Removal of Nitroimidazoles from Aqueous Solutions by Adsorption on Single-Walled Carbon Nanotubes (SWCNT) and Multi-Walled Carbon Nanotubes (MWCNT)

Carrales-Alvarado D.H.[1], Rodríguez-Ramos I.[2], And Leyva-Ramos R.[1]∗

[1] Centro de Investigación y Estudios de Posgrado, Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, Av. Dr. M. Nava No.6, San Luis Potosí, SLP 78210, México.

[2] Instituto de Catálisis y Petroleoquímica, CSIC, C/Marie Curie 2, L10, 28049 Madrid, Spain.

Corresponding author:

*e-mail: rlr@uaslp.mx

Abstract. This work was aimed at investigating the adsorption of metronidazole (MNZ) and dimetridazole, (DTZ) from water onto single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT). The MWCNTs were functionalized by attaching carboxylic groups (MWCNT-COOH) and by treating with an HNO_3 solution (MWCNT-HNO_3). The adsorption equilibrium data were obtained in a batch adsorber and were interpreted by the Freundlich, Langmuir and Radke-Prausnitz (R-P) isotherms. The R-P isotherm best fitted the experimental data since its percentage deviation was always the lowest. At T=25ºC and pH=7, the adsorption capacity of the CNTs decreased in the following order: SWCNT > MWCNT > MWCNT-HNO_3 > MWNT-COOH, and the maximum adsorption capacities of SWCNT towards MNZ and DTZ were 101 and 84 mg/g, respectively. The SWCNT had the highest adsorption capacity because SWCNT presented the largest surface area and was the only CNT with a basic surface. The basic groups activated the π-π dispersive interactions and favored the adsorption of the nitroimidazoles. The adsorption capacity of SWCNT towards MNZ increased considerably by raising the solution pH from 2 to 11, and this trend was not due to electrostatic interactions. The adsorption of both nitroimidazoles on the CNTs was predominantly due to π-π dispersive interactions.

Keywords: adsorption, nitroimidazoles, carbon nanotubes

1. Introduction

In the last years, the increase of emergent pollutants such as pharmaceutical products, cosmetics and products for domestic use, requires the development of novel adsorbents for the removal of these contaminants from water solutions. In the literature, several works have been reported about the adsorption of pharmaceutical compounds on carbon nanotubes (CNTs) with different morphology. Ncibi and Sillanpää (2015) studied the adsorption of oxytetracycline and ciprofloxacin on multi-walled carbon nanotubes (MWCNT, S_{BET} = 158 m²/g), single-walled carbon nanotubes (SWCNT, S_{BET} = 577 m²/g) and double-walled carbon nanotubes (DWCNT, S_{BET} = 382 m²/g). The SWCNT presented high adsorption capacities of 554 and 724 mg/g for the oxytetracycline and ciprofloxacin, respectively. The capacities for adsorbing both antibiotics decreased in the following order: SWCNT > DWCNT > MWCNT. Likewise, the surface areas and pore volumes of these CNTs diminished in the same order, demonstrating that the textural properties played a major role in the adsorption of antibiotics.

The surface of CNTs has been chemically modified to generate vacancy defects and incorporate functional groups to enhance the adsorption capacity and affinity of CNTs for certain compounds. The adsorption of pharmaceutical compounds on CNTs with different morphologies, textural properties and chemical nature of the surface has been reported in the literature; however, the role of the surface chemical nature of CNTs on the adsorption mechanism of the antibiotics has not been analyzed in detail.

The primary objective of this work was to study the adsorption of nitroimidazole antibiotics on single- and multi-walled carbon nanotubes having different chemical nature of their surface and textural properties.

2. Materials and Experimental Methods

2.1 Carbon Nanotubes

The CNTs used in this work were single-walled (SWCNT), multi-walled (MWCNT), carboxylated multi-walled (MWCNT-COOH) and nitrogen doped CNT (N-CNT). The SWCNT, MWCNT and MWCNT-COOH were supplied by Nanostructures & Amorphous Materials, Inc., and SUN Nanotech Co. Ltd, while the N-CNT was synthesized by a catalytic chemical vapor decomposition method reported by Faba *et al.* (2013).

The characterization of CNTs was carried out by different analytical techniques. The textural properties were evaluated by N_2 physisorption (N_2 at 77 K) using an Autosorb, Micromeritics, model ASAP 2020. The BET equation was applied to determine the surface area (S_{BET}). The total surface acidity and basicity and the pH of the point of zero charge (pH_{PZC}) were determined using previously described methods (Boehm, 1966).

2.2 Nitroimidazoles and their Quantification in Aqueous Solution

The nitroimidazole antibiotics used throughout this study were metronidazole (MNZ) and dimetridazole (DTZ), and were supplied by Sigma-Aldrich. The chemical properties of these compounds and the molecular chemical structures of the MNZ and DTZ are shown in Table 1. The molecular structures were optimized by using density functional theory (DFT). The nitroimidazole concentrations in aqueous solution were determined by UV-visible spectrophotometry, and the absorbance of the MNZ or DTZ sample was determined using a double-beam spectrophotometer, Shimadzu, UV 1800, at a wavelength of 320 nm.

2.3 Method for Obtaining the Adsorption Equilibrium Data

The experimental adsorption equilibrium data of MNZ or DTZ on the CNTs were obtained in a batch adsorber. Briefly, aqueous solutions with a known initial concentration of MNZ or DTZ ranging from 50 to 1000 mg L^{-1}, were prepared in 50 mL volumetric flasks. The batch adsorber consisted of a 50 mL centrifuge vial to which a given mass of the adsorbent and 40 mL of MNZ or DTZ solution were added. The batch adsorber was then partially immersed in a thermostatic water bath and was mechanically shaken for 15 minutes twice daily. During the adsorption experiment, the solution pH was measured periodically and was adjusted by adding few drops of 0.1 M HCl y NaOH solutions. Once the adsorption experiments reached equilibrium, the final concentration of MNZ or DTZ was quantified as described above.

The uptake of MNZ or DTZ adsorbed was calculated using the following equation:

$$q = \frac{V \, (C_{A0} - C_{Ae})}{m} \qquad (1)$$

where C_{A0} is the initial concentration of MNZ or DTZ in the solution, mg L^{-1}; C_{Ae} is the concentration of MNZ or DTZ at equilibrium, mg L^{-1}; m is the mass of adsorbent, g; q is the mass of MNZ or DTZ adsorbed, mg g^{-1}; and V is the volume of the adsorber solution, L.

3. Results and Discussion

3.1 Textural Properties of CNTs

The textural properties of the CNTs are given in Table 2. The surface areas of all the CNTs ranged from 115 to 404 m^2/g. Furthermore, the surface area of SWCNT was 2.8 and 3.5 times greater than those of MWCNT and MWCNT-COOH, respectively. The surface areas of the MWCNT and MWCNT-COOH samples were smaller because the N_2 molecules cannot access to the interlaminar spacing of the multiple tubes. The adsorption-desorption isotherms of N_2 for the N-CNT and SWCNT presented a behavior very similar to the type IIb isotherm, which is characteristic of micro and mesoporous materials. Likewise, the type IIa isotherm was observed for the adsorption-desorption of N_2 on the MWCNT and MWCNT-COOH, revealing that these CNTs were micro and macroporous materials.

3.2 Morphological Analysis of CNTs

The HRTEM images of the CNTs are depicted in Figures 1a-d. As seen in Figures 1a-b, the MWCNT and MWCNT-COOH are homogeneous, and their internal diameters were 7.9 and 9 nm, correspondingly. Both MWCNTs present obstructions in the tubes and openings through the walls.

Figure 1c illustrates the image of SWCNT showing significant morphological differences concerning MWCNTs. The N-CNTs can be observed in Figure 1d, and they exhibit a bamboo type morphology (Faba *et al.*, 2013), and its internal diameter was up to 125 nm.

3.3 Physicochemical Properties of CNTs

The concentrations of total acidic sites (carboxylic, lactonic and phenolic), total basic sites, the points of zero charge (pH_{PZC}) and the isoelectric points (pH_{IEP}) of all carbon materials are given in Table 2. It is important to highlight that SWCNT has a basic character because its pH_{PZC} was 8.99. This result was corroborated by the fact that its concentration of total acidic sites was greater than that of basic sites in SWCNT. Although, the surface nature of MWCNT, MWCNT-COOH and N-CNT was acidic since their concentrations of acidic sites were bigger than those for the basic sites, and besides, their pH_{PZC} were 3.91 5.19 and 4.10, respectively. In the case of MWCNT-COOH and SWCNT, the pH_{PZC} was higher than pH_{IEP}, revealing that the majority of acidic groups of MWCNT-COOH and SWCNT are located on the external surface. The opposite behavior was observed for MWCNT and N-CNT, indicating that the acidic sites are mainly at their internal surface.

The sample N-CNT was analyzed by XPS, and the nitrogen content was 5.03 %. Additionally, the nitrogen groups in N-CNT were pyridinic (16.33 %), pyrrolic (68.48 %) and quaternary (15.18 %). Similar results have been reported in other works regarding the synthesis of CNTs using Ni and Co as catalysts (Faba *et al.*, 2013).
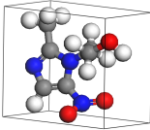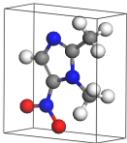
3.4 Single Adsorption Isotherms of Nitroimidazoles on Different CNTs

The experimental single adsorption equilibrium data of MNZ and DTZ on MWCNT, MWCNT-COOH, N-CNT and SWCNT at T = 25 °C and pH = 7 are depicted in Figures 2a-b, respectively. The adsorption equilibrium data were interpreted by the Freundlich, Langmuir and Radke-Prausnitz (R-P) isotherms, and the latter best fitted the adsorption equilibrium data. As seen in both figures, the adsorption capacities of CNTs towards the nitroimidazoles were highly dependent on the type and the physiochemical characteristics of CNTs. The adsorption capacity of CNTs towards both antibiotics diminished as follows: SWCNT > MWCNT > N-CNT ≈ MWCNT-COOH.

The adsorption capacities of CNTs were compared by calculating the uptake of antibiotic adsorbed at a nitroimidazole concentration at equilibrium of 4.0 mmol/L, and this capacity was denoted as Q_4. The values of Q_4 for MNZ on SWCNT, MWCNT, N-CNT and MWCNT-COOH were 0.59, 0.29, 0.25 and 0.22 mmol/g, and for DTZ were 0.55, 0.28, 0.24 and 0.21 mmol/g, respectively. These results showed that the capacity of any CNTs for adsorbing both antibiotics are very similar. For example,

the Q_4 values of SWCNT for MNZ and DTZ were 0.59 and 0.55 mmol/g, correspondingly.

Table 1. Chemical structures and physicochemical properties of MNZ and DTZ.

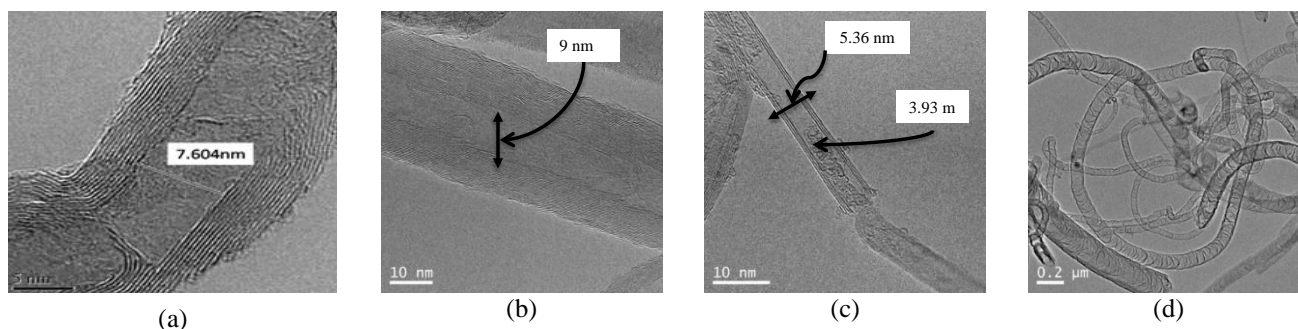| Nitroimidazole	Chemical structure	Dimensions (Å)	Molecular weight (g/mol)	Solubility in water (mol/L)	pK_{a1} [a]	pK_{a2} [b]
MNZ $C_6H_9N_3O_3$		X= 6.679 Y= 6.267 Z= 2.627	171.15	0.041	2.58	14.44
DTZ $C_5H_7N_3O_2$		X =5.364 Y=5.936 Z=1.772	141.13	0.062	2.81	-

[a, b] Dissociation constants.

Figure 1. HRTEM images of (a) MWCNT, (b) MWCNT-COOH, (c) SWCNT and (d) N-CNT.

Table 2. Textural properties and surface chemistry of the carbon nanotubes.

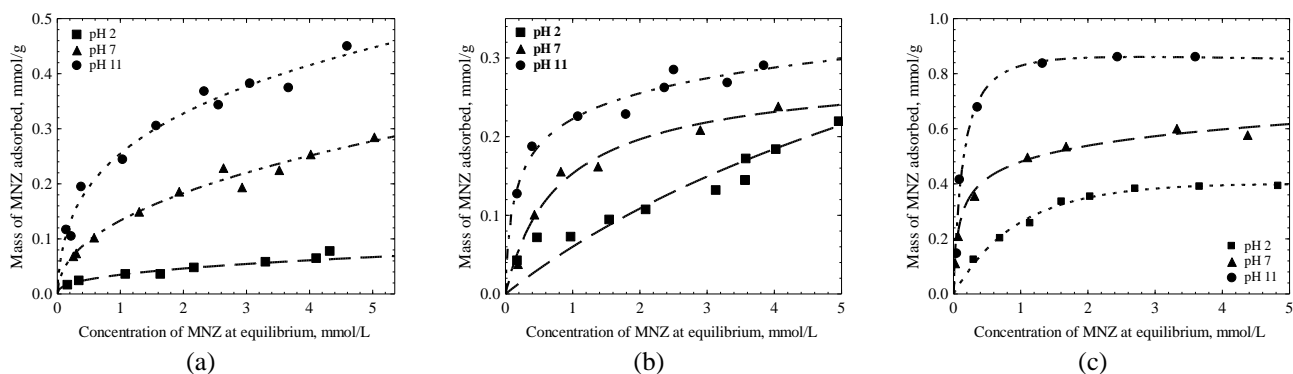| Sample	S_{BET} (m²/g)	V_p (cm³/g)	d_p (nm)	Active Sites (meq/g)					pH_{PIE}	pH_{PZC}
				Carboxylic	Lactonic	Phenolic	Total Acidic	Total Basic		
MWCNT	144	0.78	21.7	0.175	0.044	0.17	0.39	ND	8.52	3.91
MWNT-COOH	115	0.48	16.95	0.09	0.02	0.32	0.43	0.05	3.04	5.19
N-CNT	371	0.63	6.80	0.23	0.04	0.30	0.57	0.097	7.88	4.80
SWCNT	404	0.62	6.17	0.005	0.007	0.015	0.03	0.167	3.72	8.99

ND= No detected.

Figure 4. Effect of solution pH on the adsorption isotherms of MNZ on CNTs (a) N-CNT, (b) MWCNT-COOH and (c) SWCNT at T = 25 °C. The lines represent the R-P isotherm.

Carrales-Alvarado *et al*. (2014) investigated the adsorption mechanism of MNZ onto granular activated carbon (919 m^2/g), activated carbon cloth (1441 m^2/g), mesoporous activated carbon (917 m^2/g), MWCNTs (144 m^2/g) and MWCNT-HNO$_3$ modified with nitric acid solution (31 m^2/g), and reported that the adsorption capacity was dependent upon the surface area and the concentrations of carboxylic and phenolic sites (C$_{CPS}$) of the carbon materials. Additionally, it was demonstrated that the adsorption capacity increased linearly by reducing the concentration of carboxylic and phenolic sites per unit of surface area, and that π-π dispersive interactions is the main adsorption mechanism of MNZ on the carbon materials. Hence, the small adsorption capacity of MWCNT-COOH towards MNZ can be attributed to its low surface area and high concentration of carboxylic sites, the latter act as deactivating groups of π electrons of the aromatic rings of the MWCNT-COOH surface, diminishing π-π interactions. On the other hand, the SWCNT presented the greatest adsorption capacity due to its large surface area and low concentration of carboxylic sites. Furthermore, the SWCNT had the highest concentration of basic sites, which are characterized by a high concentration of electrons in their basal planes, enhancing the π-π dispersive interactions.
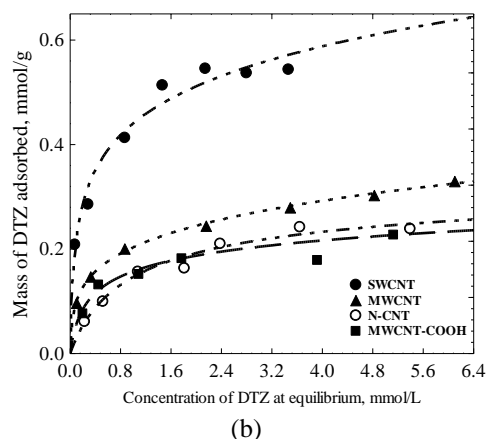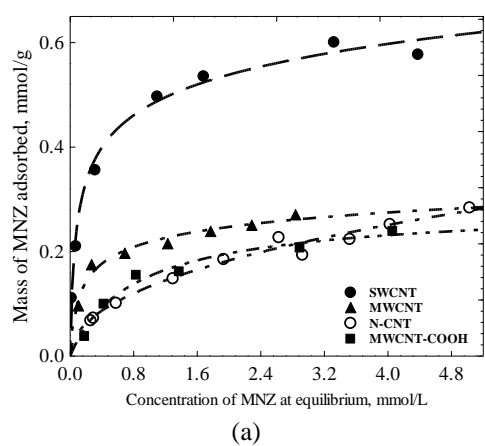

(a)

(b)

Figure 2. Single adsorption isotherms of (a) MNZ and (b) DTZ on the different CNTs at T=25 °C and pH=7. The lines represent the R-P isotherm.

Except for N-CNT, the values of Q$_4$ and S$_{BET}$ for the different CNTs decreased in the following order: SWCNT > MWCNT > MWCNT-COOH. This trend revealed that the adsorption of nitroimidazoles on CNTs is mainly due to the π-π dispersive interactions because this type of interactions are dependent upon surface area. The S$_{BET}$ of N-CNT is slightly less than that of SWCNT, and N-CNT contained phenolic and pyridinic groups, which favor the π-π dispersive interactions due to their activating character. From the above, it was expected that the adsorption capacity of N-CNT towards nitroimidazoles was very similar to that of SWCNT. However, the values of Q$_4$ showed that adsorption capacity of N-CNT was 2.12 times smaller than that of SWCNT. This result can be explained considering that the molecules of MNZ and DTZ cannot access to all surface area of N-CNT due to possibly restriction effects since the MNZ or DTZ molecules cannot enter to the narrow micropores.

In Figure 3 is graphed the adsorption capacity Q$_4$ against C$_{CPS}$ to find out the influence of the surface groups on the adsorption capacity of all CNTs towards MNZ. The data of Q$_4$ reported by Carrales-Alvarado *et al*. (2014) for the adsorption of MNZ on various carbon materials were also plotted. It is evident that the adsorption capacities of the CNTs exhibited a linear behavior with respect to C$_{CPS}$; however, the slope of the straight line for Q$_4$ is less pronounced than that of the carbon materials. Thus, the adsorption capacity of the CNTs was slightly affected by C$_{CPS}$.
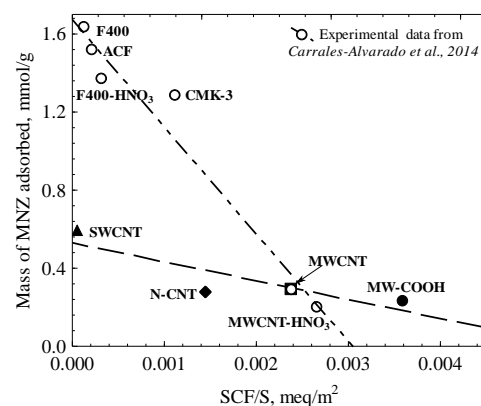

Figure 3. Effect of the C$_{CPS}$ on the adsorption capacity of the CNTs towards MNZ.

The surface area occupied by the MNZ adsorbed on the CNTs, S$_{MNZ}$, can be estimated as follows:

$$S_{MNZ} = \frac{q_m \, N_A A_p}{M_{MNZ}} \qquad (2)$$

where A$_p$ is the projected area of one molecule of MNZ, evaluated from the dimensions of MNZ listed in Table 1, 4.186×10^{-19} m^2/molecule; M$_{MNZ}$ is the molecular weight of MNZ, g/mol; N$_A$ is the Avogadro's number, 6.022×10^{23} molecules/mol; and q$_m$ is the Langmuir isotherm parameter representing maximum capacity of the CNTs for adsorbing MNZ, mol/g. Furthermore, the percentage of surface area occupied by the MNZ adsorbed (%S$_{Occup}$) was calculated from the following equation:

$$\%S_{Occup} = \frac{S_{MNZ}}{S_{BET}} \times 100\,\%\qquad\qquad (3)$$

Table 3. Percentage of surface area occupied by the MNZ adsorbed on CNTs at pH = 7 and T = 25 °C.

CNTs	q_m (mmol/g)	S_{MNZ} (m²/g)	%S_{occup}
SWCNT	0.596	150	37
N-CNT	0.280	71	19
MWCNT-COOH	0.234	59	51
MWCNT	0.291	73	51

The values of %S_{Occup} for each CNTs are given in Table 3, and it can be noticed that greatest values of %S_{Occup} were for MWCNT and MWCNT-COOH, whereas the lowest values of %S_{Occup} was for N-CNT. This indicated that the MNZ molecule could not access to micropores, so the adsorption capacity of N-CNT was reduced because of molecular size restriction

3.5 *Effect of the Solution pH on the Adsorption Capacity towards MNZ*

The effect of the solution pH on the adsorption of nitroimidazoles was only studied for MNZ because the capacity for adsorbing MNZ was very similar to that for DTZ since both nitroimidazoles have very similar molecular sizes and physicochemical properties. The adsorption isotherms of MNZ on N-CNT, MWCNT-COOH and SWCNT at T = 25 ºC and pH of 2, 7 and 11, are depicted in Figures 4a-c, respectively. As seen in these figures, the adsorption capacity of SWCNT, MWCNT-COOH and N-CNT are highly influenced by the solution pH, and the adsorption capacities increased considerably by raising the solution pH from 2 to 11. At pH = 2, the predominant species of MNZ was the cationic or protonated molecule MNZ-H⁺ so that the MNZ-H⁺ was repelled from the CNTs surface because the surfaces of SWCNT, MWCNT-COOH and N-CNT were positively charged (See values of pH_{PZC} in Table 2). However, at pH = 11, the electrostatic interactions did not affect the adsorption capacity because the preponderant species of MNZ was the neutral or undissociated molecule and the surfaces of SWCNT, MWCNT-COOH and N-CNT were negatively charged.

The adsorption capacities of MWCNT-COOH, SWCNT and N-CNT towards MNZ were enhanced 1.6, 2.1 and 7 times when the pH was raised from 2 to 11. Therefore, the effect of the pH on the adsorption capacity was influenced by the chemical characteristics of the CNTs.

The increase in the adsorption capacity may be due to the activation of the phenolic sites and hydrophobic interactions. It is very well documented that the solubility of the organic compounds reduces by increasing the solution pH so that hydrophobicity of the organic compound increases favoring the accumulation of the pharmaceutical compound on the surface of the CTNs.

4. Conclusions

The single adsorption capacity of CNTs towards MNZ and DTZ diminished in the following order: SWCNT > MWCNT > N-CNT ≈ MWCNT-COOH. Furthermore, the adsorption capacity decreased linearly with respect to the concentration of carboxylic and phenolic sites per unit surface area.

The adsorption of both antibiotics was mainly attributed to π-π dispersive interactions. Electrostatic and hydrophobic interactions affected sligthly the adsorption capacity. At pH = 2, the electrostatic repulsion reduced the adsorption of both antibiotics on all the CNTs, and the electrostatic interactions did not influence the adsorption capacity at pH = 11. The hydrophobic interactions enhance the adsorption capacity at pH > 7 due to a decrease in solubility.

Acknowledgments

References

Carrales-Alvarado D.H., Ocampo-Pérez R., Leyva-Ramos R., Rivera-Utrilla J. (2014). Removal of the antibiotic metronidazole by adsorption on various carbon materials from aqueous phase *J. Colloid Interf. Sci.* **436**, 276–285.

Faba L., Criado Y.A., Gallegos-Suárez E., Pérez-Cadenas M., Díaz E., Rodríguez-Ramos I., Guerrero-Ruiz A., Ordóñez S. (2013). *Appl. Catal. A: Gen.* **458**, 155–161.

Ncibi M.C., Sillanpää M. (2015). Optimized removal of antibiotic drugs from aqueous solutions using single, double and multi-walled carbon nanotubes. *J. Hazard Mater.* **298**, 102-110.