, especially for catalysts to be employed in liquid-phase reactions. The results published to date seem to indicate that nanostructured carbon can represent a new class of advanced materials for catalytic applications leading to more efficient and highly selective processes, therefore environmentally more benign [5–7]. Carbon nanotubes can be multi-walled, double-walled or single-walled, depending on the number (several, two or one, respectively) of graphitic layers [8]. In this work, we aimed at the preparation of platinum catalysts supported on multi-walled carbon nanotubes (MWNT) for the catalytic wet air oxidation (CWAO) of aqueous solutions with nitrogen containing pollutants (including model solutions of aniline or azo dyes) and textile wastewaters. CWAO is a known process for oxidative treatment of industrial wastewaters, due to its intrinsic efficiency in the elimination of chemical oxygen demanding species, by means of an oxidizing source under relatively mild conditions (125–220 °C, 5–50 bar) in the presence of an

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adequate catalyst. Previous studies have shown that platinum catalysts supported on activated carbon are very efficient for the CWAO of low molecular weight carboxylic acids [9], which are know to be very refractory towards oxidation.

Aniline was chosen as a model compound for preliminary catalytic tests, because it is a molecule present in several types of wastewaters, including those from the textile industry, it is highly toxic, and a known precursor used in the manufacture of dyes, including azo dyes [10]. The reports on the WAO of nitrogen-containing organic compounds in aqueous media were reviewed recently [11], and some references to the CWAO of aniline are included. However, to date there are no known reports about the elimination of aniline with Pt catalysts supported on MWNT. Therefore, we carried out a prospective study on the CWAO of aniline to select the most efficient catalyst. Further studies were then performed using the best catalyst in the CWAO of model solutions of azo dyes.

These dyes are used predominantly by textile mills but can also be found in the effluents of food, pharmaceutical, paper and printing, leather, and cosmetics industries [12,13]. It is not surprising that these compounds have become a major environmental concern. Many of these dyes find their way into the environment via wastewater treatment facilities. The effluent from textile plants normally exhibits a deep coloration, which prevents the transmission of light, thus condemning the development of aquatic life in natural environment. In the present work, we will study the degradation of three azo dyes in aqueous solution: chromotrop 2R (C2R), erionyl red B (ERB) and solophenyl green BLE 155% (SG). The chemical structures of the dyes are shown in Fig. 1. The selected azo dyes have different number of N=N double bonds, the C2R being a monoazo dye, ERB a diazo dye and SG a triazo dye.

Because these compounds retain their color and structural integrity under exposure to sunlight, soil, bacteria and sweat, they also exhibit a high resistance to microbial degradation in wastewater treatment systems [14]. Therefore, it is mandatory to reduce the amounts of aniline and azo compounds at the end of pipe effluents in textile industries before release of the wastewaters into the aquatic ecosystem.

2. Experimental

2.1. Support

MWNT were used as support in the preparation of platinum catalysts. The carbon nanotubes were produced by catalytic chemical vapour deposition of ethylene using alumina-supported iron as catalyst [3,15]. The composite material obtained from the CVD production step, consisting of nanotubes, iron and alumina, was then purified by a sulphuric acid treatment. The aim of this step was to accomplish the total dissolution of alumina and the partial elimination of iron contained in the tubes. The final material has a purity of 97%. MWNT prepared by this method have almost a complete absence of functional groups on their surface, which is a disadvantage for the preparation of carbon supported metal catalysts, due to the lack of anchoring sites. The carbon surface chemistry was therefore modified by means of an acidic treatment (HNO_3, 5 M) for 3 h under reflux, leading to the formation of carboxylic acid groups (–COOH). After oxidation, the support was washed with distilled water until neutrality of the rinsing waters for 6 h and finally dried overnight at 110 °C. The acidic surface sites created on the MWNT surface are reactive allowing easier anchoring of the platinum precursors, thus leading to higher catalyst dispersions [16]. Following this production mechanism the resulting MWNT are essentially non-porous (the inner cavity of the nanotube remains inaccessible due to the mild acidic teatment) with all the observed surface area owed to adsorption on the external surface of the tubes [17]. The oxidized MWNT were characterized by temperature programmed desorption and N_2 adsorption isotherms at 77 K, as described elsewhere [18]. The so calculated micropore volume and non-micropore surface area were 0.001 $cm^3\,g^{-1}$ and 175 $m^2\,g^{-1}$, respectively. The BET surface area of the oxidized MWNT was 175 $m^2\,g^{-1}$, as determined by the *t*-plot from the same data [18].

2.2. Catalyst preparation

The platinum was introduced by excess solution impregnation on the oxidized MWNT. Three different platinum precursors were selected and dissolved in appropriate solvents according to their solubility. Diiodo dicarbonyl platinum(II) $[PtI_2(CO)_2]$ was dissolved in toluene, dimethyl (1,5-cyclooctadiene) platinum(II) $[Pt(CH_3)_2(C_8H_{12})]$ in hexane and hydrogen hexachloroplatinate(IV) hexahydrate $[H_2PtCl_6]\cdot6H_2O$ in water. The amount of each precursor was calculated in order to obtain a final 1 wt.% Pt catalyst. The wet solid was dried overnight at 110 °C and then reduced at 350 °C for 3 h in a furnace under a flow of H_2/N_2 (10%, v/v) in order to reduce platinum.

2.3. Catalyst characterization

Determination of metal dispersion was carried out at room temperature by pulse chemisorption experiments. Pulses of H_2 were injected at regular time intervals until the area of the recorded peaks became constant.

Transmission electron microscopy (TEM) micrographs were obtained on a Philips CM12 instrument (120 keV) using carbon coated copper grids. Fairly clean MWNT can be observed after purification treatment and surface oxidation processes.
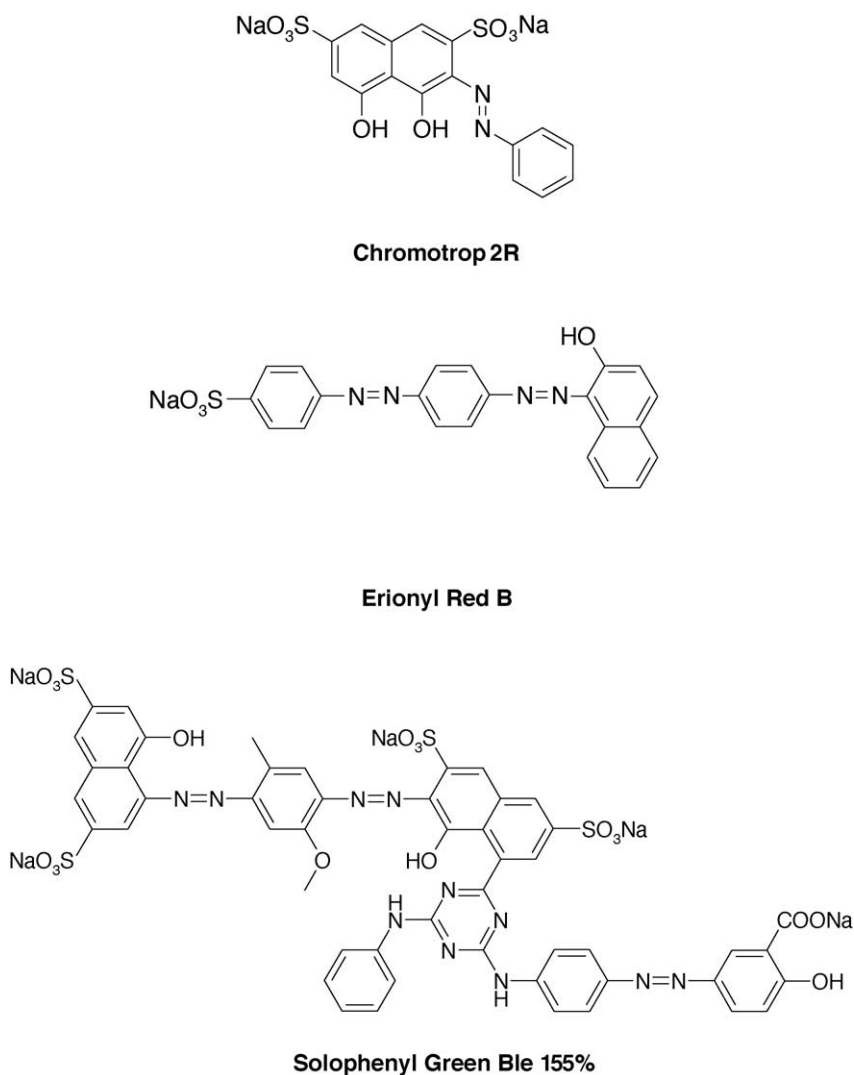
Chromotrop 2R

Erionyl Red B

Solophenyl Green Ble 155%

Fig. 1. Molecular structures of chromotrop 2R (C2R), erionyl red B (ERB) and solophenyl green BLE 155% (SG).

2.4. Catalytic wet air oxidation procedure

Catalytic wet air oxidation experiments were performed in a stainless-steel high-pressure reactor (Parr Instruments Co., USA, 4564) with a volume of $160\,cm^3$, capable of running batch experiments at pressures up to 100 bar and temperatures up to 350 °C. The reactor is equipped with a stirrer, regulated electronically, with rotation speed of 500 rpm being chosen to ensure proper mass transfer of air in the liquid phase. A constant temperature was maintained with an electronic controller. Air was used as the oxidizing agent, obtained from an air cylinder connected to the reactor.

In the non-catalyzed wet air oxidation (WAO) experiments the reactor was fed with 75 mL of aniline solutions (2 g/L), dye compounds (2 g/L) or textile wastewater. In catalytic runs, 0.8 g of catalyst was added. After feeding the reactor, heating was applied until the desired temperature was reached. Then, air was introduced into the reactor to the

desired pressure and the reaction was allowed to proceed for 2 h. At regular time intervals, liquid samples were taken from the reactor and analyzed for aniline or dye concentration and TOC content.

2.5. Product analysis

Samples resulting from aniline and dye oxidation experiments were analysed with respect to their TOC content to assess the degree of total oxidation. Since TOC analysis provides only information about the removal of total organic carbon from the liquid-phase, selectivity to non-organic compounds (S_{NOC}) was defined as $100(X_{TOC}/X_{Aniline})$ or $100(X_{TOC}/X_{dye})$, where X_{TOC}, $X_{Aniline}$ and X_{dye} are TOC, aniline and dye conversion, respectively The possibility of coke deposition in the catalyst is not excluded, although is not likely to occur. In this way, the definition accounts for all non-organic forms of carbon that can be produced (CO_2, C, . . .).

In the oxidation of textile wastewaters the parameters monitored were TOC and color. TOC was determined with a Shimadzu TOC analyzer. Total carbon (TC) was measured first, followed by inorganic carbon (IC) measurement. The TOC was calculated subtracting IC from TC. Color was measured in terms of the characteristic peaks in the UV–vis spectrum.

Aniline concentration was analyzed by gas chromatography on a capillary column (WCOT fused silica 30 m, 0.32 mm i.d., 1 μm film). Dye concentration was recorded on a JASCO V-560 UV–vis spectrophotometer with a double monochromator, double beam optical system.

3. Results and discussion

3.1. Catalyst characterization

The metal dispersions obtained for the prepared catalysts are given in Table 1. The Pt/MWNT(2) and Pt/MWNT(3) catalysts, prepared from $[Pt(CH_3)_2(C_8H_{12})]$ and $[H_2PtCl_6]\cdot6H_2O$, have higher metallic dispersions, 27.4 and 26.8%, respectively.

TEM observations (Fig. 2) are in agreement with the metallic dispersions obtained in the chemisorption experiments. The catalyst prepared from $[Pt(CH_3)_2(C_8H_{12})]$ precursor is the more homogeneous with the highest metal dispersion, containing spherical Pt metal particles with diameters ranging from 2 to 4 nm. As can be observed from the insertions, Pt/MWNT(1) prepared from $[PtI_2(CO)_2]$ contains spherical Pt particles slightly bigger, with diameters ranging from 3 to 7 nm.

3.2. CWAO of aniline

The MWNT supported platinum catalysts prepared with different platinum precursors (Table 1), were tested in the CWAO of aniline in order to characterize their performance. The catalytic results obtained at 200 °C and 6.9 bar of oxygen partial pressure are shown in Fig. 3.

The catalysts have identical performances on the long run (120 min), attaining almost complete conversion of aniline in all cases. The decay curves follow a fairly exponential decay.

In a previous work an activated carbon supported Pt catalyst was used in the CWAO of aniline under similar conditions [18] and the obtained aniline and TOC conversions are given in Table 2, for comparison purposes. It should be stressed that the amount of catalyst used in each
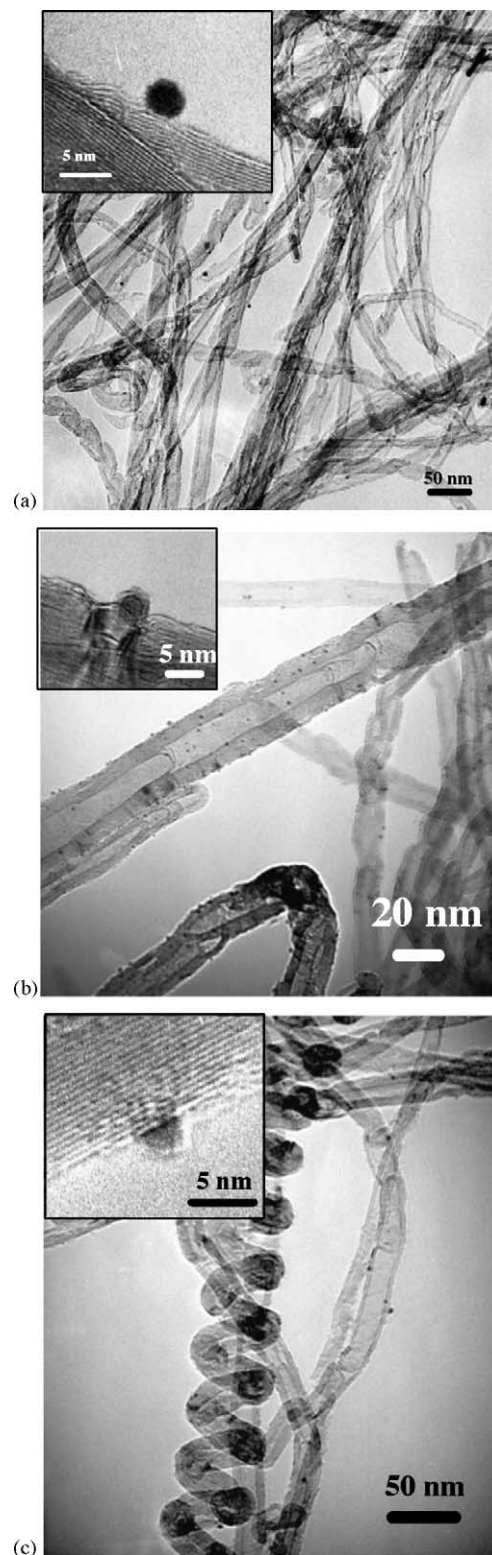

Fig. 2. TEM micrographs of (a) Pt/MWNT(1) catalyst prepared from $[PtI_2(CO)_2]$; (b) Pt/MWNT(2) catalyst prepared from $[Pt(CH_3)_2(C_8H_{12})]$; and (c) Pt/MWNT(3) prepared from $[H_2PtCl_6]\cdot6H_2O$. Insertion on the top left corner of each picture is a magnification showing a detail of a platinum particle anchored to the external MWNT surface.

Table 1
Metal dispersion of the prepared MWNT supported Pt catalysts

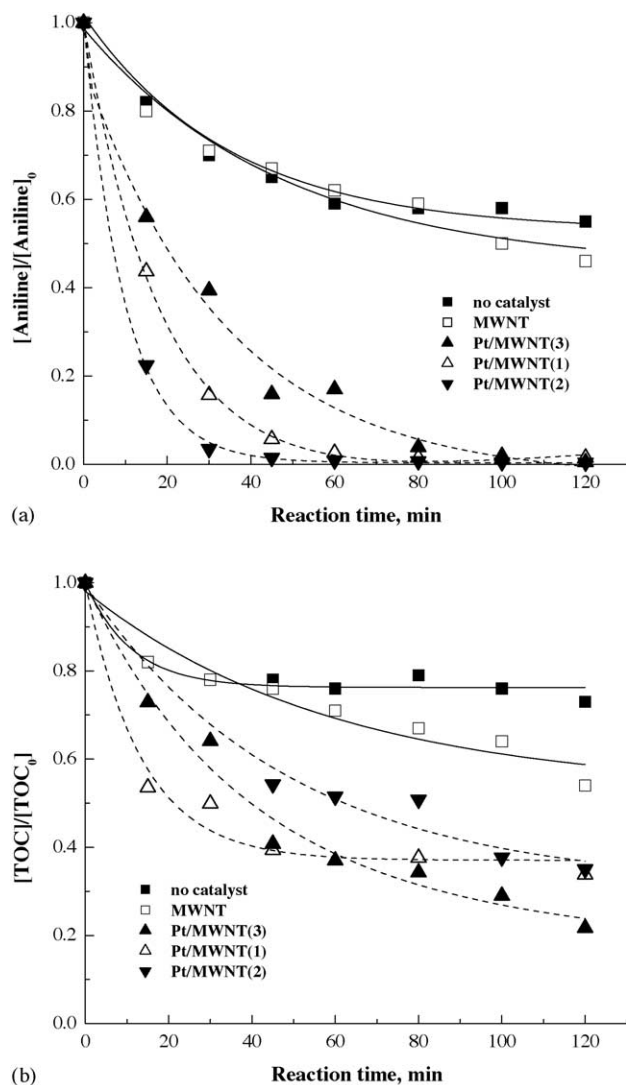| Catalyst	Precursor	Solvent	D_M (%)
Pt/MWNT(1)	$[PtI_2(CO)_2]$	Toluene	16.5
Pt/MWNT(2)	$[Pt(CH_3)_2(C_8H_{12})]$	Hexane	27.4
Pt/MWNT(3)	$[H_2PtCl_6]\cdot6H_2O$	Water	26.8

Fig. 3. CWAO of aniline at 200 °C and 6.9 bar of oxygen partial pressure using different catalysts: (a) aniline; and (b) TOC conversion.

experiment is 10.7 g/L (which is comparable to some of the existing reports for Pd supported catalysts [11]). In terms of aniline conversion all the prepared catalysts exhibit good performances with relation to those reported in the literature [11,19]. A high degree of aniline conversion is achieved either at half residence time (>83% at 60 min) or at the end of reaction (>98% at 120 min). The catalyst prepared from

Table 2
CWAO of aniline aqueous solution 2 g/L at 200 °C and 6.9 bar of oxygen partial pressure

Catalyst	$X_{Aniline}$ (%)	X_{TOC} (%)	S_{NOC} (%)
None	45.0	27.4	60.8
MWNT	54.0	45.7	84.6
Pt/MWNT(1)	98.5	66.2	67.2
Pt/MWNT(2)	99.5	65.0	65.3
Pt/MWNT(3)	99.4	78.3	78.8
Pt/AC [18]	100	94.5	94.5

Results after 120 min of reaction.

the $[H_2PtCl_6]\cdot 6H_2O$ precursor has a slightly poor performance on the short run (60 min) exhibiting only 83% conversion of aniline, compared with more than 95% for the other two. In the non-catalytic WAO of aniline, the maximum conversion attained was only 42% after 60 min, increasing to a modest 45% in the 120 min complete run. The effect of the nitric acid oxidized MWNT is negligible, barely increasing the final conversion.

If the TOC removal is considered (Fig. 3b), the conversion of aniline in the WAO after 120 min is 27.4%. In the presence of the nitric acid oxidized MWNT it increases almost to the double (45.7%). In the catalyzed process, TOC removal is always higher than 65%, the maximum value being 78.3%, for the catalyst prepared from $[H_2PtCl_6]\cdot 6H_2O$. The curves for TOC conversion do not follow the same kinetic patterns, neither the same activity order observed for aniline removal, suggesting that the different catalysts give rise to different oxidation reaction paths. Considering the fact that the examined catalysts differ in the use of various Pt precursors, these different behaviors might be due to different chemical surface properties of the synthesized catalysts. The formation and further oxidation of intermediate compounds may depend significantly on the acidic/basic properties of the catalysts surface.

The ratio $100(X_{TOC}/X_{Aniline})$ (S_{NOC}) is a good measure of the selectivity of aniline conversion to non-organic compounds. The individual values for S_{NOC} are given in Table 2. In the absence of catalyst, the selectivity towards non-organic compounds formation is 60.8%. It is worth noticing that in the presence of the nitric acid oxidized MWNT this selectivity is 84.6%. This value corresponds to the highest selectivity obtained for the CWAO of aniline under the current conditions. The selectivity obtained for the catalysts containing Pt range from 65.3 to 78.8%. This suggests, that in spite of the modest conversion obtained in the case of the oxidized MWNT, the CWAO goes through a simpler oxidation pathway.

From the literature, it was known that the WAO of aniline under more extreme conditions (same temperature but under 20 bar oxygen pressure) could lead to significant conversions [20], which is in line with our control experiments made in absence of any catalyst (lower oxygen pressure, lower aniline conversion). Somewhat better conversions are obtained in the experiment using the naked MWNT support. However, it is obvious that supporting platinum on MWNT significantly increases both aniline and TOC conversions. For the prepared catalysts the selectivity towards non-organic compounds formation (S_{NOC}) decreases following the order $[H_2PtCl_6]\cdot 6H_2O >$ $[PtI_2(CO)_2] > [Pt(CH_3)_2(C_8H_{12})]$.

The performance of the prepared catalysts can be attributed to the high external surface area and the complete absence of micropores in the MWNT providing an efficient surface contact between the aniline and the active sites, especially in liquid-phase medium where the mass transfer phenomenon becomes very significant [16]. On the other

hand, the higher external surface areas of the activated carbons are probably responsible for the higher X_{TOC} (Table 2), suggesting that modified MWNT with higher external surface area may be more efficient.

Following the observation that the best performance in X_{TOC} after 120 min of reaction was from the catalytic system prepared with [H$_2$PtCl$_6$]·6H$_2$O it was decided to use it in further studies with azo dyes and a textile wastewater.

3.3. CWAO of azo dyes

The efficiency on the oxidation of the solutions of dyes was evaluated in terms of two usually adopted indicators for global degradation performance: color bleaching by removal of the most intense absorption peaks in the 200–700 nm (UV–vis range) and TOC removal.

Since temperature is one of the operating variables with strong implications in the efficiency of the process it was decided to investigate its effect in the degradation of dyes in aqueous solutions. WAO experiments (no catalyst) were conducted at different temperatures between 100 and 200 °C at 120 min of residence time, under 6.9 bar of oxygen partial pressure and with dye concentration of 2 g/L (Fig. 4). As the reaction temperature was increased from 100 to 200 °C, a remarkable increase in the rate of degradation of all azo dyes was obtained. At 100 °C dye oxidation and TOC removal are negligible, for all dyes. At 150 °C still no oxidation or dye conversion was observed in the case of two dyes, namely SG and C2R, while for the diazo dye ERB a 28% conversion and no TOC removal was registered. At 200 °C dyes removal and TOC reduction were very high. In the case of SG, 95.1% conversion (58.7% selectivity towards non-organic compounds) with 55.8% TOC removal was observed. For ERB, the conversion was only 71.7% (13.9% selectivity towards non-organic compounds) with 10.0% TOC removal. Finally, complete dye conversion was obtained for C2R just after 60 min. For comparison purposes at 120 min, TOC removal was 88.7% and selectivity towards non-organic compounds of 88.7%. In view of these findings, it was decided to set the temperature for the CWAO at 150 °C. This temperature is enough to keep oxygen dissolved and water in the liquid phase, provided that a 6.9 bar of oxygen partial pressure (in air) is used.

In the presence of the selected Pt/MWNT catalyst, the removal rate of dye and TOC was significantly enhanced with respect to the WAO process (Fig. 5). After 120 min of reaction, almost 100% conversion was obtained for all azo dyes.

Thus, the dyes can effectively be degraded within a reasonable time at this moderate temperature with the Pt/ MWNT catalyst. At 150 °C, the removal of TOC and dye concentration decreased in the following order: diazo > monoazo > triazo, with selectivity towards non-organic compounds formation of 21.3, 63.5 and 78.1% being observed when the triazo, monoazo and diazo dyes were used, respectively (Table 3). Nevertheless, total color

removal was observed in the degradation of all azo dyes, indicating that their destruction should occur by attack of reactive oxidation species on the N=N bonds, generating small intermediate molecules. The lowest selectivity towards non-organic compounds formation was obtained in the degradation of the triazo dye (SG), because a great complexity of oxidation intermediates should be expected to occur.

3.4. CWAO of a textile wastewater

The most active catalyst Pt/MWNT(3) from [H$_2$PtCl$_6$]·6H$_2$O was used in the treatment of a real wastewater resulting from a textile plant. The removal of TOC by WAO and CWAO at 150 °C is shown in Fig. 6. In the non-catalytic process, after 120 min the TOC removal was 23.6%, and increased to 51.2% under the same conditions but in the presence of the Pt/MWNT catalyst.

Concerning color removal, it was also observed that in the WAO process 73% of the absorption in the UV–vis was removed, while color was completely removed in the CWAO. The pH remained unchanged in the WAO of the wastewater, and decreased from 6.0 to 5.4 in CWAO. The results obtained in this real case application show that the catalyst based on MWNT significantly improves TOC and color removal in CWAO.

4. Conclusions

CWAO of model solutions of aniline and three different azo dyes was efficiently performed using Pt/MWNT catalysts. The process was successfully applied to the treatment of a real wastewater from a textile plant. The most relevant findings of this study are as follows:

(1) Multi-walled carbon nanotubes can be efficiently used as metal support for catalytic reactions in liquid-phase, particularly in the oxidation of nitrogen containing pollutants.

(2) In CWAO of aniline at 200 °C and 6.9 bar of oxygen partial pressure, it is possible to achieve complete conversion after 120 min of residence time with different Pt/MWNT (1%, w/w) catalysts.

(3) Aqueous solutions of solophenyl green BLE 155%, erionyl red B and chromotrop 2R can be efficiently decolorized in CWAO at 150 °C and 6.9 bar of oxygen partial pressure, using a Pt/MWNT catalyst.

(4) Application of WAO and CWAO to the treatment of a textile effluent at 150 °C and 6.9 bar of oxygen partial pressure showed that the use of a Pt/MWNT catalyst significantly improves the TOC and color removal efficiencies. Therefore, CWAO can be considered as an option for a pre-treatment step in the treatment of textile waste waters.
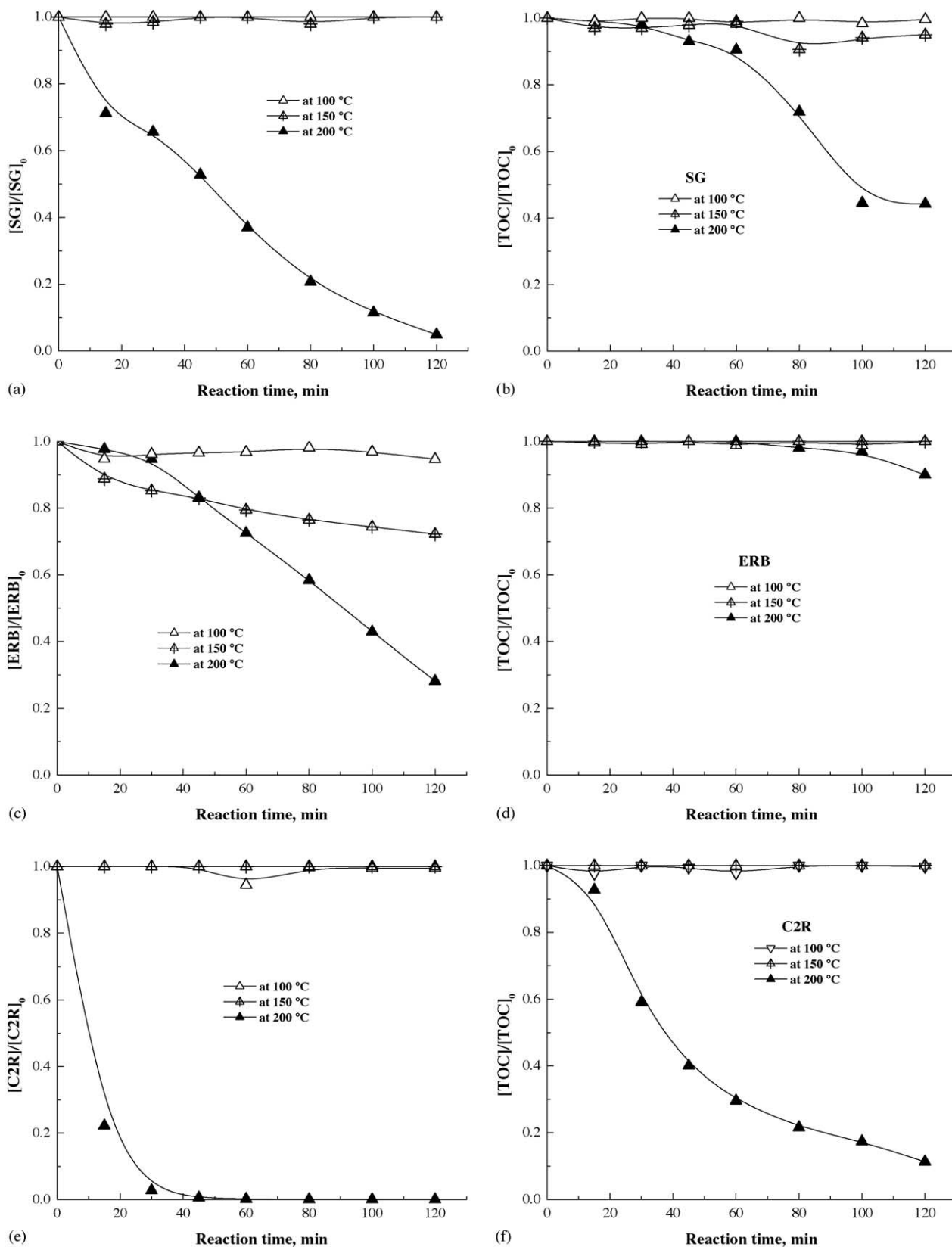
Fig. 4. WAO of aqueous solutions of: (a, b) SG; (c, d) ERB and (e, f) C2R dyes. Effect of temperature on dye (a, c, e) and TOC (b, d, f) conversion.
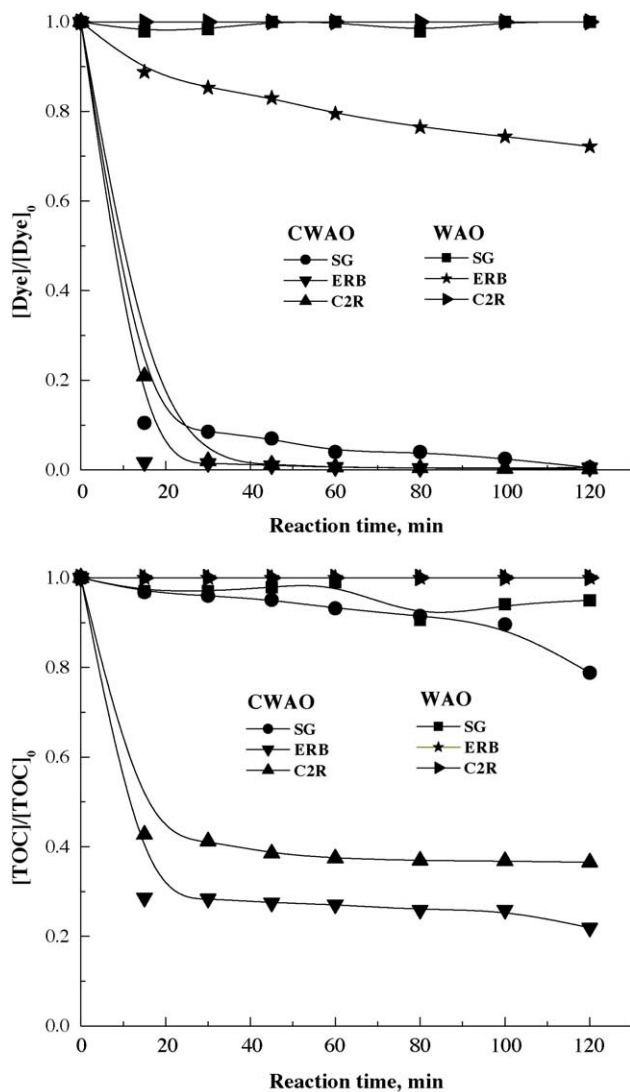
Fig. 5. CWAO of azo dyes at 150 °C and 6.9 bar of oxygen partial pressure using Pt/MWNT(3) catalyst.
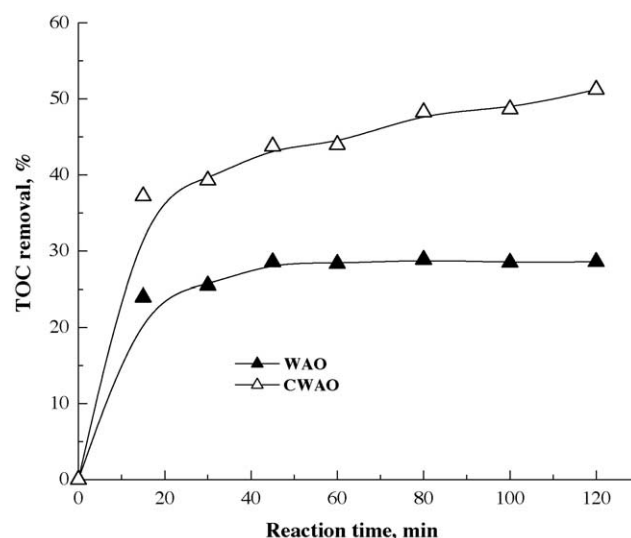

Fig. 6. TOC removal obtained in the WAO and CWAO (using Pt/MWNT(3)) of a textile wastewater at 150 °C and 6.9 bar of oxygen partial pressure.

textile wastewaters, using more elaborated processes requiring novel and efficient catalysts. The results here reported may add some insight to the development of these highly efficient catalysts of the future.

Aniline and azo dyes represent a severe threat to the aquatic environment—just a small amount of dye is enough to cause serious transparency problems in the water, condemning life in the affected eco-systems. It is therefore, necessary to develop ways of removing color and TOC from

Table 3
CWAO of aqueous dye solutions at 150 °C and 6.9 bar of oxygen partial pressure

Azo dye	Process	X_{dye} (%)	X_{TOC} (%)	S_{NOC} (%)
SG	WAO	0	0	0
	CWAO	99.5	21.2	21.3
ERB	WAO	28.0	0	0
	CWAO	99.5	78.1	78.5
C2R	WAO	0	0	0
	CWAO	100	63.5	63.5

Results after 120 min of reaction.

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