EXECUTIVE SUMMARY OF THE THESIS

Functionalized carbon nanotubes as adsorbents for wastewater remediation

TESI MAGISTRALE IN ENVIRONMENTAL AND LAND PLANNING ENGINEERING – INGEGNERIA PER L'AMBIENTE E IL TERRITORIO, TECNOLOGIE DI RISANAMENTO

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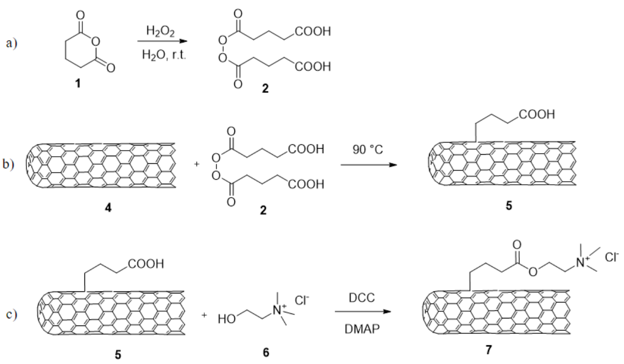
1. Introduction

Nowaday, water scarcity is a pressing global issue, with water demand experiencing exponential growth in recent years. This is due to population growth, economic and industrial development, and the finite nature of water resources [1]. Additionally, climate change is a crucial factor, as it is one of the most significant causes of the ongoing increase in droughts [2].
Therefore, it is necessary to assess new sustainable sources of water resources, like wastewater.
Despite this challenge, it persists a prevailing perception that wastewater is merely a source of pollution that necessitates treatment and disposal. Consequently, it is commonly regarded as a growing problem rather than a valuable and sustainable resource.
Fortunately, a paradigm shift is currently underway, particularly in developed countries, where advanced wastewater management practices are being adopted [3].
For these reasons, recognizing the value of wastewater and adopting innovative approaches in its management can pave the way for a more sustainable future. By going beyond traditional treatment methods, it is possible to transform wastewater into a valuable resource and contribute to the efficient use of water.
Among the most widely used tertiary wastewater treatments, there is adsorption. It's a well-known process for common adsorbents like clays, activated carbons, and zeolites, but the need for higher efficiencies has necessitated the development of increasingly high-performance materials.
Thanks to their exceptional properties and nanoscale structure, innovative materials in this category include carbonaceous nanomaterials, particularly carbon nanotubes (CNTs).
The current thesis work focuses on proposing and studying functionalization aimed at improving the adsorption efficiencies of MWCNTs and comparing them to a clay, a well-known and common adsorbent, as previously mentioned.

Hybrid materials consisting of CNTs and clay are also prepared, and their efficiency is studied.
The adsorption tests are conducted on metal cations such as Cu(II) and organic pollutants like the dyes Rhodamine B and Methyl Orange.
In the second part of the study, the obtained results are analyzed, and some preliminary hypotheses about the functioning and performance of the various adsorbents are proposed. From here, several significant insights emerge regarding potential future developments in this research.

2. MWCNTs functionalization

Surface functionalization of carbon nanotubes is a modification performed by adding functional groups to increase affinity with specific pollutants to enhance their adsorption efficiency.
MWCNTs were modified following a literature procedure [4,5]. First, by reaction of glutaric anhydride **(1)** with hydrogen peroxide, glutaryl peroxide **(2)** was prepared in good yield (scheme 1, a). Then, CNTs (CNT BASE, **4**) were modified by the free radical reaction performed at 90 °C to obtain functionalized CNTs (CNT-X-COOH, **5**), (scheme 1, b).
Choline (**6**) was introduced on the chain by esterification of the carboxylic group in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP). Modified MWCNTs were obtained (CNT-X-COL, **7**), (scheme 1, c).



Scheme 1: procedure for CNTs functionalizations.

In addition, CNT-X-COOH were converted into the corresponding salt in aqueous NaOH obtaining CNT-X-COO^- Na^+ (CNT-X-COO^-).

3. Preparation of CNTs/clay hybrid material

The ion exchange between CNT-XCOL and the clay (Montmorillonite-Nanofil 116) is performed to obtain a hybrid material. Clay is the main adsorbent for inorganic pollutants such as heavy metals. The aim is to obtain a hybrid material that could adsorb both organic and inorganic pollutants.
Two different hybrid materials have been prepared, respectively one with a 1:1 CNTs/clay ratio and the other with a 1:0.2 ratio.

4. Adsorbents used in the tests

The adsorption tests were performed on Rhodamine B, Methyl Orange, copper-ammonia complex obtained from Cu(II) sulfate and Cu(II) nitrate chosen as reference pollutants.
The tests involved the use of various types of adsorbents: pure clay, non-functionalized CNTs (CNT-BASE), nanotubes previously functionalized with carboxylic groups on the surface (CNT-COOH), and the functionalized CNT-X-COOH, CNT-X-COL, CNT-X-COO^- (Figure 1).

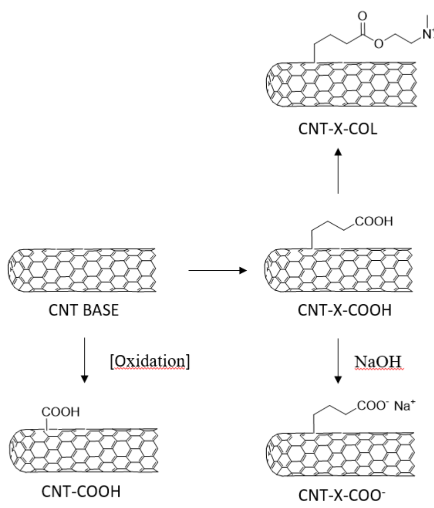


Figure 1: adsorbents used in adsorption tests.

The two carboxylated CNTs (CNT-COOH and CNT-X-COOH) were compared to explore if the introduction of a short spacer (three carbon atoms) between the nanotube surface and the functional group could affect the adsorption efficiency. Then, the positively charged CNT-X-COL and the negatively charged CNT-X-COO^- were tested to study a possible interaction with charged dyes.

The hybrid materials obtained from nanotubes and clay in ratios of 1:1 (CNT-X-COL/clay 1:1) and 1:0.2 (CNT-X-COL/clay 1:0.2) were also tested.

5. Adsorption tests

The calibration curves are determined for the four pollutants, mentioned in the previous paragraph, by means of a UV-VIS spectrophotometer and all have shown the R-squared value close to one, indicating the goodness of linear data interpolation.
The absorbance values of the solutions, after the established contact time with the adsorbent, are measured and the residual pollutant concentration is calculated using the calibration curve equations. The efficiency is calculated using the Equation 1:

$$Efficiency\ (\%) = \frac{C_0 - C_e}{C_0} \times 100$$

Equation 1.

where C_0 is the initial concentration of pollutant and C_e the final concentration of pollutant after the established contact time.

5.1. Adsorption of Rhodamine B

The five CNTs reported in figure 1 were tested using an aqueous solution of Rhodamine B (4.40 x 10^{-6} mmol/mL). The adsorption tests were carried out with a contact time of 1 hour, at room temperature (23-25 °C) and neutral pH. The amount of adsorbent is approximately 2.2 mg (Figure 3).

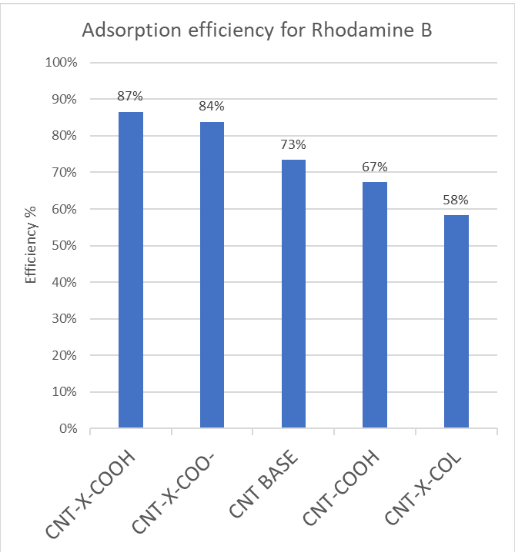


Figure 3.

The samples were analyzed at a wavelength of 553 nm (the maximum peak for Rhodamine B). As it can be seen from Figure 3, CNTs showed a different adsorbance efficiency depending on the functionalization. In particular, CNT-X-COOH revealed to the most efficient, whereas the positively charged CNT-X-COL gave the lowest value.

5.1.1. Variation of efficiency as a function of contact time

The study of the variation of efficiency as a function of contact time provides information on the adsorption mechanism.
The tests were carried out at a temperature of 24 ± 2 °C, at a neutral pH.
The adsorption of Rhodamine B on CNT BASE and CNT-X-COOH (those with the highest adsorption efficiency) at constant initial concentrations was studied as a function of contact time.
It is evident that the adsorption efficiency of CNT-X-COOH is significantly higher than that of CNT BASE (Figure 4) during all the time.

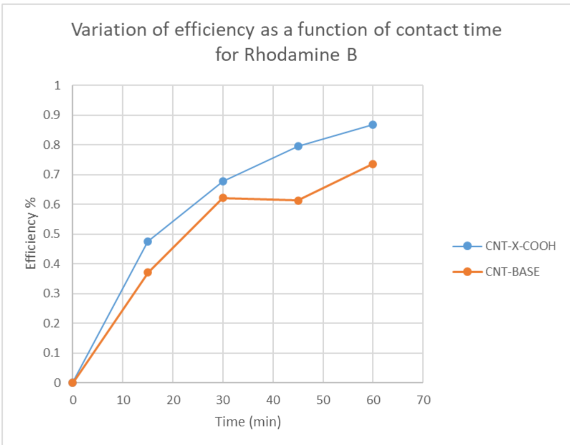


Figure 4.

Since a rather high efficiency, around 90%, was achieved for CNT-X-COOH with a contact time of one hour, it can be assumed that the system is closed to saturation equilibrium and this result is positive, in case of possible applications.
Langmuir and Temkin linearized isotherm models were used for CNT-X-COOH to study the equilibrium characteristics of adsorption, since the adsorption tests showed that these carbon nanotubes gave the best performances. Also, for CNT BASE the same models are used.

The results obtained for both adsorbents in terms of the correlation coefficient R^2 are good (in all cases >0.96).

5.2. Adsorption of Methyl Orange

The CNTs reported in figure 1 (except CNT-X-COO-) were tested using an aqueous solution of Methyl Orange. The adsorption tests were carried out with a contact time of 1 hour, using an aqueous solution (1.04×10^{-5} mmol/mL), at room temperature (23-25 °C) and neutral pH. The amount of adsorbent is approximately 2.2 mg. The samples were analyzed at a wavelength of 465 nm (the maximum peak for Methyl Orange). The results are shown in Figure 5.

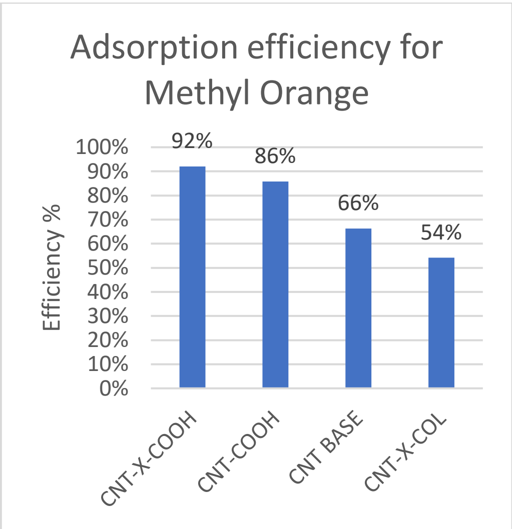


Figure 5.

Similarly, to that observed with Rhodamine B, also in this case, CNT-X-COOH showed the best performances, whereas the lowest one was that of CNT-X-COL.

5.2.1. Variation of efficiency as a function of contact time

Also, the adsorption of Methyl Orange on CNT BASE and CNT-X-COOH at constant initial concentrations was studied as a function of contact time (15, 30, 45, 60 minutes).

It is evident that also in this case, the CNT-X-COOH exhibits higher efficiencies even at intermediate times (Figure 6).

Differently from Rhodamine B, where after 1 hour the curve seems to approach the saturation equilibrium, in this case, this effect is not so evident.

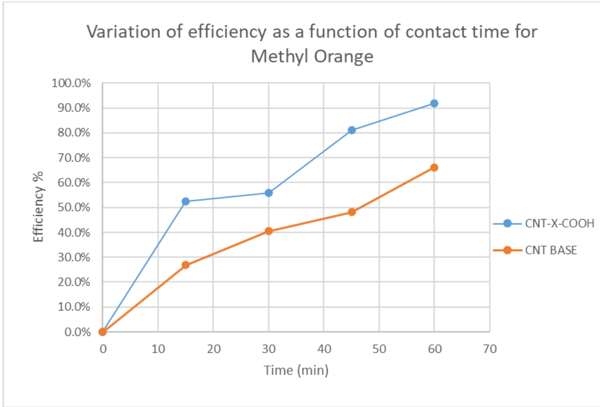


Figure 6.

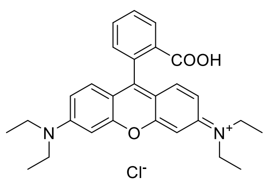
The isotherms analyzed for Methyl Orange once again include Langmuir and Temkin curves for both CNT-X-COOH and CNT BASE.

As the correlation coefficients R^2 of linearized Langmuir and Temkin isotherms for CNT-X-COOH (0.65-0.72) and CNT BASE (0.89-0.90) are not as good as in the case of Rhodamine B, it is clear that further investigations are necessary to exclude that the models are not suitable for the describing the adsorption mechanism in these cases.

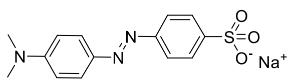
Tests were also performed over a 24-hour period and once again, CNT-X-COOH have shown higher efficiency than CNT BASE.

5.3. Discussion of results obtained with dyes

The percentage of dye removal reported above are summarized in Table 1.



Rhodamine B



Methyl Orange

Table 1.

CNT	Rhodamine B	Methyl Orange
CNT-X-COOH	87%	92%
CNT-X-COO-	84%	not performed
CNT BASE	73%	66%
CNT-COOH	67%	86%
CNT-X-COL	58%	54%

Nanotubes bearing a carboxylic group with a three-carbon chain spacer (CNT-X-COOH) revealed to be very efficient in the adsorption of both a cationic (Rhodamine B) and an anionic dye (Methyl Orange). The functionalization with a polar group increases hydrophilicity of the CNTs and at the same time, the small spacer may have the effect to promote the separation between the nanotubes that in turn could show a higher surface. Although it is not straightforward to compare different CNTs, some comments on the different efficiency can be tentatively proposed.

Regarding the study of the absorbance of Rhodamine B by CNTs, the lower efficiency of the positively charged CNT-X-COL could be simply due to the non-favorable interactions between the two positively charged adsorbent and dye. However, almost the same efficiency is observed in the case of CNT-X-COL with the anionic dye Methyl Orange. It seems that these interactions are not so important in the absorbance process. If this is true, the longer spacer in CNT-X-COL between the positive nitrogen and the nanotube surface may play a role, perhaps because the substituent chain, in this case, is too long having the effect to reduce the π-π interaction between the dye and the nanotube. The adsorption efficiency, toward Rhodamine B, of CNT-COOH and CNT-X-COOH) was compared with that of CNT BASE. In this case, only the efficiency of CNT-X-COOH was higher than that of CNT BASE, whereas for CNT-COOH the value was lower. This finding suggests that again, the interactions between the cationic dye and CNTs seems to be not the main responsible of the adsorption phenomena. The experiment performed with CNT-X-COO$^-$ gave a slight decrease of the efficiency with respect of CNT-X-COOH and this support the hypothesis discussed above. In the case of Methyl Orange (an anionic dye), CNT-COOH and CNT-X-COOH showed a higher removal efficiency compared to CNT BASE, and, at the same time, they showed a small difference in their behavior. Anyway, also in this case, CNT-X-COOH still gave the higher performances. Therefore, the spacer (C3) seems to be a structural moiety that enhances the effect of the interactions.

5.4. Adsorption of Cu(II)

The experiments are performed with a contact time of 60 minutes, using an aqueous copper-ammonia solution (0.005210 mmol/mL), at room temperature (23-25 °C) and pH 11.4. The samples are analyzed at a wavelength of 600 nm.

The adsorbents were compared in the following way: a test was conducted using 25 mg of clay, another using 50 mg of CNT-X-COL/clay 1:1 (to have the same amount of clay as in the previous test), one with 25 mg of CNT-X-COL, one using 5 mg of clay, and the last one using 30 mg of CNT-X-COL/clay 1:0.2 (to have 5 mg of clay as in the previous test). The results are shown in Figure 7.

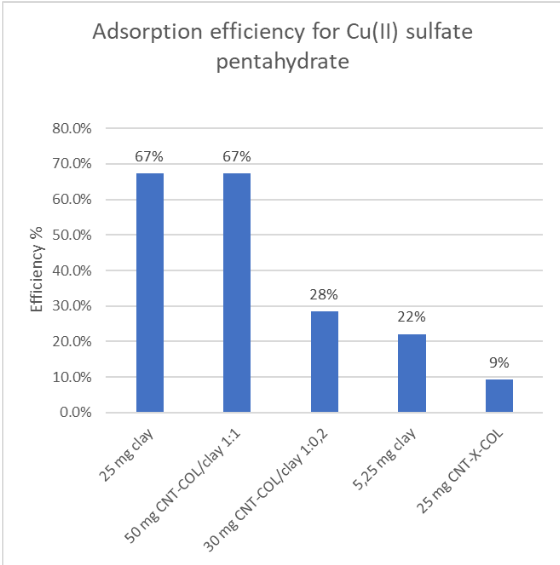


Figure 7.

5.4.1. Variation of efficiency as a function of contact time

As 60 minutes was a time sufficient to have a high removal efficiency towards organic dyes, the same contact time was used also in the case of clays. This because in a real application, the contact time must be sufficient to remove all the pollutants. Anyway, experiments with lower contact times were performed. The absorbance values of clay obtained after 30 minutes values were substantially the same of those obtained after 60 minutes. This suggests that the adsorption equilibrium has already been reached after 30 minutes.

5.5. Discussion of results obtained with Cu(II)

The lower efficiency was obtained, as expected, using the positively charged CNT-X-COL. The sample containing only clay (25 mg) shows an efficiency of 67% as well as the hybrid material containing the same amount of clay (CNT-X-COL/clay 1:1).

To the light of these results, the adsorption of copper (II) seems to be exclusively related to the amount of clay and the presence of CNT-X-COL in the hybrid material not only did not enhance the efficiency of the clay, but its removal capability seems to be negligible when the clay is present.
Thus, Scanning Electron Microscopy (SEM) observations were performed to find a possible explanation. As it can be seen (figure 8), the CNTs are completely incorporated in the clay so that the surface of the nanotube cannot interact with any compounds present in the solution to be purified.

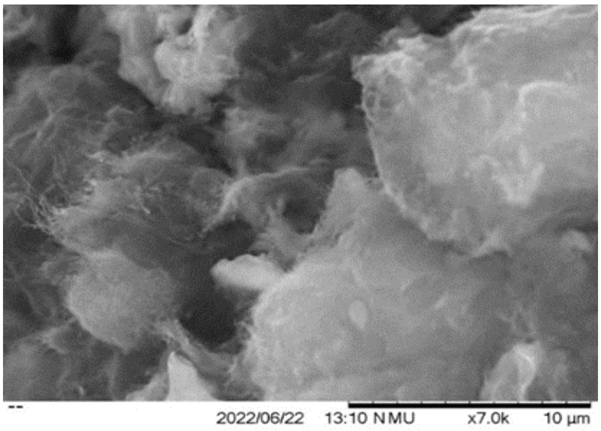


Figure 8: SEM of CNT-X-COL/clay 1:1.

The amount of clay in the hybrid material was then reduced to 20% with respect to CNT-X-COL and the absorbance efficiency was compared with that of an experiment containing only clay in the same amount. In this case, the presence of CNT in the hybrid material previously prepared seems to contribute to the adsorption efficiency.

The results obtained with the 1:0.2 CNT-X-COL/clay hybrid material seem to be promising by the applicative point of view. Nevertheless, more experiments using this hybrid material in different conditions had to be performed to complete this study.

6. Conclusion

Functionalized MWCNTs bearing carboxylic groups bound to the surface through a spacer made of three carbon atoms (CNT-X-COOH) and CNTs containing a choline moiety (CNT-X-COL) were prepared from non-functionalized nanotubes. Several experiments were performed by varying parameters such as the amount of adsorbent, the amount of pollutant, contact time and the adsorption efficiency was determined by UV-VIS measurements.
In conclusion, this study has shown that the spacer in CNT-X-COOH makes them more efficient adsorbents towards organic dyes with respect to the well-known CNT-COOH. Therefore, it is clear that appropriate functionalization significantly enhances the efficiency of non-functionalized nanotubes which have been gaining increasing interest in the scientific community in recent years due to their exceptional properties. A thorough understanding of their behavior and potential in the field of wastewater treatment could bring benefits, especially in a context where wastewater reuse is becoming increasingly important in light of climate change and water resource scarcity.
The results obtained with the 1:0.2 CNT-X-COL/clay hybrid material seem to be the most promising in the removal of copper(II). Anyway, more experiments using this material under different conditions needed be performed.

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7. Acknowledgements

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