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# TESTING MWCNT-COOH/$Fe_3O_4$ NANOCOMPOSITE FOR THE REMOVAL OF AMPICILLIN FROM SYNTHETIC AQUEOUS SOLUTIONS

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**ABSTRACT.** The aim of this paper consisted of the carbon nanotube nanocomposite testing for the removal of ampicillin from aqueous solutions. To determine the optimum experimental conditions for ampicillin adsorption on nanocomposite, several parameters were selected: the pH, initial concentration of pollutant, adsorbent dose and contact time. The high-performance liquid chromatography was used to determine the residual ampicillin concentration from aqueous solutions. The best removal of the antibiotic on the tested nanocomposite was obtained with an initial concentration of 40 mg $L^{-1}$ with 1 g $L^{-1}$, pH 2 in 20 min.

***Keywords:*** *ampicillin, adsorption, nanocomposite, carbon nanotubes, water decontamination*

## INTRODUCTION

The innovation and modern development of the antibiotic industry have seen a giant leap since the discovery of penicillin by Sir Alexander Fleming in 1928 [1]. Contamination of water with polluting agents with an increasingly high degree of toxicity, such as heavy metals, organic substances, pesticides or antibiotics, has become a major current issue that requires finding effective depollution solutions [2]. An intensively addressed field for this purpose is nanotechnology because materials with nanometric dimensions have large specific surfaces with good adsorption properties [3]. Thus, finding new water treatment technologies is essential for a sustainable

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environment and for preventing the transfer of dangerous substances in the food chain, because aquatic environments serve as “repositories” for antibiotics from the pharmaceutical industry, hospitals, animal farms, wastewater from treatment plants, municipal waste [4].

Several methods have been developed to treat antibiotic-contaminated waters, such as oxidation, degradation, electro degradation, reverse osmosis, nanofilter membranes, catalytic degradation, and adsorption [5]. Different adsorbents were used for this process, including adsorbents based on agricultural waste, nanomaterials and layered double hydroxides. The main adsorption mechanisms for antibiotic removal are the electrostatic attraction, $\pi - \pi$ interaction and hydrogen bonding. Adsorption is a widely available technique due to its high efficiency, operational simplicity and feasibility. However, the efficiency of the adsorption method is greatly affected by the properties of the adsorbents used [6, 7].

The development of carbon-based nanomaterials such as carbon nanotubes (CNTs) is of great interest for use in pollutant removal processes, due to meeting the criteria required for good adsorption: high specific surface area, large pore volume, physical interactions and strong chemicals with pollutants, etc. [8].

Ampicillin, one of the most widely used antibiotics degrades most in an acidic and basic environment, while UV light and heat have a negligible degradation effect. Time has only a slight degradation effect [9]. For this reason, it is imperative to develop effective materials for their removal from the waters. Previous studies reveal that activated carbon has excellent properties as an adsorbent for organic contaminants in water. On the other hand, CNTs having a much more porous surface than activated carbon makes them ideal candidates for the adsorption of bulky organic compounds such as bisphenol A, diclofenac, oseltamivir, sulfamethoxazole and ampicillin. The use of CNTs in adsorption, filtration or photocatalytic degradation technologies, in the case of contaminated waters, is currently limited to small-scale experiments (laboratory) and the development of a pilot system for large-scale (industry) is necessary [9, 10].

In this article, the efficiency of the MWCNT-COOH/$Fe_3O_4$ nanocomposite in removing ampicillin from synthetic water samples was investigated. The preparation and characterization method of the nanocomposite used for this study was published in a previous article [11].

## RESULTS AND DISCUSSION

Ampicillin (Figure 1) was the antibiotic selected in this study, because it is an drug from the category of broad-spectrum penicillin, with indications in various bacterial infections located at the respiratory level and otorhinolaryngological infections (bronchitis, pharyngitis, sinusitis) or infections in the digestive system and urogenital.

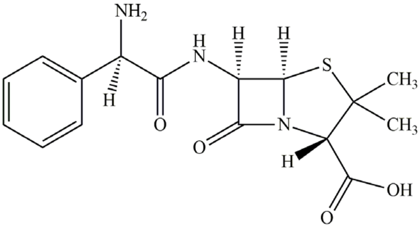

**Figure 1.** The chemical structure of ampicillin.

To establish the optimal conditions for the ampicillin adsorption process on the selected adsorbent, the influence of some physico-chemical parameters was followed.

### *Influence of pH*

An important parameter is pH because it can affects the structure of ampicillin. Thus, at pHs between 2.9 and 7.2, ampicillin was positively charged, while at pHs above 7.2, ampicillin was negatively charged [12, 13].

The experiments were carried out by varying the pH between values 2 and 10 of an initial ampicillin concentration of 40 mg $L^{-1}$. The mixtures obtained from 5 mg of adsorbent and 5 mL of ampicillin solution were stirred at 400 rpm for 20 min at a temperature of 25°C. The results obtained are presented in Figure 2.

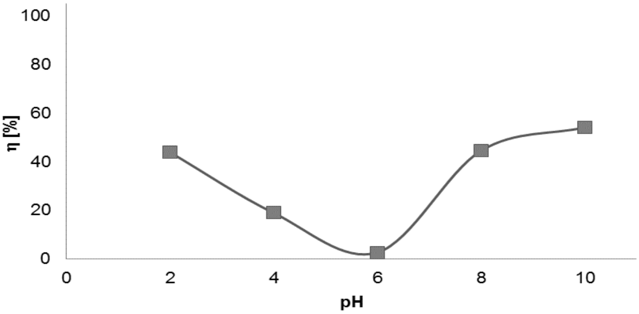

**Figure 2.** Influence of pH on the extent of ampicillin removal on CNT-COOH/$Fe_3O_4$.

The degree of ampicillin adsorption on the tested adsorbent increases in both acidic and basic media. For the following experiments, the pH value 2 was selected.

### *Influence of adsorbent dose*

This study was carried out by mixing 5 mL of ampicillin solution (40 mg L$^{-1}$, at pH 2), with different amounts of adsorbent (between 0.25 - 2 mg L$^{-1}$). The mixtures were stirred at 400 rpm at 25°C for 20 min, and the resulting solution was filtered and analyzed.

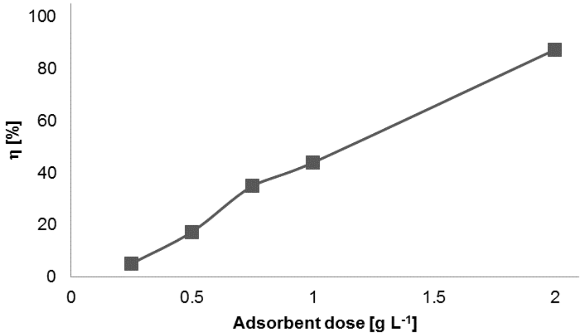

**Figure 3.** The influence of the adsorbent dose on the degree of ampicillin removal on MWCNT-COOH/$Fe_3O_4$.

The efficiency of the adsorption process increased with the increase of the adsorbent dose (Figure 3). A high degree of removal was obtained (87.2%) using an adsorbent dose of 2 g L$^{-1}$. For economic reasons, the subsequent studies were carried out using 1 g L$^{-1}$ of MWCNT-COOH/$Fe_3O_4$.

### *Influence of ampicillin initial concentration*

5 mL ampicillin solution of different concentrations (40-100 mg L$^{-1}$) at pH 2 were stirred with the amount of adsorbent established in the previous study (5 mg). The mixtures were stirred at 400 rpm for 20 min at 25°C.

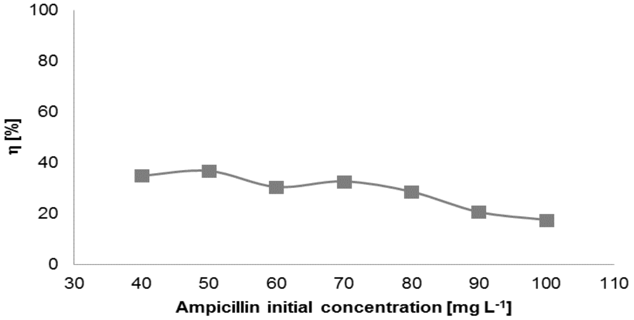

**Figure 4.** Influence of the initial concentration on the degree of ampicillin removal on MWCNT-COOH/$Fe_3O_4$.

As can be seen from Figure 4, the extent of ampicillin removal decreased with increasing initial concentration. Using MWCNT-COOH/$Fe_3O_4$ as adsorbent, the ampicillin removal degree was below 50%. For the following studies, the concentration of 40 mg $L^{-1}$ was chosen.

Since the adsorption process takes place at a very acidic pH, in this study, the degradation of ampicillin was followed over time both in the initial solution and in the solutions in which the adsorption of ampicillin was carried out with the selected adsorbent. To follow the degradation process, the solutions were chromatographically analyzed for 72 h. The results obtained are shown in Figure 5.

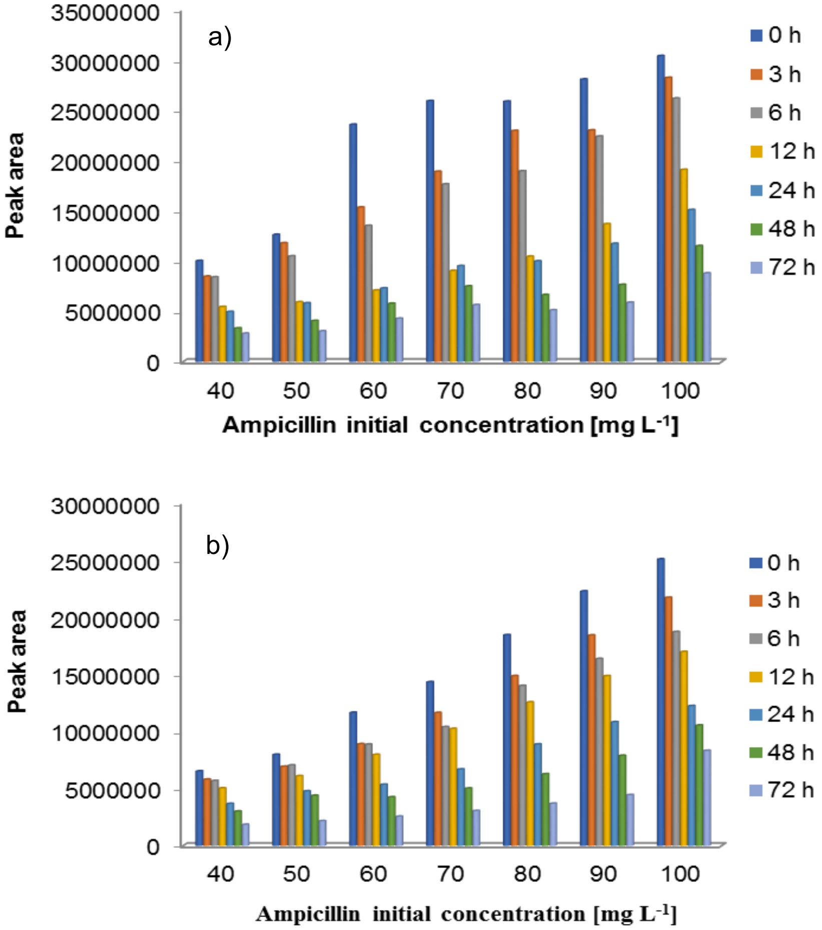

**Figure 5.** Ampicillin degradation over time: a) without adsorbent and b) with MWCNT-COOH/$Fe_3O_4$.

As can be seen (Figure 5), ampicillin degrades over time in a strongly acidic environment, but to obtain the best and fastest results, it is preferable to use especially the nanocomposite MWCNT-COOH/$Fe_3O_4$.

### *Influence of contact time*

Samples of 5 mg of MWCNT-COOH/$Fe_3O_4$ were stirred at 400 rpm with 5 mL of ampicillin solution of concentration 40 mg $L^{-1}$ at 25°C, in a time interval of 5-20 min. The solute separated a strong magnet was analyzed, and the results obtained are presented in Figure 6.

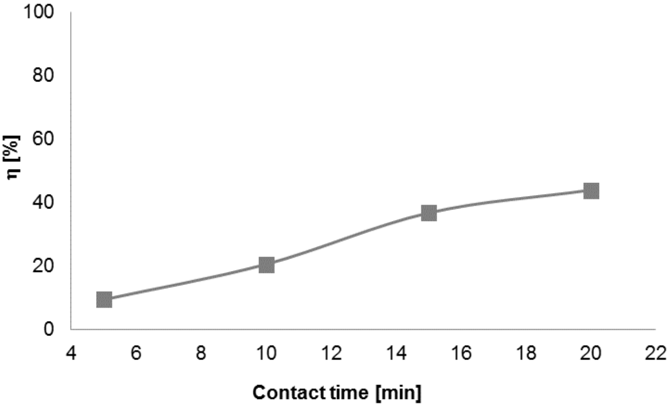

**Figure 6.** Influence of contact time on the removal degree of ampicillin on CNT-COOH/$Fe_3O_4$.

As the contact time increases, the degree of ampicillin removal on the adsorbent increases, reaching to 43.9%.

### *The proposed mechanism*

The analysis of the results obtained made possible to propose an adsorption mechanism for ampicillin on MWCNT-COOH/$Fe_3O_4$ nanocomposite. This mechanism is presented in Fig. 7. As can be seen from Fig. 7, the interaction between ampicillin and MWCNT-COOH/$Fe_3O_4$ nanocomposite can be governed by hydrogen bonds, van der Walls interactions or polar interactions. It is posibble to occur hydrogen bonding or electrostatic interactions between the functionalized carbon nanotubes and the antibiotic because the adsorbent capacity is maximum in acidic conditions (pH 2) [14, 15].

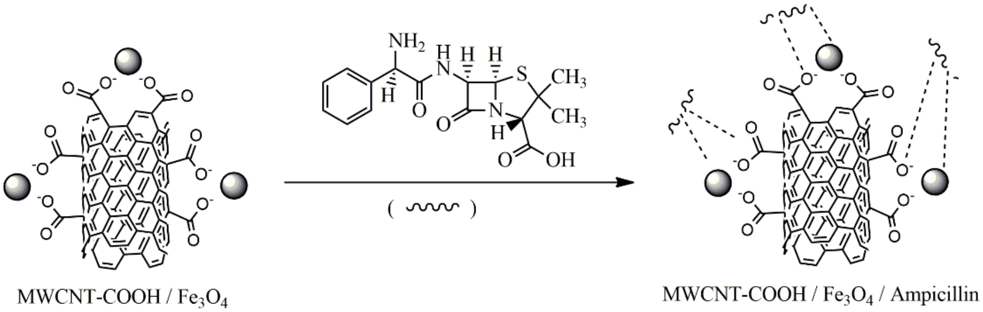

**Figure 7.** Mechanism of ampicillin adsorbtion on MWCNT-COOH/$Fe_3O_4$ nanocomposite

## CONCLUSIONS

In this paper, the adsorption performance of MWCNT-COOH/$Fe_3O_4$ nanocomposite for ampicillin removal from aqueous solutions has been assessed. To establish the optimal conditions for ampicillin removal several parameters were studied. Among the studied parameters were the pH, adsorbent dose, contact time and the initial ampicillin concentration. A degree of approx. 44% of ampicillin elimination was obtained in the following experimental conditions: 40 mg $L^{-1}$ ampicillin concentration in the aqueous solution, pH 2, 20 min of contact time with 1 g $L^{-1}$ adsorbent dose.

Considering that the concentration of ampicillin in water is much lower than that used in this experiment, as well as the magnetic properties of the nanocomposite, this can be suitable for ampicillin removal from real effluents.

## EXPERIMENTAL SECTION

### *Materials*

Injectable ampicillin was purchased from a local pharmacy. HCl and NaOH used for the pH adjustment of the aqueous solutions were purchased from Sigma-Aldrich (Germany) and VWR Chemicals, respectively. The ultrapure water obtained by a Direct-Q® 3 UV Water Purification System Merck (Germany) was used for synthetic solutions preparation used in adsorption experiments. The MWCNT functionalized with COOH groups and MWCNT-COOH/$Fe_3O_4$ nanocomposites were synthesized in our laboratory according with the methods published in our previous paper [11].

### *Adsorption studies*

The adsorption process was carried out under static conditions (“batch technique”) consisting of contacting a synthetic aqueous solution of the studied pollutant species with the adsorbent in a Berzelius glass. The mixture was stirred (400 rpm/min) for a certain time, after which the two phases were separated with the help of a magnet, and the solute was analyzed.

The efficiency of the adsorption process is given by the degree of removal of the pollutant, which is calculated with the relation:

$$\eta\,(\%) = \frac{(C_0 - C_t)}{C_0}100$$

where: η (%) represents the degree of removal/retention of the pollutant, $C_0$ and $C_t$ (mg $L^{-1}$) represent the concentration of the pollutant in the solution at the initial moment and at time t (min).

### *Ampicillin determination*

Analysis of ampicillin was performed using a Shimadzu LC2010 high-performance liquid chromatograph. The analysis of ampicillin from synthetic water samples was carried out on a Nucleodur column (100 × 3 mm, 3 µm) thermostated at 30°C. The mobile phase used was ultrapure water with 0.1% formic acid (A) and acetonitrile (B). Ampicillin was eluted with the elution gradient shown in Table 1 at a flow rate of 0.5 mL $min^{-1}$. The equilibration time of the column was 5 min and the injection volume used was 20 µL. Three chromatograms were recorded for each sample.

**Table 1.** Gradient program used for chromatographic separation of ampicillin. Mobile phase: ultrapure water with 0.1% formic acid (A) and acetonitrile (B).

| **Time (min)** | **A (%)** | **B (%)** |
|---|---|---|
| 0:00 | 95 | 5 |
| 1:00 | 95 | 5 |
| 9:00 | 80 | 20 |
| 10:00 | 95 | 5 |
| 15:00 | Stop | Stop |

**ACKNOWLEDGMENTS**

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