

Application of membrane filters in determination of the adsorption of tetracycline hydrochloride on graphene oxide

Mirza Dedic¹, Sanjin Gutic², Armina Gicevic¹, Ervina Becic¹, Belma Imamovic¹, Damir Markovic¹, Nermina Ziga-Smajic¹

¹ University of Sarajevo, Faculty of Pharmacy, Sarajevo, Bosnia and Herzegovina

² University of Sarajevo, Faculty of Science, Sarajevo, Bosnia and Herzegovina

Corresponding author: Mirza Dedic (mirza.dedic@ffsa.unsa.ba)

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Abstract

This paper shows the use of membrane filters in adsorption of solution of tetracycline hydrochloride on graphene materials. The adsorption process was monitored at different wavelengths, different pH values at certain time intervals.

The absorbances of the solutions were measured by UV-Vis spectrophotometry at two wavelengths (275 nm and 356 nm), and three pH values (pH 4, pH 7 and pH 10) every 90 minutes for 6 hours of monitoring, with constant stirring in an ultrasonic bath.

The results showed decrease in absorbance at both wavelength and in all three pH values which proved the adsorption of tetracycline hydrochloride on GO and rGO. The largest decrease in absorbance was 98.1%. The most suitable pH value for adsorption was pH 4.

This paper used a unique approach to filtration through membrane filters, which in the future could lead to the development of membrane filters based on graphene materials.

Keywords

spectrophotometry, antibiotics, purifiers, nanomaterial

Introduction

Due to its strong valence and flexibility, carbon has a large number of allotropic modifications, such as graphite, diamond, fullerene, graphene, carbon nanotubes, etc. Carbon allotropes have different physical, chemical and morphological properties (Garg 2014). Graphite is the first known carbon allotrope, and it represents a structure composed of several two-dimensional layers of sp² hybridized carbon atoms arranged in a hexagonal lattice. Each of the individual layers in the graphite structure re-

presents graphene (Du et al. 2013). Graphene is an allotropic modification of carbon. It is a single layer of densely packed carbon atoms connected into a honeycomb-shaped hexagonal structure, with a bond length between carbon atoms of 0.142 nm (Figure 1). Graphene layers form graphite. Graphene is the thinnest known carbon allotrope, and it also has a very large theoretical specific surface area ($\approx 2630 \text{ m}^2 \text{ g}^{-1}$) (Zheng et al. 2015). There is graphene oxide and reduced graphene oxide. Compared to GO, rGO contains less oxygen functional groups and a higher percentage of defects.

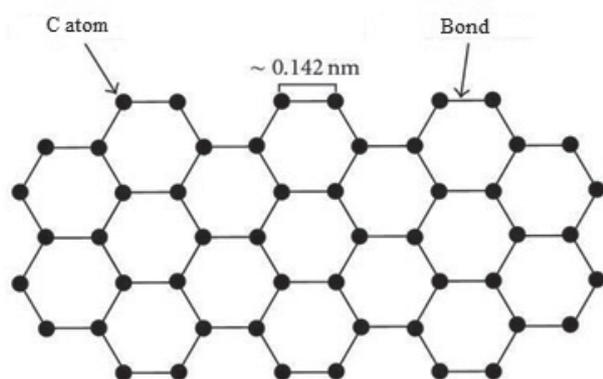


Figure 1. Structure of graphene in the form of a hexagonal lattice (Garg et al. 2016).

Due to their overuse, antibiotics have become one of the most common pollutants, and among them tetracyclines have very important place (Zhu et al. 2018). Because of that, more and more attention is paid to the techniques for their analysis. Therefore, there is a need for an efficient method of adsorption of antibiotics from wastewater. This could help solving the problem of developing bacterial resistance to antibiotics and disrupting the stability of microorganisms naturally present in the environment caused by antibiotics.

The results of previous studies of the ability of graphene to adsorb antibiotics show that graphene has a high efficiency of antibiotic removal and that the main factor for the degree of adsorption is the number of aromatic rings in the antibiotic structure, and the main mechanism of adsorption is the creation of π - π interactions (Peng et al. 2016; Ye and Zhu 2017).

Materials and methods

Chemicals

Graphite flakes – Sigma-Aldrich (Germany); Hydrofluoric acid (HF) min. 40% – Alkaloid Skopje (North Macedonia); Phosphate acid (H_3PO_4) min. 85% – Merck (Germany); Sulfuric acid (H_2SO_4) 95–97% – Kemika Zagreb (Croatia); Potassium permanganate (KMnO_4) – Merck (Germany); Hydrogen peroxide (H_2O_2) 30% – Alkaloid Skopje (North Macedonia); Ethanol ($\text{C}_2\text{H}_5\text{OH}$) 96% – Alkaloid Skopje (North Macedonia); Diethyl ether ($(\text{C}_2\text{H}_5)_2\text{O}$) – Alkaloid Skopje (North Macedonia); Argon (Ar) – Messer (Germany); Standard tetracycline hydrochloride ($\text{C}_{22}\text{H}_{25}\text{C}_1\text{N}_2\text{O}_8$) – Sigma-Aldrich (Germany).

Apparatus

Spectrophotometer – Spectronic Genesys 2, Spectronic Instruments, Milton Roy Company (USA); FTIR spectrophotometer – Perkin Elmer Spectrum BX FTIR (USA); DXR Raman Microscope, Thermo Scientific (USA); Diffractometer – UltimaIV Rigaku X-ray Diffractometer (USA).

Graphene oxide synthesis

Graphene oxide was synthesized by a modified Hummers method. For synthesis of graphene oxide natural graphite was used. The material left after this procedure was divided into two parts. One portion of graphene oxide (15 mL) was left as an aqueous suspension and the other portion was dispersed in 96% ethanol, then coagulated with diethyl ether. After filtration by vacuum pump at room temperature, the solid obtained on the filter was dried overnight at 50 °C and 63 mg of graphene oxide was obtained.

Thermal reduction of graphene oxide

To reduce the obtained graphene oxide, a thermal method was used, which is based on direct heating of graphene oxide to high temperatures in an inert atmosphere. Prior to heating, argon was added to the graphene oxide. Graphene oxide and reduced graphene oxide were prepared in concentrations of 0.8 mg ml⁻¹.

Tetracycline hydrochloride stock solution

A standard solution of tetracycline hydrochloride was prepared at concentration of 1 mg ml⁻¹. This solution was diluted with buffers. Dilutions of 0.01 mg ml⁻¹ were prepared from the standard tetracycline hydrochloride solution (1 mg ml⁻¹) with appropriate buffers (pH 4, 7 and 10).

Preparation of buffer solutions

For the purpose of examining the influence of the pH value on the adsorption of tetracycline hydrochloride on GO and rGO, solutions of acetate, phosphate and ammonia buffer (pH 4, 7 and 10) were prepared.

Preparation of samples for spectrophotometric analysis

Samples for spectrophotometric analysis were made by mixing prepared solutions of tetracycline hydrochloride (0.01 mg ml⁻¹) and aqueous solutions of GO and rGO (0.8 mg ml⁻¹).

For each individual measurement, 2.4 ml of tetracycline hydrochloride solution and 0.3 ml of GO or rGO were used, which adjusted the ratio of concentrations of adsorbents (GO and rGO) and adsorbed substance (tetracycline hydrochloride) which was 10:1.

UV-VIS Spectrophotometric analysis

The reduction of tetracycline hydrochloride content was monitored using a UV-Vis spectrophotometer, measuring the absorbance at selected wavelengths ($\lambda = 275$ nm and 356 nm), every 90 minutes for 6 hours of monitoring, with constant stirring in an ultrasonic bath for establishing a balance between the adsorbent and the adsorbed substance.

After equilibration, the mixture was centrifuged for 10 min at 15.000 rpm, and the supernatant was collected and filtered by disposable membrane filters with a pore size of 0.20 μm and then the absorbance was measured.

Results

Characterization of the obtained graphene oxide (GO) and reduced graphene oxide (rGO) was performed by infrared spectroscopy with Fourier transform (FTIR), Raman spectroscopy and X-ray diffraction (XRD).

The spectrum of tetracycline hydrochloride was obtained by UV-Vis spectrophotometry which gave insight about the absorption maxima, which were used in further analysis (Figure 2).

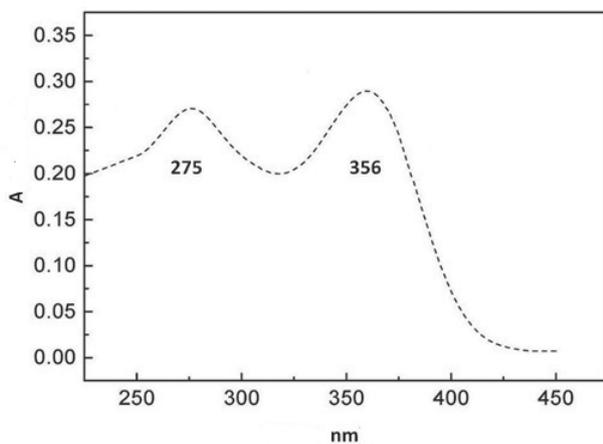


Figure 2. UV-Vis absorption spectrum of tetracycline hydrochloride.

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectrogram (Figures 3, 4) showed the presence of a number of functional groups characteristic for graphene materials including hydroxyl (3400 cm⁻¹), ether,

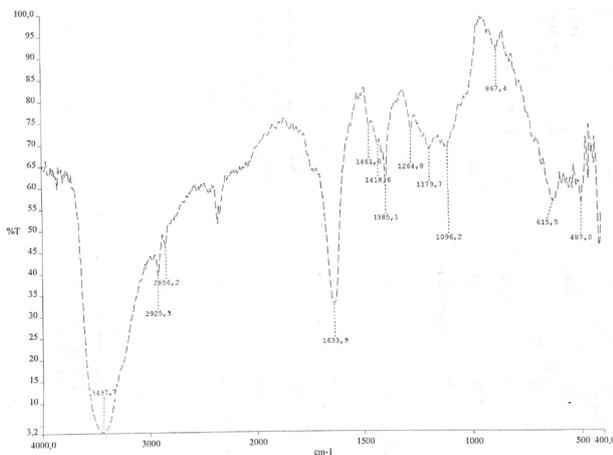


Figure 3. FTIR spectrum of graphene oxide.

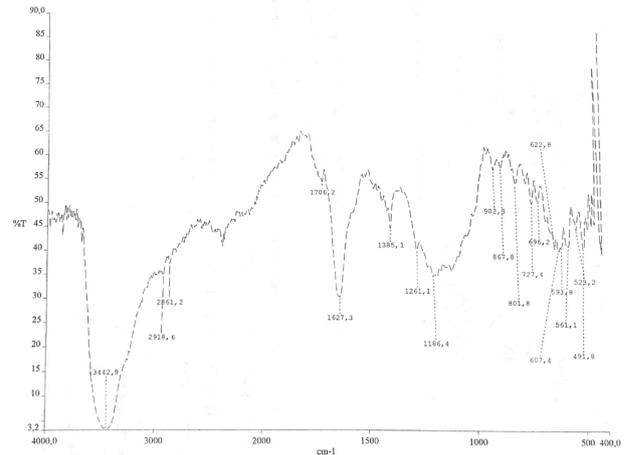


Figure 4. FTIR spectrogram of thermally reduced graphene oxide.

epoxy (1200 -1300 cm⁻¹) and quinone group (1633 cm⁻¹), as well as the presence of CH groups whose absorption bands can be seen at 2925 cm⁻¹ and 2856 cm⁻¹.

Raman spectroscopy

Raman spectra of GO (Figure 5) and rGO (Figure 6) show characteristic bands for these materials. The first originates from deformations in the structure of the graphene layer, and it is located at about 1350 cm⁻¹ (D band), the

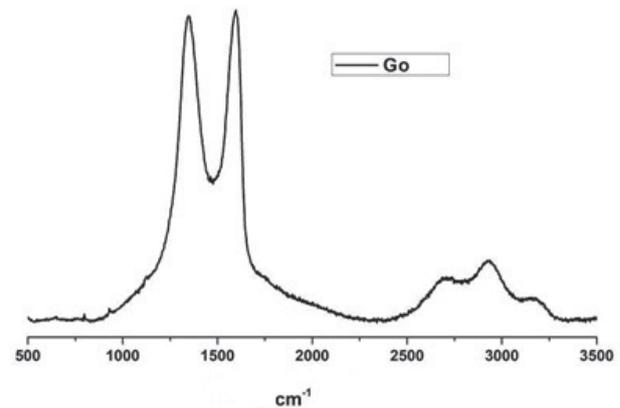


Figure 5. Raman spectrum of graphene oxide.

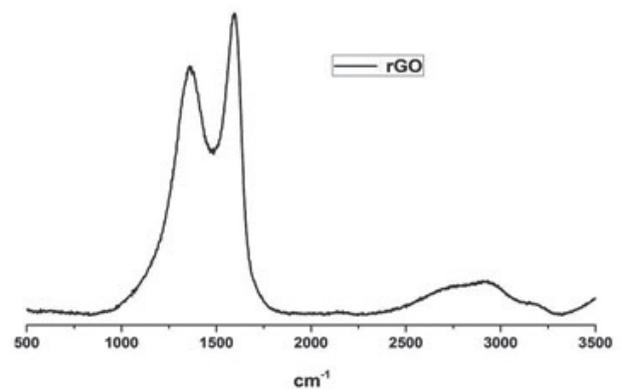


Figure 6. Raman spectrum of thermally reduced graphene oxide.

second is at about 1580 cm^{-1} (G band), and a wide band is observed at about 2700 cm^{-1} (2D or G' band) (Claramunt et al. 2015).

X-ray diffraction (XRD)

Characterization of graphene materials by X-ray diffraction was performed using a diffractometer equipped with a Cu $K\alpha_{1.2}$ radiation source, with a voltage generator of 40.0 kV and a current generator of 40.0 mA. Scanning was performed in continuous mode, in the range of $3\text{--}90^\circ$, with a step of 0.02° and a scanning speed of 2° min^{-1} (Gutić 2016). A very intense diffraction at $2\theta = 10.50^\circ$ appeared on the GO diffractogram (Figure 7). This diffraction corresponds to an interlayer spacing of about 0.9 nm, which is almost three times higher than in graphite (0.34 nm). On the diffractogram of thermally reduced graphene oxide (Figure 8) there is no intense diffraction at $2\theta = 10.50^\circ$, but there is a wide diffraction between $2\theta = 18.50^\circ$ and 23.50° .

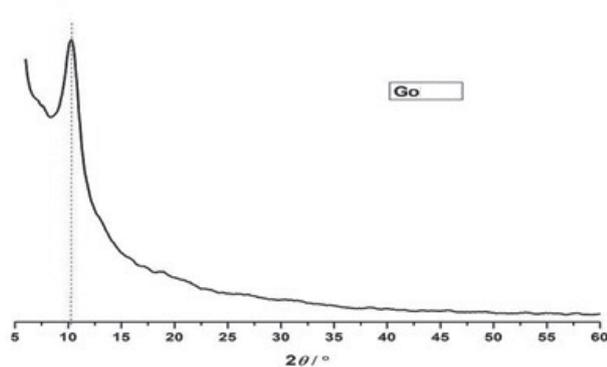


Figure 7. Diffractogram of graphene oxide.

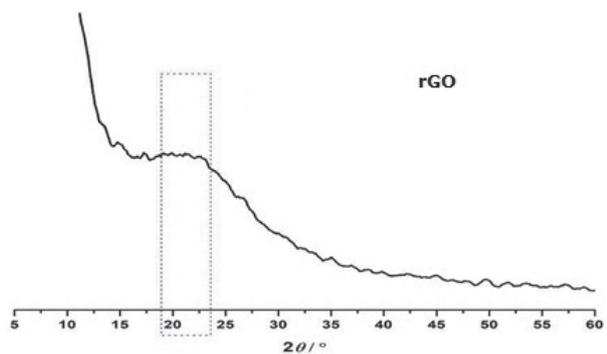


Figure 8. Diffractogram of thermally reduced graphene oxide.

Adsorption of tetracycline hydrochloride on graphene oxide

Table 1 shows the absorbances of tetracycline hydrochloride (TC) before and after the addition of GO. Absorbances were monitored at two wavelengths (275 nm and 356 nm) and two pH values (pH 4 and 7). Absorbances were

Table 1. Absorbance of tetracycline hydrochloride before and after addition of graphene oxide.

$\lambda=275\text{ nm}$		pH=4	pH=7
Absorbance A (TC)		A=0,374	A=0,492
Absorbance A (TC+GO)	Time	Mean	Mean
	$t\text{ (h)}$	Absorbance (n=3)	Absorbance (n=3)
	t_0	A=0,142	A=0,238
	$t_1=1,5$	A=0,192	A=0,252
	$t_2=3,0$	A=0,176	A=0,246
	$t_3=4,5$	A=0,175	A=0,275
$t_4=6,0$	A=0,108	A=0,276	
$\lambda=356\text{ nm}$		pH=4	pH=7
Absorbance A (TC)		A=0,351	A=0,338
Absorbance A (TC+GO)	Time	Mean	Mean
	$t\text{ (h)}$	Absorbance (n=3)	Absorbance (n=3)
	t_0	A=0,101	A=0,189
	$t_1=1,5$	A=0,137	A=0,200
	$t_2=3,0$	A=0,122	A=0,172
	$t_3=4,5$	A=0,067	A=0,180
$t_4=6,0$	A=0,043	A=0,201	

also monitored at pH 10, but these results had not been taken into consideration because coagulation of prepared solutions happened. Acidic and neutral solutions of GO are much more transparent than solutions in basic medium. The reason for that is pH dependent visible aggregation that occurs in acidic, but not in basic medium which makes acidic and neutral GO solution much more transparent because of the significant reduction in the number density of GO scattering centers. (Shih et al. 2012). This made acidic and neutral solutions of GO convenient for using UV-Vis spectrophotometry in determination of adsorption of tetracycline hydrochloride on GO.

Adsorption of tetracycline hydrochloride on reduced graphene oxide

Table 2 shows the absorbances of tetracycline hydrochloride (TC) before and after the addition of rGO monitored at two wavelengths (275 nm and 356 nm) and three pH values (pH 4, 7 and 10).

Table 2. Absorption of tetracycline hydrochloride before and after the addition of thermally reduced graphene oxide.

$\lambda=275\text{ nm}$		pH=4	pH=7	pH=10
Absorbance A(TC)		A=0,391	A=0,530	A=0,423
Absorbance A (TC+rGO)	Time	Mean	Mean	Mean
	$t\text{ (h)}$	Absorbance (n=3)	Absorbance (n=3)	Absorbance (n=3)
	t_0	A=0,069	A=0,207	A=0,143
	$t_1=1,5$	A=0,045	A=0,194	A=0,137
	$t_2=3,0$	A=0,038	A=0,156	A=0,119
	$t_3=4,5$	A=0,024	A=0,171	A=0,124
$t_4=6,0$	A=0,009	A=0,203	A=0,053	
$\lambda=356\text{ nm}$		pH=4	pH=7	pH=10
Absorbance A (TC)		A=0,315	A=0,266	A=0,187
Absorbance A (TC+rGO)	Time	Mean	Mean	Mean
	$t\text{ (h)}$	Absorbance (n=3)	Absorbance (n=3)	Absorbance (n=3)
	t_0	A=0,062	A=0,062	A=0,065
	$t_1=1,5$	A=0,017	A=0,033	A=0,058
	$t_2=3,0$	A=0,013	A=0,021	A=0,048
	$t_3=4,5$	A=0,007	A=0,021	A=0,042
$t_4=6,0$	A=0,006	A=0,024	A=0,024	

Discussion

Characterization of the obtained graphene materials was performed by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and X-ray diffraction (XRD). The characterization provides data about the presence of certain functional groups, as well as about the defects in the structure of graphene oxide, which is a useful phenomenon if this material is going to be used as an adsorbent. In addition to the presence of characteristic functional groups, the reduction of graphene oxide was proven and performed by FTIR analysis. An indication for reduction is reduced intensity of absorption at 2856 cm^{-1} and 2925 cm^{-1} of reduced graphene oxide compared to graphene oxide. This absorption originates from C-H stretching. FTIR analysis showed that after thermal reduction of GO, a large number of oxygen-containing functional groups remain mostly on the marginal regions of rGO layers, which, in addition to π - π interactions, enables electrostatic interactions with organic and inorganic molecules, and with various atoms and ions (Huizar-Félix et al. 2019). Unlike FTIR analysis, which provides information about the present functional groups, Raman spectroscopy provides information about defects, edge planes, layer thickness and orientation, stress and thermal conductivity of graphene materials (Gutić 2016). The present D band of the Raman spectrum refers to gaps, i.e. lack of atoms or ions in the structure, impurities or other defects in the graphene structure, such as oxygen-containing groups, while the G band shows the structural integrity of sp^2 hybridized carbon atoms. The third characteristic band is 2D, which is associated with the thickness of graphene (Figures 5, 6) (Peng et al. 2016). Unlike the D band, the activation of the 2D band does not require the presence of defects and it can always be registered in the Raman spectrum of graphene. The symmetrical 2D band and its high intensity indicate the existence of monolayer graphene. Since the thermal reduction of GO is a fast process, it prevents significant stacking of graphene layers, which is manifested on the rGO spectrogram by reducing the intensity of the 2D band (Gutić 2016).

The degree of defects at the graphene plane can be better estimated by the intensity ratio of the D and G bands (ID / IG). Although it is somewhat logical to expect that during the reduction of GO there will be a decrease in the intensity of the D band, because the removal of basal functional groups restores the graphene structure, the opposite happens. During the reduction there is an increase in ID / IG ratio (Gutić S et al. 2016). This phenomenon occurs because the reduction not only removes oxygen basal groups, but also side reactions happen. These reactions involve the release of CO and CO_2 , which means that part of the carbon, is also broken down from the graphene oxide structure, thus the number of defects observed from the Raman spectra is increased. In summary, based on the high intensity of the D band, and the ID / IG ratio,

it can be determined that rGO with a high percentage of defects is formed during thermal reduction (Gutić 2016). The high degree of structural defect contributes to the increase of the adsorption capacity of rGO.

In order to characterize graphene materials, XRD analysis of the crystal structure of graphene nanomaterials was performed, which is a good way to estimate the distance between the layers of graphene in the material. Unlike graphene oxide, graphite has a strong maximum of the basal plane at $2\theta = 26.6^\circ$, with a distance between layers of 0.34 nm. The lack of this peak in graphene oxide is proof of the complete oxidation of graphite. A very intense diffraction at $2\theta = 10.50^\circ$ appears on the GO diffractogram (Figure 7) and this is an undoubted indication of complete exfoliation of graphene layers. On the diffractogram of reduced graphene oxide, there is a wide peak between $2\theta = 18.50^\circ$ and 23.50° , which indicates random stacking of graphene sheets. This peak corresponds to a layer spacing of 0.34 nm as a result of the removal of oxygen atoms that entered the graphite structure during the intercalation process. This confirms the process of reducing graphene oxide to graphene (Thema et al. 2012).

Graphene oxide of these characteristics was mixed with a solution of tetracycline hydrochloride in an ultrasonic bath, and then the mixture was centrifuged. The supernatant was decanted and filtered through disposable membrane filters with a pore size of $0.20\text{ }\mu\text{m}$. The absorbance was then measured and it was found that there was a sharp drop in both wavelengths in the initial time t_0 (graphs 1 and 2). The decrease in absorbance is proof that the content of tetracycline hydrochloride is reduced, which means that the adsorption of tetracycline hydrochloride on GO has occurred. After that, the absorbances were decreasing and increasing during six hours of monitoring at both wavelengths, which could mean that in the mixture of aqueous tetracycline hydrochloride solution and graphene oxide suspension there was a partial desorption with GO as a result of constant mixing of samples in an ultrasonic bath. This leaves room for further testing and determination of graphene oxide adsorption kinetics. However, the occurrence of desorption did not significantly reduce the overall decrease in absorbance, and the adsorption process was dominant, given the fact that each increase in absorbance was negligible in comparison to its initial decrease after mixing the solution with the GO suspension. From the beginning to the end of the measurement there is a trend of decreasing absorbance, which was the greatest in the initial time t_0 , and then it was weaker. This was expected, given the fact that at the beginning there are the freest places to establish interactions between adsorbent and adsorbed substance.

The research showed that the acidic medium (pH 4) is the most suitable for the adsorption processes of tetracycline hydrochloride on GO. The largest decrease in absorbances at pH 4 was after initial mixing of tetracycline hydrochloride samples with GO (decreased by 62.1 % at

275 nm and by 71.2 % at 356 nm), and a lower absorbance value was registered after 6 hours of mixing tetracycline hydrochloride and graphene oxide with a decrease of 71.12 % at 275 nm and 87.75 % at 356 nm. In the neutral medium (pH 7) there was also a decrease in tetracycline hydrochloride after the initial adsorption on GO, at time t_0 (decreased by 51.6 % at 275 nm and by 44.1 % at 356 nm).

The same pattern happens with thermally reduced graphene oxide where occurs a significant decrease in the absorbance of tetracycline hydrochloride in the initial time t_0 , immediately after mixing tetracycline hydrochloride with rGO. The decrease in absorbance also is the evidence that the content of tetracycline hydrochloride has been reduced, which means that the adsorption of tetracycline hydrochloride on rGO has occurred. In contrast to the results of measurements after adsorption of tetracycline hydrochloride to GO, which showed a random decrease and increase in the values of the measured absorbances, after its thermal reduction these phenomenon is less present. A constant decrease in tetracycline hydrochloride absorbance was observed during the 6 h measurement, at both wavelengths (275 and 356 nm) and at two pH values (pH 4 and 10), while a slight increase in absorbance was observed at pH 7 after the third hour. This increase is negligible compared to the initial decrease in absorbance after mixing the tetracycline hydrochloride solution with rGO.

Regarding the influence of pH value on adsorption, in this case also, the acidic medium (pH 4) proved to be the most suitable. At both wavelengths, the decrease in absorbance at pH 4 was greatest after the initial mixing of the tetracycline hydrochloride with rGO (decreased by 82.4% at 275 nm, and by 80.2% at 356 nm). The downward trend of the measured absorbances continued in other measurements, and the lowest value of absorbance in both cases was measured after 6 hours (decreased by 97.7% at 275 nm and by 98.1% at 356 nm). In the neutral medium (pH 7) there was also the largest decrease in the absorbance of the tetracycline hydrochloride solution after the initial adsorption on rGO, at time t_0 (decreased by 61% at 275 nm, and by 76.7% at 356 nm). As with GO, the lowest absorbance at both wavelengths was measured after 3 hours of mixing (decreased by 70.57% at 275 nm and by 92.10% at 356 nm), followed by an increase in absorbance. In the base medium (pH 10), the decrease in absorbance, as well as in the acidic medium, was constant and there was no process of desorption of tetracycline hydrochloride from the rGO surface. The initial decrease in absorbance was the most significant in this case (decreased by 66.2% at 275 nm, and by 65.3% at 356 nm), and the lowest values of absorbance at both wavelengths were measured after 6 hours (decreased by 87.47% at 275 nm, and by 87.17% at 356 nm).

The results of testing the adsorption capacity of graphene oxide before and after its thermal reduction show that this material, under the stated conditions, can be used as an adsorbent for the tested antibiotic. A high rate of adsorption is observed during the first measurements which is probably due to the availability of large areas of

graphene oxide for antibiotic molecules at the beginning of the process. The adsorption rate gradually decreases until all existing graphene surfaces become occupied and after that a constant adsorption rate is observed. The increased number of aromatic rings in the structure of antibiotics also contributes to the increased rate of adsorption (Peng et al. 2016).

In both cases (graphene oxide and thermally reduced graphene oxide), pH 4 was the most suitable medium for the adsorption of tetracycline hydrochloride. Under these conditions, adsorption process is performed through the hydrogen bonds and the π - π stacking effect. By increasing pH, the number of hydrogen bonds is reduced due to the generation of OH⁻, thus the adsorption is lower.

Thermal reduction of graphene oxide contributed to slightly better adsorption of tetracycline hydrochloride on this material, because reduced graphene oxide has more π locations. During the reduction of graphene oxide, a noticeable change in color occurs, which is an indicator of the recovery of the π electronic system, which is crucial for adsorption (Gutić 2016). The cause of slightly higher adsorption of reduced graphene oxide compared to graphene oxide is the high degree of defects in its structure which was detected during the characterization of the material.

Amino groups in the structure of the adsorbent form bonds with oxygen and nitrogen atoms present in the structure of tetracycline hydrochloride. Thanks to its unique structure, graphene oxide can improve the adsorption of certain substances. A large number of epoxy, carboxyl, hydroxyl groups and delocalized π conjugate structures on the surface of graphene oxide increase the adsorption efficiency and affinity for substances that have an aromatic ring in the structure, such as tetracycline hydrochloride (Peng et al. 2016; Ye and Zhu 2017; Zhu et al. 2018).

The approach to filtration in this paper was unique, very cheap and simple, which speeds up and reduces the cost of the analysis process. Membrane filters are otherwise used in different purposes, and this would give them a new application. Testing could be continued in this direction, so that filtration systems with adsorbents based on graphene materials could be developed. Disposable and reusable filters could be made for analysis for different types of samples in medicine, pharmacy, biology, chemistry, in laboratory or field conditions. It should be noted that this experiment was performed with graphene material that was synthesized by the modified Hummers method, and the specific graphene material was confirmed by characterization.

Conclusion

Spectrophotometric analysis determined the ability of adsorption of tetracycline hydrochloride from an aqueous solution to graphene oxide. Adsorption was most intense in acidic medium (pH 4). An increase in the extent of adsorption was also observed after thermal reduction of graphene oxide due to an increase in the number of π sites. The results showed that graphene materials have high

efficiency in the removal of tetracycline hydrochloride and that the main factor for the degree of adsorption is the number of aromatic rings in its structure, and the main mechanism of adsorption is the formation of π - π interactions. In this paper, a unique approach to filtration was used,

using membrane filters, which showed a new type of application of these filters and opened the possibility for the development of filtration systems with adsorbents based on graphene materials. These results could be used in the future to analyze graphene materials as potential purifiers.

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