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Hydrotalcites: a highly efficient ecomaterial for effluent treatment originated from carbon nanotubes chemical processing

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Abstract. It has been reported that a mixture of carboxylated carbonaceous fragments (CCFs), so called oxidation debris, are generated during carbon nanotubes chemical processing using oxidant agents such as HNO₃. The elimination of these fragments from carbon nanotubes surface has been point out to be a crucial step for an effective functionalization of the nanotubes as well as for improving the material. However, this process can introduce a potential environmental problem related water contamination because these CCFs can be viewed as a mixture of carbonaceous polyaromatic systems similar to humic substances and dissolved organic matter (DOM). The negative aspects of humic substances and DOM to water quality and wastewater treatment are well known. Since carbon nanotubes industry expands at high rates it is expected that effluent containing oxidation debris will increase since HNO₃ chemical processing is the most applied method for purification and functionalization of carbon nanotubes. In this work, we have demonstrated that Hydrotalcites (HT) are highly efficient to remove oxidation debris from effluent solution originated from HNO₃-treated multiwalled carbon nanotubes. The strategy presented here is a contribution towards green chemistry practices and life cycle studies in carbon nanotubes field.

1. Introduction

Safety issues are important in nanotechnology and they need to be addressed before the products originating from this emerging technology platform come to the market on a large scale. Many aspects including ethics and new ways of preventing waste generation either during fabrication or manipulation of nanomaterials are key points. The starting step for any nanotechnology outcome begins with nanomaterials fabrication and/or processing (purification, functionalization, etc). Safe disposal and recycling strategies should be present in order to achieve sustainable development of this emerging technology. In this regard, one should think about the full life cycle of the nanomaterials and this assessment demands green strategies that would prevent society from facing serious health and environmental problems in the future [1]. Therefore, the sustainable development of nanotechnologies will depend on developing the ability to control both health and environmental risks, thus not creating...
or at least minimizing future problems similar to those that people have faced from many of the
technologies developed in the last century.

Carbon nanotubes are among the most promising materials for nanotechnologies and their
applications in electronics, materials, and biotechnology demands chemical treatments (purification
and oxidation) of the as-prepared samples and nitric acid treatment is one of the most applied methods
for achieving this goal [2]. Recent work has pointed out that the treatment of carbon nanotubes with
concentrated nitric acid generates a mixture of oxygenated polyaromatic-like fragments. These
polyaromatic-like compounds have been called “oxidation debris” or carboxylated carbonaceous
fragments (CCFs) and they play an important role in the functionalization of carbon nanotubes
because these fragments adsorb on the nanotubes surface [3-5]. The removal of these fragments from
the carbon nanotubes surface is crucial for developing nanotubes surface chemistry and studies about
their removal from the nanotubes have been reported [6-8].

Although the removal of oxidation debris from the carbon nanotubes surface is not a currently
standard procedure for applications of oxidized carbon nanotubes, this procedure can be largely
applied in carbon nanotubes field to improvement of the material quality. However, the industrial
implementation of this procedure can introduces a potential environmental problem because these
CCFs can be viewed as a mixture of carbonaceous polyaromatic systems similar to dissolved organic
matter (DOM) and humic substances which play an important role in water quality and wastewater
treatment [9, 10] as well as on the interaction with many environmental pollutants [11-13]. Since the
carbon nanotubes mass production and application is growing very fast it is very important to find a
safe way of handling this emerging residue that would be generated in the chemical processing of
these oxidized carbon nanotubes. Therefore, the investigation of removal process of oxidation debris
compounds is important in view of contributing to the development of a proactive, safe and
environmental friendly carbon nanotubes-based technology.

In this paper we address this problem using a layered double hydroxide material, the so called
Hydrotalcites (HT), for removing the oxidation debris from sodium hydroxide solution (effluent
originated from carbon nanotubes chemical processing). These layered materials are important
ecomaterials [14] and opened up many possibilities of removing pollutant species from water not only
through adsorption on the external surface of the layers but also through an intercalation process [15-
17]. The use of this ecofriendly material is a strategy that contributes to address the issue of a safe
cycle-end nanomaterials disposal [18, 19].

2. Experimental

All chemicals (reagent grade, Synth or Vetec) were used as received, without further purification.
Commercially available chemical vapour deposition (CVD) grown multiwall carbon nanotubes
(MWCNT) [Ctube 100, CNT Co. Ltd., Incheon – South Korea] were used.

2.1. Nitric acid treatment of Multiwalled carbon nanotubes.

The MWCNT (1.0 g) were refluxed in HNO₃ 7.0 mol/L (200 mL) for 24 h at 140 °C. After cooling to
room temperature, they were filtered through a 0.2 µm PTFE membrane and washed with deionized
water until neutral pH of the filtrate was reached. The oxidized MWCNT were dried in vaccum system
for 24 h.

2.2. Preparation of oxidation debris effluent stock-solution.

The oxidation debris stock-solution was prepared according to the method described by Verdejo et al
[5]. Briefly, the nitric acid oxidized MWCNT (0.25 g) were homogenized in 0.1 mol/L of sodium
hydroxide solution (200 mL). Then the mixture was sonicated in an ultrasound bath [Cole-palmer
8891] for 15 min. After it was submitted to strong magnetic stirring for 1 h. The colored filtrate
(orange-brown) was obtained using standard filtration system through a 0.2 µm PVDF membrane.
This filtrate has considered to be oxidation debris or CCFs compounds (effluent stock solution) and
was used in further adsorption studies.
2.3. Hydrotalcites synthesis.

Mg–Al-based hydrotalcite with a Mg$^{2+}$/Al$^{3+}$ molar ratio equal to 2 was prepared by the co-precipitation method at variable pH. An aqueous solution (100 ml) containing 0.1 mol of Mg(NO$_3$)$_2$•6H$_2$O and 0.05 mol of Al(NO$_3$)$_3$•9H$_2$O was added dropwise under vigorous mechanical stirring into a 2.0 mol/L NaOH solution (150 ml). After addition of the nitrates the mixture was kept at room temperature and maintained for 2 h under stirring for ageing. The solid product was separated by centrifugation and washed several times with deionized water until pH 7–8. Finally, the solids were dried at 40 °C for 48 h and crushed above 150 meshes. The same procedure was adopted for the chloride and sulfate samples, using magnesium and aluminium chlorides and sulphates solutions respectively. The Mg$^{2+}$/Al$^{3+}$ molar ratio was kept equal to 2 and so were the synthesis, ageing and drying conditions.

2.4. Adsorption experiments.

Adsorption experiments of oxidation debris onto hydrotalcites were carried out in centrifuge tubes containing 5.0 mL of effluent stock-solution at room temperature under magnetic stirring. Then, the effect of three parameters were evaluated: (i) interlayer anion SO$_4^{2-}$, NO$_3^-$ and Cl$^-$, (ii) contact time: 30 min, 60 min and 90 min and (iii) HT/ effluent stock-solution volume ratio = 1.0, 5.0 and 10 g/L. These tubes were subsequently centrifuged at 3500 rpm for 10 min. The adsorbed oxidation debris or CCFs concentration was evaluated using UV-vis spectrometer at 500 nm wavelength and expressed as percentage of the removal.

2.5. Characterization methods.

Absorption spectra of solutions were obtained using a UV-visible spectrophotometer [Shimadzu model UV-1650 PC]. X-ray powder diffraction (XRD) patterns were obtained with a Shimadzu XRD6000 diffractometer, using Cu Kr (1.5406 Å) radiation operating with 30 mA and 40 kV. A scan rate of 1°/min was employed. The Fourier transform infrared (FT-IR) spectra were recorded using a Bomem MB spectrometer in the 4000-400 cm$^{-1}$ frequency range. A total of 34 scans and a resolution of 4 cm$^{-1}$ were employed in obtaining the spectra. The KBr solid was used to prepare the samples for FT-IR analysis.

3. Results and Discussions

Chemical oxidation of carbon nanotubes using HNO$_3$ has been used for purifying, cutting and functionalizing carbon nanotubes aiming to improve their dispersion in water and other solvents. Dillon et al. [20] observed that treatment of carbon nanotubes with nitric acid produces a uniform functionalized coating of disordered carbon on the nanotubes sidewalls. Recently it has been shown that this functionalized coating (oxidation debris), is indeed the major carrier of the COOH groups present in the sample, and that it can be easily removed from tube surface by base aqueous wash such as NaOH [21, 22]. The colored (orange-brown) sodium hydroxide filtrate shown in the insert to Figure 1 contains oxidation debris compounds resulting from the oxidative fragmentation of MWCNT using 7.0 mol/L HNO$_3$ for 24 h at 140 °C. UV-visible absorption spectrum (Figure 1) of the alkaline filtrate (effluent originated from carbon nanotubes chemical processing) exhibits a broad adsorption profile, with a shoulder at about 280 nm. The spectrum indicates the presence of a molecular chromophore containing a system of conjugated double or triple bonds or polycyclic aromatic substances. This spectral characteristic supports the identification that CCFs or oxidation debris were generated during acid oxidation [23].

The colored oxidation debris dispersion is a potential water contaminant and it must be remediated before being returned to the aquatic environment. The implementation of green chemistry principles seems to be an appropriated strategy towards sustainability, which includes the use of ecofriendly materials for treating wastewater or effluents such as the oxidation debris. Hydrotalcites have these characteristic and they appear as natural candidates to be tested as sorbent material for removal of oxidation debris from wastewater. HT compounds have positively charged layers and the interlayer space is negatively charged thus leading to a system with a rich adsorption and intercalation chemistry.
Many studies have been devoted to investigating the ability of HT to remove harmful oxyanions such as, humic substances, phenols, herbicides, pesticides, boron, textile dyes, among other anionic pollutants from water [24, 25]. In this sense, the HT materials were synthesized by co-precipitation method of nitrate, sulfate and chloride solutions of magnesium and aluminium. The obtained solids were named HT-NO\(_3\), HT-SO\(_4\) and HT-Cl, respectively. XRD and FT-IR analysis have confirmed that Hydrotalcites structures were obtained (Figure 2).

Figure 1. (a) Filtration system used to separation of oxidation debris from oxidized multiwalled carbon nanotubes. The arrow indicates the oxidation debris effluent; (b) UV-vis absorption spectrum of oxidation debris effluent stock-solution filtrate wash originated from oxidized multiwall carbon nanotubes (see text). [Inset: Oxidation debris effluent stock-solution].

Figure 2. (A) X-ray diffraction patterns and (B) FT-IR spectroscopy of the as-prepared Hydrotalcites.

Table 1. Percentage of oxidation debris removal as a function of interlayer anion, contact time and HT/effluent stock-solution volume ratio.

<table>
<thead>
<tr>
<th>HT/Volume Ratio</th>
<th>HT-NO(_3) (%)</th>
<th>HT-SO(_4) (%)</th>
<th>HT-Cl (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 min</td>
<td>60 min</td>
<td>90 min</td>
</tr>
<tr>
<td>1.0 g/L</td>
<td>63.8</td>
<td>90.4</td>
<td>94.4</td>
</tr>
<tr>
<td>5.0 g/L</td>
<td>86.5</td>
<td>100</td>
<td>97.2</td>
</tr>
<tr>
<td>10 g/L</td>
<td>95.0</td>
<td>100</td>
<td>99.4</td>
</tr>
</tbody>
</table>
Since oxidation debris is a mixture of carboxylated carbonaceous fragments (negatively charged) we have evaluated the potential of our synthetic Hydrotalcites (positively charged) to remove these fragments dispersed in NaOH solution (effluent stock-solution). The amount of oxidation debris removed by the hydrotalcites from an effluent stock-solution increase by increasing the HT quantity and contact time as shown in Table 1. All HT samples prepared were found to be highly efficient for removing oxidation debris compounds reaching the complete removal after 60 min. For 30 min test it was observed the highest removal efficient levels for HT-SO\textsubscript{4} (superior to 80%). Quantitative (Table 1) and qualitative data inspection (Figure 3), indicate that Hydrotalcites are very efficient as sorbents for these oxidation debris compounds from carbon nanotubes.

**Figure 3.** Qualitative assessment of oxidation debris removal as a function of Hydrotalcite (HT-NO\textsubscript{3}) content: (A) 0.1 g/L; (B) 1.0 g/L; (C) 5.0 g/L; (D) 7.0 g/L; (E) 10 g/L; (F) 15 g/L; (G) 20 g/L. All systems were submitted to 30 minutes of magnetic stirring starting with a 5 mL of oxidation debris effluent stock-solution.

In order to get further insights into the adsorption mechanism we have performed X-ray diffraction (for probing interlayer distance) and FT-IR spectroscopy (for probing interlamellar species) for as-prepared and debris-adsorbed HT-NO\textsubscript{3} (Figure 4). We can observe that after the interaction with oxidation debris residue the X-ray pattern does not exhibit significant change. Both angular position and relative intensity of the various diffraction peaks are the same thus indicating that the oxidation debris residues are likely to be adsorbed on the HT-NO\textsubscript{3} surface rather than intercalated in the interlayer space. The infrared spectra for both samples are quite similar thus suggesting that the species in the interlamellar space are not affected by the presence of oxidation debris.

By comparing the FT-IR spectra for as-prepared samples and debris-adsorbed HT-NO\textsubscript{3} we can observe a change in the band about 1640 cm\(^{-1}\) that is related to H-O-H deformation mode from water. For the debris-adsorbed sample we observe a new peak located at 1590 cm\(^{-1}\) (marked with a down arrow) which can be attributed to C=C vibration from the fragments (oxidation debris) adsorbed on the Mg-Al HT-NO\textsubscript{3}. However, a peak related to C=O from the carboxylic groups, which are expected to saturate the edges of carbon fragments, was not observed. By combining X-ray and FT-IR data we came to the conclusion that the basic mechanism of removing oxidation debris from the base aqueous solution is by adsorption rather than by intercalation.

The results showed that Mg-Al-based HT can be efficiently used for removing oxidation debris dispersed in base aqueous solution and this protocol offers to both the scientific and technological community a safe and clean strategy for not releasing in the environment these dissolved organic matter (DOM) species look like humic substances and polyaromatic compounds. These HTs materials are already available in the market with competitive costs so the remediation of this effluent can be applied in both laboratory and industrial scales. Hydrotalcites also exhibit a striking property which is called memory effect in which some the products of their thermal decomposition at a given temperature experience a spontaneous structural reconstruction when placed in aqueous medium and this phenomenon is well-known for Mg-Al hydrotalcites [26, 27]. We have performed recycling tests using HT-NO\textsubscript{3} (10 g/L for 90 min), with thermal treatment for 2 h at 500 °C after each cycle. The solid was reused for three cycles with oxidation debris effluent stock-solution and the removal efficiency
was superior to 97% (data not showed). These results open up the possibility of removing the oxidation debris from the HTs (through thermal decomposition) because the HT has the ability to reconstruct back to their parent structure makes the HT suitable materials for producing recyclable sorbents. In addition, it was found that both pH and molar concentration of the NaOH solution after removing the oxidation debris with HT remains practically unchanged. These results suggest that the reuse of this solution (process water) is feasible for subsequent treatments of oxidized carbon nanotubes. The reuse of this process water can lead to: saving water and diminishing effluent waste.

![Figure 4](image-url)  
(a) X-ray diffraction patterns and (b) FT-IR spectroscopy data of as-prepared (lower trace) and debris-adsorbed (upper trace) HT-NO$_3$.

**4. Conclusions**

In summary, we have proposed a very efficient, simple and ecofriendly strategy using Hydrotalcites for effluent treatment originated from carbon nanotubes chemical processing. Since the industrial production of carbon nanotubes has already reached tons per year this work point out a way of removing the dissolved carbonaceous residues that nanotubes-based technology will generate. Finally, the results described here can be straightforwardly transferred to graphene oxide technology which is pointed out to be an important industry in the near future.

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