Semi-Continuous Adsorption Processes with Multi-Walled Carbon Nanotubes for the Treatment of Water Contaminated by an Organic Textile Dye

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Abstract: Adsorbent columns, containing different amounts of multi-walled carbon nanotubes (MWCNTs), in a semicontinuous process were studied. The optimal conditions for the discoloration of water contaminated by an azoic organic textile dye were investigated. In particular, as representative of contaminated water, a highly concentrated solution of Reactive Black 5 (RB5) equal to 37 mg/L was utilized. A predetermined volume of dye solution, equal to 100 mL, was subjected to repeated cycles of adsorption until the eluted solution became colorless. This adsorption operation was carried out for different types of columns. Adsorbent performances as a function of characteristics of each column were investigated. For each column, the optimum quantity of MWCNTs, maximum volume of treatable solution, carbon usage rate (CUR), empty bed contact time (EBCT), and adsorption capacity were determined. The permeate was characterized by UV-VIS analysis and TOC analysis, while adsorbent material (MWCNTs) was characterized by thermogravimetric TG-DTA analysis. The column containing 2.5 g of carbon nanotubes was revealed to be the best one for the total amount of Reactive Black 5 adsorbed, i.e., 55 mg/g \(_{(\text{MWCNTs})}\). The research has shown the high adsorption efficiency of carbon nanotubes toward RB5 dye, highlighting the degradation of the dye molecule and the stratification, inside the columns, of the adsorbed compound.

Keywords: multi-walled carbon nanotubes; dye; RB-5; textile wastewater; adsorption

1. Introduction

The problems linked to the purification of wastewater from the textile industry today represent a factor of high environmental impact and a dangerous element that should not be underestimated due to the possible environmental impacts. Every year, 20% of the synthetic dyes used in textile production are lost in the waste [1–3], with residual concentrations between 10 and 50 mg/L [4]. The main difficulty in treating these wastewaters with classical purification methods is due to their heterogeneous composition [5]. In particular, the high content of coloring materials in wastewater could decrease the adsorption efficiency of these types of adsorbent materials. In fact, the use of textile dyeing baths of increasingly stronger reactive dyes, with a low degradation behavior, increases their reactive capacity but could complicate their removal from wastewater [6]. The dyes most used in numerous industrial applications [7] are the azo-compounds, characterized by the presence of one or more \(-\text{N} = \text{N}-\) bonds, representing ca. 60–70% of the dyes used [8,9]. The presence of these materials in wastewater generates the phenomena of ionization and microbiological and chemical oxidation, forming polluting byproducts [10,11]. Furthermore, dyes are toxic, mutagenic, and carcinogenic to a large number of living organisms [12]. Therefore, specific techniques are needed that help the usual purification methods.
Textile wastewater treatments are carried out through different processes such as biological [13–19], oxidative [20–22], coagulation [23–26], flocculation [27], membranes [28,29], and photocatalysis [30–36].

Adsorption is one of the most important and efficient purification techniques applied to various nonbiodegradable polluting compounds, producing high-quality water. There are several materials that can be used for adsorption. Among these are microporous materials [37–47]. Activated carbon is commonly used for these applications [48–51]. Other adsorbent materials like silica [52], chitosan [53–55], and natural materials [56–59] are used. Carbon nanotubes are achieving great success, as they are very versatile materials and applicable in many fields [60]. They can generally be used as reinforcing fibers [61–65] and as a material capable of efficiently adsorbing different substances [66–73]. A particular application for which carbon nanotubes have shown promise is the removal of dyes in wastewater [74–78].

In our previous work, the removal of Reactive Black 5 (RB5) dye from aqueous solutions with carbon nanotubes in static systems was investigated by evaluating the influence of the nature of the carbon nanotubes, the initial concentrations of dye, the stirring speed, and the times on the adsorption process [78].

In this work, in particular, we wanted to continue the previous research [78] by studying the absorption of the Reactive Black 5 dye from aqueous solutions with carbon nanotubes in semicontinuous processes, in order to search for the optimal conditions for the purification of water contaminated.

Reactive black-5 dye was chosen as the representative dye present in textile wastewater. It was chosen because it is one of the most common dyes used in the textile industry thanks to the presence of reactive groups in the molecule that promote the formation of covalent bonds with fibers. Furthermore, it also was chosen for its high solubility in water, which allowed us to prepare its aqueous solutions to be used in the experimental procedures [79].

For this purpose, different adsorption columns were studied and subjected to different adsorption cycles that were suspended only when the permeate was colorless. The characteristics of each column were studied and compared.

2. Materials and Methods

The research was carried out through several consecutive steps. In the first phase, the raw materials were chosen and prepared. Subsequently, adsorption columns with different quantities and types of nanotubes were prepared. Adsorption tests in a semicontinuous process followed. Finally, the permeates and retentates were characterized. The details of the different steps of the research are below.

2.1. Materials

The multi-walled carbon nanotubes (MWCNTs) used in this experiment were the same ones synthesized and characterized as reported in previous articles [67,78]. Briefly, they were synthesized using the catalytic chemical vapor deposition technique (CCVD) and obtained with a purity of 95%. They had a specific BET area of 108.70 m$^2$/g and an average pore width of 103.70 Å.

Further information on the characteristics of the nanotubes used can be found in [80].

The dye solution was prepared using Reactive Black 5 (Sigma Aldrich, Darmstadt, Germany), at a final concentration of 37 mg/L, as a representative of wastewater, which generally has concentrations ranging between 10 and 50 mg/L [4]. The silica gel spheres used were 2–5 mm in diameter (white Disidry silica gel, Firenze, Italy).

2.2. Preparation of Adsorbent Columns

The adsorption columns were prepared by compacting a layer of MWCNTs inside the columns, with variable quantity and thickness. A layer of silica gel spheres was added over the carbon nanotube layer inside each column to ensure the maintenance of the carbon
nanotube compaction and to achieve a uniform impact of the dye solution on the section of the nanotube layer.

The quantities of carbon nanotubes were chosen after a series of preliminary tests that had the criteria of preparing columns as efficient as possible and with the minimum quantities.

The borosilicate filter at the base of the column during the tests prevented the nanotubes from being carried away by the flow of the RB5 solution in the permeate, thus becoming pollutants themselves.

To exclude the passage of carbon nanotubes through the borosilicate filter, preliminary tests were carried out before the adsorption tests with a dispersion of carbon nanotubes in water. The use of water only and not of the dye solution was adopted to prevent the color of the dye solution from covering and not making any passage of the nanotubes visible through the filter. However, permeate and no loss of nanotubes through the filter were consistently observed.

In total, five different adsorbent columns were prepared. The weight/volume ratio of the MWCNTs compacted in the different columns was kept almost constant, between 0.16–0.18 [g/cm³]. Table 1 and Figure 1 show the characteristics and schematic representation of the adsorption columns, respectively.

**Table 1.** Characteristics and composition of the adsorption columns.

|               | C1    | C2    | C3    | C4    | C5    |
|---------------|-------|-------|-------|-------|-------|
| Column diameter [cm] | 2.00  | 2.00  | 2.00  | 2.00  | 2.00  |
| Height of silica spheres layer [cm] | 2.50  | 2.50  | 2.50  | 2.50  | 2.50  |
| Height of MWCNT layer [cm] | 4.50  | 2.25  | 1.40  | 1.00  | 0.40  |
| Volume of MWCNT layer [cm³] | 14.14 | 7.07  | 4.40  | 3.14  | 1.26  |
| Weight of MWCNT layer [g] | 2.50  | 1.25  | 0.75  | 0.50  | 0.20  |

**Figure 1.** Schematic representation of the different adsorption columns.

### 2.3. Adsorption System

The adsorption system consisted of a graduated Pyrex glass column loaded for each cycle with 100 mL of Reactive Black 5 solution with a concentration of 37 mg/L. The passage of the solution inside the columns was guaranteed thanks to the use of a peristaltic pump.

The descent of the RB5 solution through the adsorbent column, prepared in the manner described above, was facilitated by means of a vacuum pump connected to the flask where the permeate was collected. The tests were carried out in the laboratory at room temperature (about 20 °C). Different adsorption cycles were repeated. The first adsorption cycle began with dried carbon nanotubes. The process was powered semicontinuously;
after every 100 mL of treated solution, the process was blocked to allow the collection of the permeate and subsequently loaded with another new 100 mL of Reactive Black 5 solution.

The adsorption cycles were blocked when the permeate was visually colorless, confirming the saturation of the nanotubes. Each single test was repeated twice and took into account the average value of the data obtained. The lack of color in the permeate was visually verified by comparing the permeate with a distilled water sample taken as a reference. Both the sample and the reference were subjected to the same light on a white background and compared.

Furthermore, the maximum quantities of retainable dye in the various columns were calculated according to the volumes of solution treated until the color reappeared. This choice was made on the basis of current wastewater regulations that establish the total absence of turbidity and color of the wastewater. Figure 2 shows a schematic illustration of adsorption system.

![Scheme of the adsorption system.](image)

**2.4. Instruments**

After each adsorption cycle, the permeates were recovered and analyzed by UV spectrophotometer (UV-3100PC Shimadzu, Kyoto, Japan) to measure the residual concentrations of dye. UV analyses were performed considering the three characteristic peaks of Reactive Black 5 at 307, 481, and 600 nm.

After all the adsorption cycles were carried out, the MWCNTs were recovered and placed in an oven at 80 °C for 24 h to allow the evaporation of the water content.

Subsequently, a thermogravimetric analysis (TG) and a differential thermal analysis (DTA) (Shimadzu-60, Kyoto, Japan) were carried out in order to detect the weight losses and the thermal characteristics of the nanotubes after the adsorption tests at different depths of the nanotube layer present in the column (high, medium, low). An air flow of 50 mL/min and heating rate of 10 °C/min were utilized.

Total organic carbon (TOC) and total inorganic carbon (TIC) content were measured by a TC analyzer (Shimadzu, Kyoto, Japan). The analysis was carried out through oxidative catalytic combustion and the non-dispersive infrared gas measurement device (NDIR) method; acidification was carried out using 0.1 M HCl, and the combustion temperature was 680 °C, allowing us to calculate the TOC value after evaluating the TOC and TIC.

**3. Results and Discussion**

**3.1. Evaluation of Hydraulic Parameters**

Table 2 reports the number of adsorption cycles carried out in the different columns that allowed us to obtain a visually colorless permeate, together with the respective total volume of treated solution. The adsorption columns C1, C2, C3, and C4 showed a total decolorization of the solution already at the first adsorption cycle, while for the C5 column, a colored permeate was observed, even if the solution in any case presented a certain degree
of discoloration. Increasing the amount of MWCNTs in the columns increased the number of repeatable cycles that allowed for a colorless permeate. In fact, the C1 column, with the highest quantity of nanotubes (2.5 g), reached the highest number of cycles, corresponding to 38, while the C4 column, with 0.5 g of MWCNTs, needed only one adsorption cycle. The total volume of solution that can be treated by column C1 was the highest (3.8 L), while that which could be treated with column C4 was the lowest (0.1 L), excluding column C5, which, as already mentioned, already presented, at the first cycle, no ability to completely decolorize the solution. Columns C4 and C5, however, allowed us to define the minimum quantity of MWCNTs necessary to perform at least one adsorption cycle, which was found to be equal to 0.5 g. Figure 3 reports the permeation times for each cycle performed on columns C1, C2, and C3. The permeation time was calculated as the sum of the times used by each single adsorption cycle up to the last cycle; that is, until the solution was no longer colorless. Since the time for column C4 related to a single cycle and was equal to 12 min, and since the C5 column did not produce a decolored solution in the first cycle, they were not graphed.

Table 2. Number of adsorption cycles of 100 mL of Reactive Black 5 [37 mg/L] solution and total volume treated.

| Adsorption Column | Number of Adsorption Cycles | Total Volume Treated [L] |
|-------------------|-----------------------------|-------------------------|
| C1                | 38                          | 3.8                     |
| C2                | 9                           | 0.9                     |
| C3                | 6                           | 0.6                     |
| C4                | 1                           | 0.1                     |
| C5                | 0                           | 0.0                     |

Figure 3. Permeation times as a function of number of cycles for different columns.
It is evident that in column C1, the most representative in terms of adsorption cycles carried out, there was an increase in permeation times as a function of the cycles carried out, even if characterized by a swinging sawtooth trend. This behavior of the C1 column can be associated with an alternation of clogging and rupture of the MWCNT layer, due to the creation of preferential pathways in it, which were subsequently recompacted in consecutive cycles. For columns C2 and C3, the trend remained substantially constant, settling on an average value for the permeation times of between 65 and 70 min. Table 3 reports the carbon usage rate (CUR) values calculated using the following Equation (1):

\[ CUR = \frac{M_{\text{ads}}}{Q \cdot t} \]  

where \( Q \) is the average flow rate, \( M_{\text{ads}} \) is the weight of the adsorbent layer of nanotubes, and \( t \) is total permeation time (as the sum of the permeation times of each single cycle) until the colorless permeate is maintained. The data obtained show that the CUR decreased as the amount of nanotubes in the column increased. The highest value was obtained for column C4 (5.0 g/L), while the lowest value was obtained for column C1 (0.66 g/L).

| Column | \( M_{\text{ads}} \) [g] | \( V_{\text{Treated}} \) [L] | \( V_{\text{ads}} \) \( \times 10^{-6} \) | \( A \) \( \times 10^{-4} \) | \( Q \) [L/h] | Time [h] | CUR [g/L] | \( J \) \( \text{m}^3/\text{m}^2 \cdot \text{h} \) | EBCT [min] |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| C1     | 2.5             | 3.8             | 14.14           | 3.14            | 0.0194          | 195.7           | 0.66            | 0.066           | 43.687          |
| C2     | 1.25            | 0.9             | 7.07            | 3.14            | 0.0947          | 9.5             | 1.39            | 0.301           | 4.477           |
| C3     | 0.75            | 0.6             | 4.40            | 3.14            | 0.0869          | 6.9             | 1.25            | 0.278           | 3.036           |
| C4     | 0.50            | 0.1             | 3.14            | 3.14            | 0.5             | 0.2             | 5.00            | 1.591           | 0.377           |

The flux \( (J, \text{Equation (2)}) \) and the empty bed contact time \( (\text{EBCT, \text{Equation (3)}) \) were calculated as:

\[ J = \frac{Q}{A} \]  

\[ \text{EBCT} = \frac{V_{\text{ads}}}{Q} \]  

where \( Q \) is the average flow rate crossing the transversal section of column, \( A \) is the area of the section, and \( V_{\text{ads}} \) is the volume filled by MWCNTs. Table 3 reports the flux and EBCT for different adsorption columns.

The reported data show that there was a decrease in flow \( (J) \) and a decrease in the EBCT as the amount of nanotubes in the column increased.

The values of the hydraulic parameters show a dependence on the quantity of nanotubes present in the columns. In short, it was found that the contact times, the total treatable volume and the empty bed contact time increased with an increase in the quantity of nanotubes, while the value of the carbon usage rate was inversely proportional.

However, it should be emphasized that these dependencies were not linearly proportional to the quantities of nanotubes, but these parameters underwent a sort of amplification, even for small increases in carbon nanotubes. This is because when the nanotubes are not dispersed, unlike what happens in the case of a batch system, but are compacted in a column, a small increase in their quantity leads as a consequence, in addition to the increase in the adsorbent material that determines a greater adsorption, to an amplification of the resistances that oppose the descent of the solution. This results in a longer contact time and EBCT. The synergistic action of the increase in the adsorbent material and in the contact times leads to a marked improvement in the adsorption capacity.

For example, by comparing the data of the treatable volume in columns C1 and C2, it can be seen that a doubling of the quantities of carbon nanotubes inside the column did not lead to a doubling of the treatable volume, but rather a volume that was about 4 times greater.
3.2. Characterization of Permeate

The permeate concentration was evaluated by a UV-VIS quantitative spectroscopic analysis. Figure 4 shows the concentrations of Reactive Black 5 in the permeates after different adsorption cycles.

![Figure 4. Concentration of Reactive Black 5 in permeates as a function of the numbers of cycles; colorless (gray) and colored (blue) solutions are shown.](image)

The reported data show that the C1, C2, C3, and C4 columns exceeded a concentration of 3.5 mg/L of Reactive Black 5 in the permeate after 38, 9, 6, and 1 cycles, respectively. This concentration coincided with the limit beyond which the permeate was no longer visually colorless. Column C5 is not shown in the graph because it returned a colored permeate in the first cycle, with a concentration of 7 mg/L, demonstrating the ineffectiveness of adsorption. The amounts of dye in the permeate and retentate dye were calculated and are reported in Table 4.

**Table 4. Total amount of permeate and retentate RB5 and hydraulic ratio for different columns.**

| Column | V_treated [L] | Total Weight of RB5 Utilized [mg] | Total Permeate RB5 [mg] | Total Retentate RB5 [mg] | \( R \) [mg_{ret}/g_{MWCNTs}] |
|--------|---------------|-----------------------------------|------------------------|-------------------------|-------------------------------|
| C1     | 3.8           | 140.6                             | 1.978                  | 138.622                 | 55.44                         |
| C2     | 0.9           | 33.3                              | 0.234                  | 33.066                  | 26.45                         |
| C3     | 0.6           | 22.2                              | 0.250                  | 21.950                  | 29.27                         |
| C4     | 0.1           | 3.7                               | 0.181                  | 3.519                   | 7.04                          |

The removal of dye was almost total until the achievement of chromatic change, after which the substance not adsorbed considerably increased. The adsorption capacity \( q_e \) (Equation (4)) was calculated as the ratio between the amount of permeate dye until...
the color change and the amount of MWCNTs used in the column, using the following equation:

\[
q_e = \frac{m_{\text{permeate}}}{m_{\text{MWCNTs}}} = \left( \frac{C_i - C_f}{m_{\text{MWCNTs}}} \right) \times V
\]  

(4)

where \( C_i \) is the concentration of mother liquor (mg/L), \( C_f \) is the final concentration of permeate (mg/L), and \( V \) is the volume of treated solution (L). Figure 5 reports the adsorption capacity as a function of number of cycles.

![Figure 5](image)

**Figure 5.** Adsorption capacity as a function of number of cycles.

The obtained exploitation values from the ratio (R) between retained substance until color change (\( \text{mg}_{\text{Ret}} \)) and the amount of MWCNTs (\( m_{\text{MWCNTs}} \)) used in the column were calculated (Table 4).

The column C1 ensured a better use of MWCNTs. The efficiency of removal of columns (RE) for each cycle is plotted in Figure 6. It was obtained using Equation (5):

\[
RE \ (% \) = \left( \frac{C_i - C_f}{C_i} \right) \times 100
\]  

(5)

where \( C_i \) and \( C_f \) are the initial and final concentrations, respectively.
Two important results can be noted. The first is that all of the adsorbent columns showed a good removal efficiency. The second is that the removal efficiency increased with the number of cycles. This suggests that the adsorptivity of the MWCNTs increased with the number of cycles.

Permeate values were further investigated by means of total carbon (TOC), inorganic carbon (IC), and total organic carbon (TOC) analysis. In particular, the initial solution of the RB5 dye and the permeates of the columns at different numbers of cycles were subjected to analysis. Table 5 reports the values related to this analysis.

The data obtained allow us to say that during the adsorption process, two factors intervened simultaneously: the quantity of nanotubes used and the contact times. By increasing the thickness of the nanotubes inside the column, the solution found a greater resistance to its descent, which also led to an increase in contact times. Both the greater quantity of nanotubes and the longer contact times create the conditions for a greater adsorption. The adsorption was due to the great van der Waals forces between the dye and the carbon nanotubes.

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Two important results can be noted. The first is that all of the adsorbent columns reported an excess of inorganic carbon (IC) compared to that obtained in the mother liquor of RB5. It also stabilized at low values after an initial high peak in the first filtration step. This result is probably related to a leaching effect of the MWCNTs.

Initially, the TOC was partially decreased compared to the mother liquor of RB5. Then it increased as the permeate was close to the color-change state. The TOC variation, for permeate and mother liquor, was to assume a degradation of dye molecule inside MWCNT layer, where a chromophore group was adsorbed at least, as demonstrated by UV-VIS, while part of organic carbon (OC) could remain in the permeate passing through the MWCNT layer. It is possible to hypothesize that inorganic carbon is generated by the decomposition of the dye into carbonates, bicarbonates, and dissolved CO2, as discussed in previous works [78].
Table 5. TOC, IC, and TC of permeate in the adsorption columns after different cycles. Cx-yy: x is the name of the column, and yy is the number of cycles.

| Sample | TC [mg/L] | IC [mg/L] | TOC [mg/L] |
|--------|-----------|-----------|------------|
| RB5    | 9.539     | 0.247     | 9.292      |
| C1-01  | 13.190    | 7.333     | 5.859      |
| C1-15  | 3.522     | 1.508     | 2.014      |
| C1-24  | 3.508     | 1.909     | 1.600      |
| C1-36  | 2.864     | 1.237     | 1.627      |
| C1-37  | 3.079     | 1.123     | 1.956      |
| C1-38  | 3.532     | 1.342     | 2.190      |
| C1-39  | 3.749     | 1.395     | 2.354      |
| C1-41  | 5.458     | 1.380     | 4.078      |
| C2-01  | 3.890     | 3.292     | 0.599      |
| C2-09  | 3.421     | 1.815     | 1.606      |
| C2-10  | 3.890     | 1.970     | 1.920      |
| C3-01  | 4.836     | 2.953     | 1.883      |
| C3-06  | 5.463     | 1.374     | 4.089      |
| C3-07  | 4.260     | 0.713     | 3.548      |
| C4-01  | 2.018     | 1.228     | 0.790      |
| C4-02  | 3.150     | 1.006     | 2.144      |
| C5-01  | 5.391     | 0.589     | 4.812      |

3.3. Characterization of MWCNTs Layer

The carbon nanotube layers were characterized by means of a thermal analysis to study the method of dye adsorption. TG and DTA analyses were carried out at different heights of the MWCNT layers to define the stratigraphic trend of adsorption inside each column. The MWCNTs related to the last cycle before the color change were chosen for the analyses. The samples number was considered as a function of height of the MWCNT layer. Figure 7 shows the samples taken in the different columns.

Figure 7. Samples taken in the different layers of MWCNTs.

A comparison between the different TG curves of samples was possible. A TG curve of the pure RB5 dye is presented in Figure 8.
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![Figure 7. Samples taken in the different layers of MWCNTs.](image)

A comparison between the different TG curves of samples was possible. A TG curve of the pure RB5 dye is presented in Figure 8.

![Figure 8. TG curves of samples as a function of height of the MWCNT layer.](image)

From the graphs shown in Figure 8, it is possible to observe that the lower layers tended to have a smaller weight loss. This trend is most noticeable in the columns that had the highest total layer of MWCNTs. In fact, in column C1, which had a total layer of MWCNTs equal to 4.5 cm, the difference between the first and last layer was equal to 11.96%, while in column C4, which had a total layer equal to 0.4 cm, the difference was equal to 0.13% (Table 6).
Table 6. Relative weight losses of TG curves.

| Layer   | Total Weight Loss [%] | Height of Total MWCNT Layer in the Column [cm] | Difference Weight Loss between High and Low Layer (%) |
|---------|-----------------------|-----------------------------------------------|------------------------------------------------------|
| C1-Low  | 82.05                 |                                               |                                                      |
| C1-Medium | 90.43               | 4.50                                          | 11.96                                                |
| C1-High | 94.01                 |                                               |                                                      |
| C2-Low  | 86.58                 |                                               |                                                      |
| C2-Medium | 87.25               | 2.25                                          | 7.88                                                 |
| C2-High | 94.46                 |                                               |                                                      |
| C3-Low  | 89.51                 |                                               | 0.24                                                 |
| C3-High | 89.75                 | 1.4                                           |                                                      |
| C4-Low  | 92.12                 |                                               | 0.13                                                 |
| C4-High | 92.25                 |                                               |                                                      |
| C5      | 92.42                 | 0.4                                           |                                                      |

To confirm this inhomogeneity of the layers, Figure 9 shows the DTA thermal analyses for the C1 column only, as it is characterized by a higher nanotube layer, which allowed a more effective distinction of the three layers.

Figure 9. DTA curves of C1 column for different height of layers (high, medium, and low).
DTA curves for the C1 column show two exothermal peaks at ca. 446 °C and 580 °C, very close to those of RB5 at 413 °C and 617 °C, respectively (Figure 9). The thermal analysis of the middle part of the MWCNT layer presented the same thermal behavior but the intensities of the exothermal peak of DTA curve were lower. The deeper layer presented exothermal peaks of DTA curve that were very low, almost invisible. This could be due to a smaller amount of dye adsorbed at this MWCNT layer. This observation was the same for all of the analyzed columns. Figure 10 shows a zoom of the DTA peaks at ca. 446 °C, comparing the several heights for each column to highlight better the variation of exothermal peaks for each column.

In Figure 10, it can be seen that the DTA curves, near the peak around 446 °C, characteristic of the RB5 dye, tended to have more intense peaks for the upper layers, confirming a greater adsorption than in the lower layers.

This nonhomogeneity in the nanotube filters, in which the higher layers had a greater weight loss and therefore a greater adsorption, can be attributed to the fact that the solution, as it arrived in the deeper layers of the filter, flowed outwards in a faster way by having an increasingly smaller layer in front that opposed its passage. On the other hand, in the higher layers of the filter, the descent of the solution was hindered by the lower layers. All this determined, within the filter, different contact times of the solution, which were greater in the higher layers and less in the lower ones. This gradient of contact times within the filter generated a stratification of the dye, which was more evident at greater thicknesses of the layer.
In a recent review, it was reported that carbon nanotubes appear to be the best and most appropriate adsorbent materials for the removal of Reactive Black 5 dye, which has a rapid adsorption rate as its main feature [81]. By comparing our data with those reported in the literature [74–82], where adsorption processes in static conditions are studied in the latter, it was possible to deduce that they were consistent, and to confirm a great propensity of carbon nanotubes to treat of water contaminated by Reactive Black 5.

The semicontinuous adsorption process, studied in particular in this work, has shown that the rapid removal rate and efficiency of carbon nanotubes was maintained even after several consecutive adsorption cycles, and that, for example, a column containing only 2.5 g of nanotubes was able to treat 3.8 L of Reactive Black 5 solution, with a concentration equal to 37mg/L.

We are not aware of any research that has used columns of carbon nanotubes in semicontinuous processes for the treatment of water specifically contaminated by Reactive Black 5. However, studies reported in the literature have used similar experimental conditions, although for the removal of other substances, such as NOMs (natural organic matter) [83], glimepiride [84], or heavy metals [85], and achieved results consistent with those reported by us, in which the quantity of carbon nanotubes, and therefore the height of the read in the column, played the fundamental role capable of amplifying the adsorption capacity.

The data obtained in this research are encouraging for a potential implementation of a continuous plant characterized by several columns that alternate during the regeneration phases of the nanotubes.

4. Conclusions

Various columns packed with different amounts of MWCNT, i.e., 2.5 g, 1.25 g, 0.75 g, 0.5 g, and 0.2 g (C1, C2, C3, C4, and C5, respectively), were studied to optimize the purification process of waters contaminated by Reactive Black 5 dye. In the first three columns, one cycle was sufficient to decolorate the dark-blue solution of Reactive Black 5, while the last two columns gave a response at the minimum quantity of MWCNTs to be used, i.e., 0.5 g. For each column, the optimum quantity of MWCNTs was determined in order to efficiently adsorb 1 L of solution. The best adsorbent column was revealed to be C1, with a 0.66 g/L carbon usage rate (CUR). Moreover, the C1 column had discolored 3.8 L of solution before the solution changed color from transparent to blue, and later a stacking occurred that diminished the flux of the liquid. C1 was revealed to be the best regarding the total amount of Reactive Black 5 adsorbed, i.e., 55 mg/g

In agreement with previous research [78], the data obtained confirmed that the dye underwent partial destruction, even during the adsorption process in semicontinuous conditions. Finally, the TG and DTA techniques showed unequivocally that the amount of adsorbed colorant decreased in the columns from superior to the lower layers of MWCNTs.

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