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Adsorption of oxytetracycline and ciprofloxacin on carbon-based nanomaterials as affected by pH

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Abstract: With the increase in use and application of carbon nanomaterials and the frequent presence of fluoroquinolones and tetracyclines antibiotics in the aquatic environment, their interactions have attracted extensive attention. In this study, adsorption of two antibiotics: oxytetracycline (OTC) and ciprofloxacin (CIP) by four carbon-based nanomaterials (graphene oxide, reduced graphene oxide, multiwalled carbon-nanotubes, oxidized multiwalled carbon-nanotubes) affected by pH was investigated. The experiment was performed in two steps: (i) adsorption of OTC and CIP at different pH values, (ii) adsorption isotherm studies of both antibiotics on four carbon-based nanomaterials. Both steps were conducted using the batch equilibration technique. The results showed that the adsorption of both antibiotics on studied adsorbents was highly pH-dependent. The highest adsorption was obtained at pH 7.0, implying the importance of the zwitterionic antibiotics forms to adsorption. Antibiotics adsorption isotherms at three given pH values followed the order of pH 7.0 > 1.0 > 11.0, which confirmed zwitterionic species of OTC and CIP as having the greatest ability to adsorb on carbonaceous nanomaterials. Electrostatic interaction, π-π EDA interaction, hydrophobic interaction for both antibiotics, and additionally hydrogen bond for CIP were possible mechanisms responsible for OTC and CIP adsorption onto studied nanomaterials. These results should be important to understand and assess the fate and interaction of carbon-based nanomaterials in the aquatic environment. This study can also be important for the use of carbon nanomaterials to remove antibiotics from the environment.

Introduction

Ciprofloxacin (CIP) is a broad-spectrum antibiotic belonging to the fluoroquinolones class, which is widely used in the medical practice for treating infections caused by various Gram-positive and Gram-negative bacteria (Zhang et al. 2018). Fluoroquinolones play an important role in global medicine because their consumption is approximately 7% of the total consumption of antimicrobial agents (Szymańska et al. 2019; Felis et al. 2020). Due to their hydrophilic properties, fluoroquinolones can be mobile in an aquatic environment, thus they are detected in surface water, groundwater, and even in drinking water (Watkinson et al. 2009; Hanna et al. 2018; Reis et al. 2019). Mobility in the environment caused ciprofloxacin to be listed on the second EU watch list (EU Decision, 2018/840 of June 5, 2018). However, the wastewater treatment plants (WWTPs) are recognized to be important as the main reservoir of ciprofloxacin. It was reported that ciprofloxacin was detected in the effluent of 90% of WWTPs located in the EU (Loos et al. 2013). Its concentration in various wastewaters is between ng L^{-1} – µg L^{-1} (Watkinson et al. 2009; Verlicchi et al. 2013). The removal efficiency of CIP at conventional WWTPs is 90% (Michale et al. 2013). However, these antibiotics are mainly removed by adsorption on activated sludge flocs. It is noted that CIP can be adsorbed on activated sludge up to 80% (Golet et al. 2003; Michael et al. 2013).

Tetracyclines can form complexes with metal ions such as calcium, iron, magnesium, which present a strong affinity to activated sludge (Felis et al. 2020). These chelating properties caused tetracyclines to be relatively well removed in conventional WWTPs (up to 90%), mainly by sorption onto sludge flocs (Michael et al. 2013). Oxytetracycline (OTC) is one of the most often used antibiotics belonging to the tetracycline class. An extremely high concentration of OTC was found in the effluent from OTC manufacturer, where 50 mg L^{-1} was observed (Li et al. 2008), while in the livestock farm its concentration was estimated at 2.1 mg L^{-1}. Therefore, both oxytetracycline and ciprofloxacin pose a serious hazard to the aquatic environment, thus there is need to remove them effectively.

For the past few decades, many materials have been studied to remove antibiotics from the environment via catalysis oxidation process (Lemańska et al. 2021) or adsorption, such as activated carbon (Ahmed 2017), carbon nanotubes (Ji et al.

2010, Liu et al. 2016), graphene oxide (GO) (Liu et al. 2016), bentonite (Genç and Dogan, 2013) and biochar (Zheng et al. 2013). With the development of nanotechnology, new materials have emerged with new properties, which also allow for modification of current materials. Nowadays, nanomaterials are wildly used in biomedicine, electronics, mechanical engineering, photonics, energy generation, and storage due to their excellent electrical and mechanical properties. The most commonly used carbon-based nanomaterials are those based on graphene, which is characterized by 2D-atomic crystal structure with sp^2 networks (Papageorgiou et al. 2017). Basic graphene is polar and hydrophobic, so to improve its dispersibility in aqueous media its needs to be oxidized with, for example, chemical oxidation (Lalwani et al. 2016). Moreover, chemical oxidation and exfoliation of graphite followed by reduction have been indicated to be promising for reduced graphene oxide (rGO) production (Liu et al. 2016). On the other hand, increasing production of graphene nanomaterials (GNMs) caused their release into environment which poses a serious problem because of their toxicity. Moreover, the prevalence of environmental organic pollutants which can be adsorbed on graphene nanomaterials may cause both GNMs and organic pollutants to be spread further in the environment. Moreover, the interaction between graphene nanomaterials and organic pollutants may increase the toxicity of both GNMs and organic pollutants (Zhao et al. 2014). Thus, such interaction needs to be in-depth evaluated.

Rostamain and Behnejadu (2018) studied the adsorption of three antibiotics: ciprofloxacin, tetracycline, and doxycycline by GO nanosheets and revealed that the adsorption process is a pH-dependent. Similar statement was presented by Liu et al. (2016), who investigated adsorption of two sulfonamides (sulphapyridine and sulfathiazole) on graphene-based nanomaterials (rGO, SWCNTs). Thus, it can be expected that OTC and CIP adsorption onto rGO and multiwalled carbon nanotubes (MWCNTs) was also pH-dependent because similar composition of these carbon-nanomaterials consisted of graphene sheets. Therefore, rGO and GO as well as MWCNTs have been proven as an efficient adsorbent for various environmental pollutants such as pharmaceutical, nitroaromatic compounds, and phenolic compounds due to the conjugation π region sites and functional groups. The four possible adsorption interactions between antibiotics and carbon-based nanomaterials are described: (i) inducing π-π interaction of antibiotics and π electron of nanomaterials aromatic ring, (ii) hydrogen bonding of antibiotic and hydrogen ion from carboxyl or hydroxyl group of nanomaterials, (iii) hydrophobic interaction of antibiotics with hydrophobic groups of nanomaterials, (iv) electrostatic interaction of antibiotics with carboxyl groups at different pH for cationic attraction (Wang et al. 2019).

Therefore, in this work, it was investigated how pH affects sorption of two commonly used antibiotics (oxytetracycline, OTC; ciprofloxacin, CIP) by four carbon-based nanomaterials. Both antibiotics are commonly used in medicine, veterinary and animal breeding resulting in their detection in a different part of the environment (Felis et al. 2020). Previous studies have mainly focused on one type of carbon nanomaterials (GO or CNTs), without comparing themselves. Therefore, the novelty of this study is to compare the sorption ability of four different carbon-based nanomaterials including reduced graphene oxide (rGO), graphene oxide (GO), multi-walled carbon nanotubes (MWCNTs), and oxidized multiwalled carbon nanotubes (oMWCTNs). The adsorption efficiency of the studied nanomaterials has been explored by taking into account different pH values. This study will provide the comparison of the sorption effectiveness of two antibiotics which belong to different classes and will be useful to understand the behavior of antibiotics sorption at different pH conditions.

Materials and methods

Test compounds

Commercially available GO, rGO (Nano Carbon, Poland) and MWCNTs (Nanocyl NC7000™, Belgium) were used. MWCNTs were functionalized by oxidative treatments with a mixture of nitric acid (HNO_3) and sulfuric acid solution (H_2SO_4) (1:3; v/v), then the mixture was refluxed using the heating mantle for the periods 5 to 90 minutes and cooling to room temperature for 15 minutes. Next, the mixture was poured onto distilled water (2 L) to quenching, filtrated out under diminished pressure (pore size 0.2 μm), then rinsed with distilled water and dried at 85°C to the constant weight (at least 12 h) (Kolanowska et al. 2019. OTC (CAS: 79-57-2) and CIP (CAS: 85721-33-1) were selected as the representative antibiotics of tetracycline and fluoroquinolone class, respectively because of their prevalence and high concentration in the environment reaching a few μg L^{-1} (Felis et al. 2020). Oxytetracycline and ciprofloxacin were purchased from Alfa-Aesar and Acros Organic, respectively with purities of 96% and 98%, respectively, and used as received. The chemical structures and some physicochemical properties are shown in Table 1.

Adsorption experiments

Adsorption experiments were conducted using the batch equilibration technique in 100 mL bottles. Stock solutions (100 mg L^{-1}) of OTC and CIP were prepared by background solution containing 20 mM NaCl and 200 mg L^{-1} NaN_3, to avoid possible microbial biodegradation. To reveal the effect of pH on adsorption of OTC and CIP on carbon-based nanomaterials, the nanomaterials were added to the solution with 50 mg L^{-1} antibiotics and the pH solution was adjusted in the range 1.0–12.0 (with an interval of 1) with using 10% NaOH and 10% HCl. The concentration of antibiotics was adjusted to experimental needs, while such a wide pH range was selected to find the optimum value at which the highest sorption efficiency occurs. Antibiotics adsorption isotherm study was performed at pH 1.0, 7.0, and 12.0 with the initial concentrations of both OTC and CIP at 2, 3, 5, 6, 10, 15, 20, 40, 50, 75, 100 mg L^{-1}. The 100 mL of antibiotics solution at defined concentration was poured into the 100 mL glass bottles, which defined amounts of nanomaterials (rGO, GO, MWCNTs. oMWCNTs) were added. Next, pH was adjusted. All samples were incubated in the dark and mixed on the magnetic stirrer (150 rpm, room temperature) for 1 day. After incubation, the samples were centrifuged for 15 min at 3000 rpm for further measurements and additionally filtrated out (pore size 0.22 μm). The concentration of antibiotics was analyzed spectrophotometrically using UV-Vis spectrophotometer (UV5600, Shanhai Metash Instruments Co., Lld) at the maximum wavelength of 350 nm

for OTC and 276 nm for CIP via measuring the concentration by plotting a calibration curve.

Contribution of OTC and CIP to adsorption

To investigate the adsorption affinity of OTC and CIP at a given pH, the distribution adsorption coefficient, K_d, was calculated from the following equation:

$$K_d = \frac{(C_0 - C_e)V}{C_e m} \quad (1)$$

where C_0 is the initial concentration of antibiotics (mg L^{-1}), C_e is the concentration of adsorbate at equilibrium (mg L^{-1}), V is the volume of antibiotic solution (mL), and m is the mass of adsorbent (g).

Adsorption isotherm data fitting

In this study two models were used to fit the experimental data.

The Langmuir and Freundlich isotherms were represented by the equation 2 and 3, respectively (Langmuir, 1918; Freundlich, 1906):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

$$q_e = K_F C_e^n \quad (3)$$

where q_e (mg g^{-1}) is the amount of adsorbed substance per unit mass of the adsorbent, C_e (mg L^{-1}) is the concentration of adsorbate at equilibrium, q_m (mg g^{-1}) is the maximum adsorption capacity and K_L (L mg^{-1}) is Langmuir adsorption affinity parameter K_F ((mg g^{-1})(L $mg^{-1})^{1/n}$) and n is the Freundlich adsorption constants.

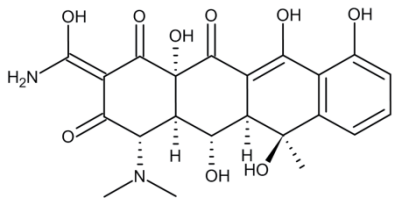
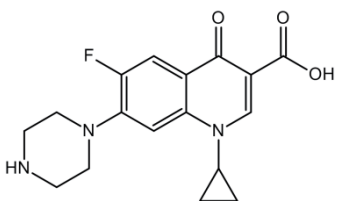
Results and discussion

Effect of pH on OTC and CIP adsorption

Previous studies have reported that pH could significantly affect the adsorption of antibiotics on carbon-based nanomaterials (Zheng et al. 2013; Liu et al, 2014; Liu et al. 2016). The effects of pH on K_d values of OTC and CIP adsorbed onto the four carbon nanomaterials are shown in Figure 1. The obtained results show that K_d values of both OTC and CIP for all adsorbents exhibited a similar pH-dependent pattern, first increased with pH from 1 to 7 and then slightly dropped with pH from 8 to 12. Similar results were presented by Yadav et al. (2018), who found that at neutral pH (pH = 7.0) both CIP and NOR (norfloxacin) showed the highest sorption capacity on graphene. pH affected the adsorption capacity of antibiotics by influencing surface binding sites, surface charges of adsorbents, aqueous chemistry, and the molecules of antibiotics molecules (Yadav et al. 2018; Figueroa et al. 2005). Depending on the pH of the solution, both OTC and CIP can occur in three forms: cationic, zwitterionic, and anionic. The presence of ionized forms of both antibiotics results from having different pK_a values: pK_{a1} = 6.1 and pK_{a2} = 8.7 for CIP and pK_{a1} = 3.57, pK_{a2} = 7.49 and pK_{a3} = 9.44 for OTC. At lower pH, CIP exists in the cationic form due to protonation of the amine group in the piperazine molecule, while at higher pH, it exists as an anion due to deprotonation of the carboxyl group. At pH = 7.0, the zwitterionic form is the dominant species due to the charge balance over the carboxyl and amino groups (Yadav et al. 2018). Meanwhile, increasing pH can simplify the deprotonation of charged enol and amine groups in OTC and carboxyl group in the studied adsorbates. The electron-acceptor ability of these molecules was impaired by suppressing the cation – π bond, increasing pH, and π-π stacking with nanomaterials (Gao et al. 2012; Rostamian and Behnejad, 2018). However, with pH increasing from 1 to 7, electrostatic interaction takes place, so adsorption of CIP increases (Rostamian and Behnejad, 2018). Thus, this allows us to state that the zwitterionic form of both OTC and CIP may have an important contribution to the adsorption onto carbon-based nanomaterials.

According to the used nanomaterials, K_d values for both OTC and CIP exhibit similar pH-dependent model following the order of rGO > GO > MWCNTs > oMWCNTs, which is mostly in accordance with the surface area and micropore volume of these nanomaterials. Table 2 presents examples of the literature data of the surface area and micropore volume of

Table 1. The basic physico-chemical characteristics of OTC and CIP

	Oxytetracycline	Ciprofloxacin
Chemical formula	$C_{22}H_{24}N_2O_9$	$C_{17}H_{18}FN_3O_3$
Chemical structures		
CAS number	79-57-2	85721-33-1
Molecular weight (g mol^{-1})	460.44	331.38
pKa	pK_{a1}=3.27 pK_{a2}=7.32 pK_{a3}=9.11	pK_{a1}=6.09 pK_{a2}=8.74
Log K_{ow}	-0.90	0.28

the studied nanomaterial. These results indicate that the surface interaction and micropore filling of the studied nanomaterials played an important role in the adsorption of both OTC and CIP. Similar results were presented by Liu et al. (2016), who obtained a higher adsorption capacity of rGO than MWCNTs for sulphapyridine and sulfathiazole, paying special attention to the difference in the surface area and micropore volume between these nanomaterials. These results are also in line with oxygen-containing functional group of nanomaterials, because both GO and rGO contain much more oxygen group than MWCNTs and oMWCNTs, which may suggest that higher surface oxygen content increases the adsorption of studied antibiotics, which is in contradiction with the previous research results. Numerous studies have shown that number of oxygen functional groups content decrease the adsorption of organic chemicals on carbon-based nanomaterials (Franz et al 2000; Zhu et al. 2005) by hydrogen bonding, water adsorption, and dispersive–repulsive interactions (Sheng et al. 2010). Previous studies of adsorption aromatic chemicals on carbon nanomaterial suggested that surface oxygen complexes on activated carbon increase the affinity of water to this material, which reduces the accessibility for aromatic adsorbates, causing lower adsorption capacity (Franz et al. 2000). Moreover, Liu et al. (2016) to better understand the factor which controls the differences in adsorption of sulphapyridine and sulfathiazole onto five adsorbents (2 × rGO, MWCNTs, SWCNTs, graphite), normalized the adsorption isotherms by surfaced area and micropore volume. These results have shown that although rGO has more oxygen content than MWCNTs, the normalized adsorption results were overlapped, suggesting the limited role of the oxygen-containing functional groups in adsorption.

Adsorption isotherm test

The adsorption isotherm is curtail because it gives information on how adsorbed molecules are distributed between the liquid and solid phase when the equilibrium is reached in the adsorption process (Sheng et al. 2010). These tests were conducted in three different pH values to provide the essential

Table 2. Literature data of surface area and micropore volume of studied carbon-based nanomaterials. [a]BET (Brunauer-Emmett-Teller) method, [b]BJH (Barrett-Joyner-Halenda) method.

Carbon-based nanomaterials	Surface area ($m^2\ g^{-1}$)	Micropore volume ($m^3\ g^{-1}$)	References
rGO	325–331[a] 364	0.118–0.133	Liu et al. 2016, 2014 Smajic et al. 2018
GO	332 32a	 0.11[b]	Xu et al. 2011 Li et al. 2013
MWCNTs	117[a] 177[a] 72[a]	0.053 0.54[b] 0.41[b]	Liu et al. 2016, 2014 Li et al. 2013 Sheng et al. 2010
oMWCNTs	121[a]	0.49[b]	Sheng et al. 2010

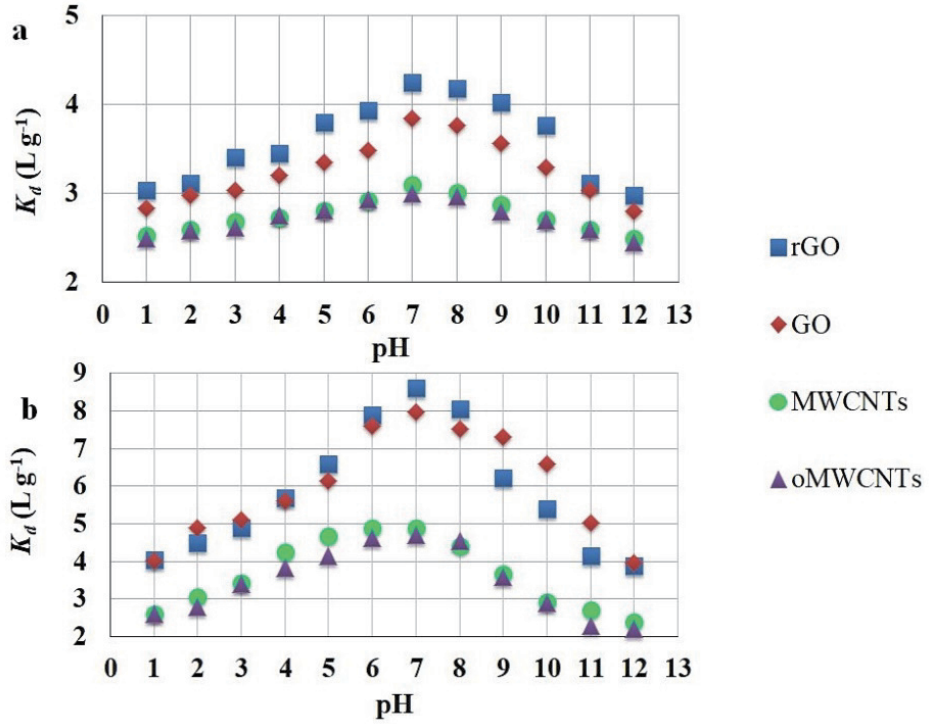


Fig. 1. pH-dependent OTC (a) and CIP (b) adsorption onto rGO, GO, MWCNTs, oMWCNTs. The initial concentration of both OTC and CIP was 50 mg L^{-1}. The experiment was conducted at room temperature.

information on the adsorption behaviors of both OTC and CIP because the highest adsorption of both antibiotics was reached at pH 7.0, which might suggest that the zwitterionic form of both OTC and CIP was more favorable to the adsorbents. Moreover, at pH 1.0 and 12.0, OTC and CIP were mostly in the cationic and anionic form, respectively, which had a significant effect on adsorption capacity (Figueroa et al. 2004; Wang et al. 2011).

As can be seen from Table 3 and Table 4 the experimental data of OTC and CIP adsorption on four carbon-based nanomaterials at three pH values are well fitted by both Langmuir and Freundlich isotherm models. The isotherms for all nanomaterials are nonlinear for the antibiotics studied in this work, which may suggest a heterogeneous adsorption site of the adsorbents. Due to their strong hydrophobicity, nanomaterials of different sizes can form aggregated structures (Sheng et al. 2010). Such heterogeneous sites can create different adsorption energies for antibiotic adsorption. For example, Gnihotret al. (2004) stated that heterogeneity of MWCNTs can occur: (i) in the void space inside the nanotubes, (ii) in the interstitial intervals between adjacent nanotubes, (iii) on the grooves of the nanotube bundle periphery, (iv) on the curved surface of the nanotube periphery.

Comparing the parameters for the isotherm models (Table 2, 3), higher maximum adsorption capacity (q_m) is presented by CIP rather than OTC. Because CIP has a planar configuration, it should be possible to form a π-π stack between the studied nanomaterials and the benzene rings of CIP and reveal more adsorption sites (Carabineiro et al. 2012). Meanwhile, different absorption behavior of ciprofloxacin (CIP), tetracycline (TC), and doxycycline (DOC) onto GO nanosheets were studied by Rostamian and Behnejad (2018), and similar results were found. They obtained the maximum adsorption capacity of antibiotics as follows: CIP > DOC > TC, which confirms that CIP has a better capacity than tetracycline antibiotics.

Compared with the Langmuir isotherm model, the Freundlich model slightly better described the adsorption isotherm, due to higher R^2 values (near the value 0.9999) for both OTC and CIP. Therefore, the following discussion was based on the Freundlich adsorption isotherms. As shown in Figure 2, the adsorption of OTC and CIP at three given pH values followed an order of pH 7.0 > 1.0 > 12.0, indicating that used carbon-nanomaterials possessed the highest adsorption capacity to neutral-charge molecules followed by positively and negatively charges form of OTC and CIP. Similar results were also found in adsorption of norfloxacin and sulfamethoxazole by functionalized CNTs (Zhang et al. 2010; Wang et al. 2010) and also sulphapyridine and sulfathiazole by rGO and CNTs (Liu et al. 2016).

The chemical structure of studied carbon-based nanomaterials, i.e., the atoms and oxygen-containing groups that have high chemical activity and adsorption capacity located on the surface of the nanomaterials allow for chemical adsorption mechanism (Wang et al. 2019). Adsorption mechanism of carbon-based adsorbents, such as rGO and GO can be interpreted by the π-π electron-donor-acceptor (EDA) interaction (Ji et al. 2009; Wang et al. 2010, Sheng et al. 2010; Liu et al. 2016). Analyzing the chemical structure of CIP (Table 1), it was found that the benzene rings include fluorine group and nitrogen-heteroaromatic ring, which can be a π-electron-acceptor due to the strong electron-rejecting ability of nitrogen and fluorine. Meanwhile, groups that contain oxygen such as -OH and -COOH, exist on the surface of GO and rGO. These groups make the benzene rings become π-electron donors, while the -COOH groups make the benzene rings as π-electron acceptors to abolish π-π bonds (Pan and Xing, 2009; a et al. 2015). During the chemical reduction, the high oxidability of -COOH groups makes them removed. Therefore, residual hydroxyl groups on GO and rGO surface make the benzene ring rich in the π-electron ring, which plays a significant role in π-π electron donor-acceptor interaction (Ma et al. 2015). Similar to ciprofloxacin, oxytetracycline can also form π-π (EDA) interactions with GO and rGO because the conjugated enone structures of the oxytetracycline molecule can function as π-electron-acceptors due to the strong electron donating ability of the ketone group, and thus interact strongly with the GO and rGO (π-electron-donor) surface of carbon adsorbents to form π-π EDA interactions (Ji et al. 2009).

According to the obtained results, ciprofloxacin has higher adsorption than oxytetracycline, it should be an additional adsorption mechanism. Thus, some studies suggest that hydrogen bond plays an important role in the process of organic pollutants sorption (Ji et al. 2009; Wang et al. 2011). Previous studies have shown that CIP with two -C=O and one -OH groups can form a hydrogen bond with the oxygen-containing groups that are on carbon nanomaterial. Polar functional groups in CIP such as -NH and -OH can play the role of acceptors in forming hydrogen-bonding with -OH on rGO and GO. However, due to the fact that some carbon-based nanomaterials such as MWCNTs and graphene exclude oxygen functional groups on the surface, their ability for hydrogen-bonding interaction on adsorption may not be significant. Moreover, hydrophilic functional groups of carbon-based materials may form hydrogen bonds with water molecules, resulting in the competitive sorption of water with organic substances, what was described above (Ma et al. 2015).

It should be noted that adsorption of both OTC and CIP at pH 1.0 and 12.0 was much lower than that at pH 7.0. Therefore, the contribution of π-π EDA interaction at both low and high pH should be overcome by different mechanisms. Electrostatic interaction has been shown as a possible adsorption mechanism of ionic organic compounds on carbon-based nanomaterials. At pH 1.0 and 12.0, both OTC and CIP are positively and negatively charged, respectively. Due to the relatively high content of oxygen-containing functional groups, the surface of all nanomaterials can be protonated and deprotonated at pH 1.0 and 12.0, respectively. Thus, electrostatic repulsion between the same charges of antibiotics and adsorbents may be responsible for less adsorption at pH 1.0 and 12.0 compared to pH 7.0.

Conclusions

Based on the study, the following conclusions can be made:

- pH has a significant effect on the adsorption of oxytetracycline (OTC) and ciprofloxacin (CIP) onto reduced graphene oxide (rGO), graphene oxide (GO), multiwalled carbon nanotubes (MWCNTs) and oxidized multiwalled carbon nanotubes (oMWCTNs).

Table 3. Adsorption isotherm parameters for adsorption of OTC on carbon-nanomaterials at given pHs (1.0, 7.0, 12.0)

pH	Adsorbent	Langmuir			Freundlich		
		q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F ((mg g^{-1})(L mg^{-1}))$^{1/n}$)	n	R^2
pH 1	rGO	62.09	0.078	0.986	9.22	0.41	0.9935
	GO	55.08	0.081	0.971	10.15	0.36	0.9903
	MWCNTs	20.77	0.017	0.991	6.18	0.25	0.9920
	oMWCNTs	22.56	0.015	0.993	6.01	0.28	0.9875
pH 7	rGO	82.64	0.002	0.977	13.55	0.38	0.9934
	GO	66.07	0.002	0.989	12.55	0.35	0.9914
	MWCNTs	43.10	0.004	0.989	11.02	0.29	0.9839
	oMWCNTs	52.97	0.005	0.974	8.35	0.39	0.9957
pH 12	rGO	27.59	0.033	0.947	2.06	0.56	0.9933
	GO	21.91	0.032	0.991	3.01	0.42	0.9955
	MWCNTs	9.95	0.086	0.981	2.82	0.26	0.9946
	oMWCNTs	9.19	6.112	0.971	1.51	0.38	0.9971

Table 4. Adsorption isotherm parameters for adsorption of CIP on carbon-nanomaterials at given pHs (1.0, 7.0, 12.0)

pH	Adsorbent	Langmuir			Freundlich		
		q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F ((mg g^{-1})(L mg^{-1}))$^{1/n}$)	n	R^2
pH 1	rGO	70.41	0.085	0.988	11.33	0.28	0.9876
	GO	65.24	0.069	0.979	9.37	0.41	0.9782
	MWCNTs	21.71	0.017	0.987	6.18	0.26	0.9808
	oMWCNTs	25.29	0.016	0.979	6.43	0.28	0.9644
pH 7	rGO	99.26	0.001	0.943	17.85	0.36	0.9310
	GO	79.78	0.002	0.979	1.41	0.36	0.9926
	MWCNTs	50.44	0.005	0.986	8.17	0.39	0.9884
	oMWCNTs	55.83	0.004	0.978	9.13	0.38	0.9924
pH 12	rGO	28.56	0.018	0.983	3.79	0.43	0.9834
	GO	24.22	0.026	0.980	14.94	0.45	0.9955
	MWCNTs	10.69	0.082	0.974	3.02	0.26	0.9858
	oMWCNTs	9.04	8.780	0.972	2.45	0.27	0.9892

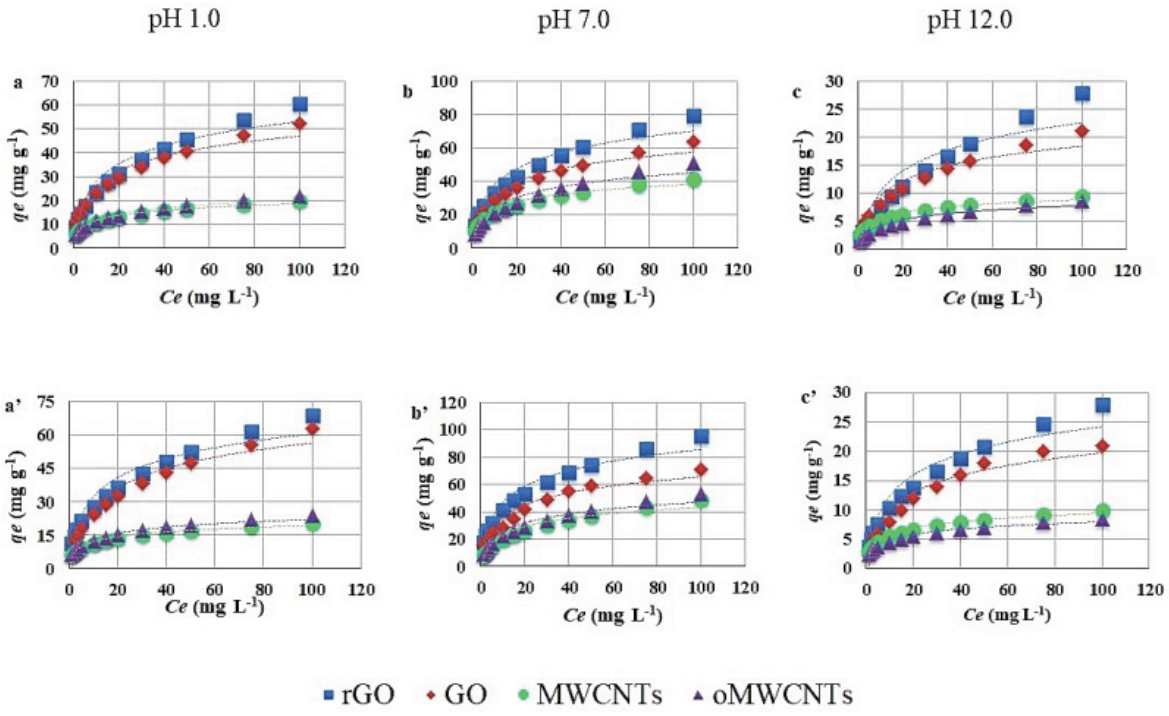


Fig. 2. Freundlich adsorption isotherm for the adsorption of OTC (a, b and c) and CIP (a', b' and c') at pH 1.0, 7.0 and 12.0

- The neutral form of both OTC and CIP, occurring at pH 7.0, presented the strongest adsorption affinity and high contributions to the overall adsorption of these antibiotics.
- The adsorption mechanism is connected with electrostatic interaction, π-π EDA interaction, and hydrophobic interaction for both, OTC and CIP. Additionally, a hydrogen bond for CIP adsorption on studied nanomaterials was revealed.
- The best adsorption capacity for both antibiotics (OTC and CIP) was presented by rGO.

The results of this work can be useful to better understand the interaction between carbon nanomaterials and antibiotics in the aquatic environment and allow us to look at carbon nanomaterials as potential adsorbents to remove antibiotics from the aquatic environment. As the highest sorption efficiency was found at neutral pH, carbon nanomaterials can be used, for example, to remove antibiotics from wastewater whose pH ~ 7.0. However, future research studies should focus on the possibility of immobilizing nanomaterials so that they do not enter the environment and research on more complex environmental matrices containing other organic, inorganic compounds should be conducted

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