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The use of modified multi-walled carbon nanotubes for the removal of selected pharmaceuticals from the aqueous environment

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ABSTRACT

Adsorptive removal of two popular painkillers such as ibuprofen and paracetamol from aqueous solutions on carbon nanotubes (CNT) as well as carbon nanotubes functionalized with hydroxyl (CNT-OH) and carboxyl (CNT-COOH) groups was investigated. The effects of solution pH and ionic strength were studied. Adsorption kinetics and equilibrium study were also carried out. It was observed that the adsorption of both the drugs on all three adsorbents was strongly pH-dependent while the ionic strength of the solution did not affect the adsorption efficiency. Adsorption kinetic data were analyzed using pseudo-first-order and pseudo-second-order equations and the results showed that adsorption kinetics followed the pseudo-second-order model. The Langmuir, Freundlich and Sips models were applied to describe the adsorption isotherm of the ibuprofen and paracetamol on the CNTs. The Langmuir isotherm provided the best correlation for the adsorption of drugs on all of the adsorbents, and the adsorption efficiency of ibuprofen and paracetamol increased in the order: CNT-OH < CNT < CNT-COOH. The adsorption capacities for CNT, CNT-OH, and CNT-COOH were found to be 50.76, 43.67 and 61.35 mg/g for ibuprofen, and 29.85, 17.95 and 38.76 mg/g for paracetamol, respectively.

Keywords: Ibuprofen; Paracetamol; Adsorption; Carbon nanotubes

1. Introduction

The development of medicine entails an increase in the production and consumption of drugs. The pharmaceutical market is one of the most dynamically developing industries in Poland, Europe, and the world. It should also be emphasized that about 34% of the pharmaceutical market are OTC (over-the-counter) drugs, that is, over-the-counter drugs, including both pharmaceutical products and personal care products (PPCP – Pharmaceutical and Personal Care Products), of which 26% are painkillers [1]. Among this group of non-steroidal anti-inflammatory drugs (NSAIDs), which include ibuprofen, ketoprofen, naproxen, diclofenac, and paracetamol are among the most commonly prescribed and taken painkillers and anti-inflammatory drugs. Already in the 1990s, it was estimated that about 30 million people worldwide used these drugs every day [2].

The effect of the growing consumption of drugs is their presence in the environment. Drug residues and metabolites of their biotransformation (sometimes more toxic than the original form) end up in raw and treated wastewater, as well as in surface and drinking waters [3–5]. Although most drugs do not cause significant acute toxicity to aquatic organisms, they are chronic and therefore seriously hazardous to the environment. The lack of legal regulations

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related to the determination of environmentally safe values of pharmaceutical substances in wastewater discharged into municipal sewage systems or water receivers causes an uncontrolled increase in the load of these pollutants in the environment. In the literature, pharmaceuticals present in waters are included in the group of so-called "Emerging Contaminants" defined as newly emerging contaminants or contaminants of emerging concern – contaminants that cause concern about environmental quality (changes) [6]. For this reason, it is necessary both to monitor the presence of these substances and their metabolites in the environment and their effects on living organisms and to remove them from water and wastewater.

Among the NSAIDs, the third most popular, most prescribed, and most sold OTC drug in the world is ibuprofen (α-methyl-4-(isobutyl)phenylacetic acid. This drug is excreted from the body in the form of metabolites such as carboxyibuprofen, hydroxyibuprofen, and carboxy hydratropic acid, and about 15% unchanged. Paracetamol (acetaminophen, 4-acetamidophenol) is an equally popular NSAID. In the USA, where paracetamol is one of the 200 most commonly used pharmaceuticals, its consumption in 2001–2005 reached about 29 billion doses [7,8]. The source of the presence of paracetamol and its decomposition product, 4-aminophenol, is additionally the production of dyes and photographic materials [9]. Numerous studies [4,10–12] have shown that the content of these drugs in sewage sludge, soils, and surface waters ranges from ng/L to μg/L, which is a significant threat to living organisms. The largest amounts of pharmaceuticals, including NSAIDs, are found in municipal wastewater from households, healthcare facilities, and industrial waste from pharmaceutical plants. Although concentrations of pharmaceuticals in domestic wastewater are traceable, there is a problem with their removal, as conventional wastewater treatment plants using physical and biological wastewater treatment methods are not designed to remove micropollutants. A study by Tauxe-Wuersch et al. [13] on the disposal of drugs such as mefenamic acid, ibuprofen, ketoprofen, diclofenac, and clofibric acid at three plants demonstrated that none of the drugs were completely removed from wastewater. These results are confirmed by studies of treated wastewater and sewage sludge after the biological process in wastewater treatment plants carried out by Samaras et al. [14] and Pereira et al. [15]. Lipophilic drugs are better absorbed on sediment, while acidic drugs such as NSAIDs remain in the aqueous phase.

For this reason, the effective removal of pharmaceuticals from wastewater as well as water requires the expansion of existing solutions to involve physical and chemical methods, including membrane bioreactors [16], bioreactors with an overhead bed [17], biofiltration [18], as well as oxidation processes, including methods of advanced oxidation processes (AOP) [19], electrocoagulation [20] and adsorption.

Adsorption as a method of removing pharmaceuticals from water and sewage has been the subject of numerous studies, which results both from the efficiency of this process and the wide range of available sorbents, such as activated carbons, zeolites, and clay materials [21]. Currently, among the available sorbents used to remove pharmaceuticals from the water phase, more and more attention is paid to nanomaterials [6,22], including nanocarbon sorbents [23,24]. Undoubtedly, the most widely used sorbent for the removal of inorganic and organic pollutants, including drugs from the water phase, is activated carbon, which translates into its use in water and wastewater treatment technologies [25]. Despite its many advantages, its application has its limitations since it is a non-selective sorbent, and its production, especially concerning formed carbons, is not neutral to the environment. For this reason, there are more and more studies indicating the possibility of using other carbon materials as pharmaceutical sorbents, such as graphene [26,27] and carbon nanotubes [28–33] used directly or as components of composites. Carbon nanotubes are a material made by folding a single-layer graphite plane. This material is characterized by excellent mechanical and electrical properties, elasticity, tensile and flexural strength, and the fact that it does not dissolve in water or organic solvents. In addition, they have a large specific surface area, uniform pore distribution, and a high surface area-to-weight ratio. Both the nature of the porous structure and the size of the specific surface area and the possibility of its modification make nanotubes one of the most promising functional nanomaterials. By introducing functional groups (carboxyl, hydroxyl, or amine), you can significantly change the hydrophobic–hydrophilic properties and surface charge, which allows you to obtain selective sorbents dedicated to the binding of a specific group of organic and inorganic compounds. The use of carbon nanotubes can be a potential alternative to conventional sorbents due to comparable and often higher sorption capacity, and the possibility of surface modification, which in turn translates into the possibility of obtaining selective sorbents. In literature, various functionalized carbon nanotubes were successfully used to remove various pollutants from water [34–36]. Despite numerous studies, it is still important to clarify the influence of the surface chemistry of the nanotubes used, as well as the conditions of the sorption process and the physico-chemical properties of selected organic substances, including pharmaceuticals that are micropollutants in the aqueous environment, on the effectiveness and efficiency of the sorption process.

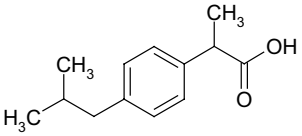
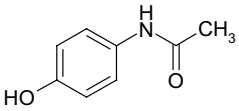
Therefore, the present study investigated the adsorptive removal efficiency of two popular painkillers, such as ibuprofen and paracetamol, identified as contaminants in the aqueous environment, on commercial carbon nanotubes (CNTs) and carbon nanotubes functionalized with hydroxyl groups (CNT-OH) and carboxyl groups (CNT-COOH). The effects of solution pH and ionic strength were investigated. Adsorption kinetics and equilibria were also investigated.

2. Experimental

2.1. Materials and methods

The analytical grade ibuprofen (99% purity) was received from Sigma-Aldrich (USA) while paracetamol (98% purity) was purchased from Acros Organics (Belgium). The structural formulas and most important properties of the two compounds are shown in Table 1. All other high-purity chemicals and reagents were purchased from Chempur (Poland).

Table 1
Physico-chemical properties of the drugs

	Ibuprofen	Paracetamol
CAS No.	15687-27-1	103-90-2
Empirical formula	$C_{13}H_{18}O_2$	$C_8H_9NO_2$
Structure		
Molecular weight (g/mol)	206.28	151.165
pKa	4.9	9.4

Three kinds of multi-walled carbon nanotubes with different surface chemistry (non-modified, OH functionalized and COOH functionalized) were obtained from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences (Chengdu, China).

2.2. Adsorbents characterization

The porosity of the multi-walled carbon nanotubes was characterized using low-temperature nitrogen adsorption–desorption isotherms (ASAP 2020, Micromeritics, Norcross, GA, USA). Determination of the surface-bonded oxygen content was carried out using a scanning electron microscope (Philips XL30/LaB6, Amsterdam, Netherlands) coupled with an energy-dispersive X-ray spectrometer (DX4i/EDAX device).

To determine the point of zero charge of CNTs, sodium chloride solutions (0.02 L) of 0.01 mol/L with different pH values ($pH_{initial}$) were prepared, into which 0.02 g of each adsorbent was introduced. The samples were shaken for 24 h and then filtered through filter paper. Their pH was measured again (pH_{final}). The final pH was plotted against the initial pH and the intersection point of the obtained curve was taken as the point of zero charge (pH_{PZC}).

2.3. Adsorption studies

Adsorption experiments were performed in glass Erlenmeyer flasks, into which 0.02 L of ibuprofen or paracetamol solution of appropriate concentration and 0.01 g of CNTs were introduced. Such prepared mixtures were shaken at 200 rpm at 23°C. After 8 h (or after a well-defined time in kinetic studies), the mixtures were filtered through filter paper and the obtained transparent filtrate was measured, thus establishing the equilibrium concentration (C_e). The amount of ibuprofen or paracetamol that was adsorbed on CNTs surface under equilibrium conditions (q_e) or after time t (q_t) was calculated based on Eqs. (1) and (2):

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

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where q_e – the amount of drug adsorbed at equilibrium (mg/g), q_t – the amount of drug adsorbed after time t (mg/g), C_0 – initial concentration of ibuprofen or paracetamol in solution (mg/L), C_e – equilibrium concentration (mg/L), V – the volume of the solution (L), m – the mass of the CNTs (g).

Experiments on the effects of pH and ionic strength on the adsorption of ibuprofen and paracetamol on CNTs were carried out in the same way. Solutions of adsorbates were prepared with different pHs ranging from 2.3 to 11.0 and with different concentrations of sodium sulfate (from 0 to 0.2 mol/L). The initial concentrations of the adsorbates were 25 mg/L.

UV-Vis spectrophotometry (Carry 3E model, Varian, USA) was used to quantify ibuprofen and paracetamol in solutions. The obtained calibration curves for ibuprofen and paracetamol recorded at wavelengths of 222 and 244 nm, respectively, were straight-line in the tested concentration range (2–30 mg/L). The calibration curves were described by the following equations: $y = 0.039x + 0.029$ ($R^2 = 0.997$) for ibuprofen and $y = 0.061x + 0.021$ ($R^2 = 0.999$) for paracetamol.

3. Results and discussion

3.1. Characterization of adsorbents

The nitrogen adsorption–desorption isotherms on the CNTs determined at 77 K are presented in Fig. 1. The specific surface area (S_{BET}) and constant C were calculated by using the Brunauer–Emmett–Teller (BET) equation, and the total pore volume (V_t) was obtained from the amount of nitrogen adsorbed at $P/P_0 = 0.98$. Additionally, the specific surface area for a single point was determined. The obtained values of the above parameters characterizing the porosity of the CNT, CNT-OH, and CNT-COOH are listed in Table 2. The chemical composition of all three CNTs samples' surfaces was presented in Table 3.

The obtained results indicate that the differences in the specific surface area are relatively small compared to the differences in the oxygen content. The S_{BET} value for CNT-OH and CNT-COOH samples was lower than for CNT by 12% and 15%, respectively. On the other hand, the content of oxygen bound to their surface for CNT-OH and CNT-COOH samples is respectively 3 and 3.5 times higher than for CNT. The differences in the surface chemistry of the multi-walled carbon nanotubes used were investigated using the

Fourier-transform infrared spectroscopy method and discussed by Kan et al. [37].

3.2. Adsorption kinetics

Kinetic studies were conducted for initial concentrations of ibuprofen and paracetamol of 25 mg/L. The obtained results are shown in Fig. 2 as a graph of q_t dependence as a function of time. As can be seen, the adsorption of both drugs on carbon nanotubes was very fast (in the first 15 min), and then slows down and reaches equilibrium after about 30 min.

To describe the adsorption kinetics, the two most popular kinetic equations were used: the pseudo-first-order (3) and the pseudo-second-order (4), which can be expressed as follows [38]:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{4}$$

where k_1 and k_2 are the pseudo-first-order (min^{-1}) and the pseudo-second-order rate constants (g/mg·min), respectively.

The values of the correlation coefficients R^2, the rate constants (k_1 and k_2) as well as the adsorption amount q_e – experimental ($q_{e(exp)}$) and obtained from the kinetic equation ($q_{e(cal)}$), are shown in Table 4.

Significantly higher R^2 values (≥0.997), as well as a greater agreement between $q_{e(cal)}$ values and experimental

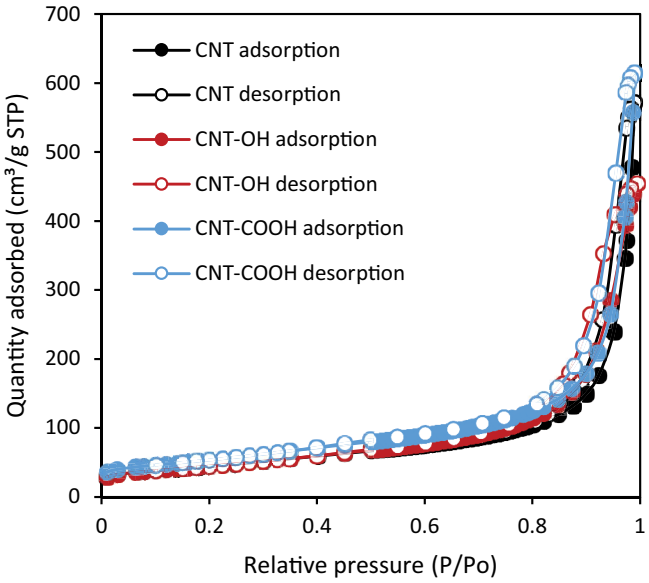


Fig. 1. Nitrogen adsorption–desorption isotherms at 77 K of multi-walled carbon nanotubes.

Table 2
Textural parameters of the multi-walled carbon nanotubes obtained from N_2 adsorption isotherms

Carbon nanotubes	S (single point) (m^2/g)	S_{BET} (m^2/g)	C	V_t (cm^3/g)
CNT	179	182	149	0.798
CNT-OH	158	160	154	0.651
CNT-COOH	154	155	168	0.618

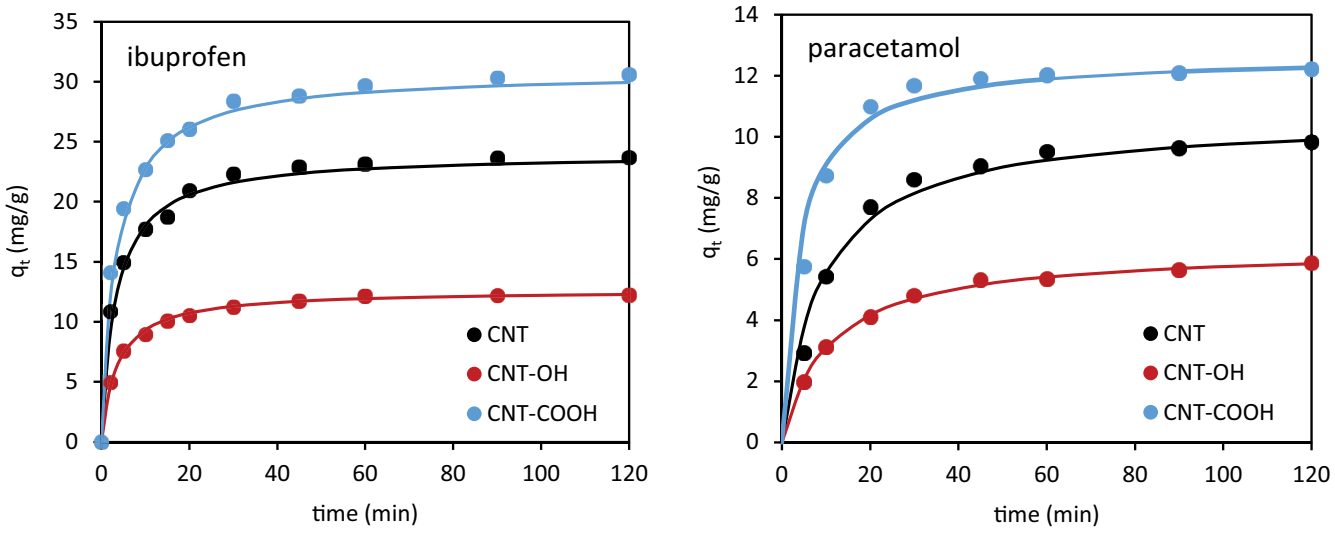


Fig. 2. Effect of contact time on the adsorption of ibuprofen and paracetamol on the multi-walled carbon nanotubes (line – fitting of pseudo-second-order kinetic model).

$q_{e(exp)}$ values, were obtained for the pseudo-second-order equation. Thus, it can be concluded that the adsorption of both drugs on CNTs followed the pseudo-second-order kinetic model. The values of adsorption rate constants k_2 obtained for ibuprofen increased in the order CNT-COOH < CNT < CNT-OH, while the adsorption rate values observed for paracetamol increased in the order CNT < CNT-COOH < CNT-OH.

The process of adsorption from solution involves several successive steps such as transport from the bulk phase to the boundary layer, diffusion in the boundary film, intraparticle diffusion, and final adsorption (localization of adsorbate molecules on the active sites of the adsorbent) [38]. The last of the adsorption stages occurs fastest, so it does not affect the adsorption kinetics. The kinetics is determined by the slowest processes and therefore film diffusion and/or intraparticle diffusion play a crucial role. To study the adsorption mechanism and to find out the rate-limiting step of ibuprofen and paracetamol adsorption on CNTs the Weber–Morris and the Boyd kinetic models were used [38].

The Weber–Morris model is given by the following equation:

$$q_t = k_i t^{0,5} + C_i \quad (5)$$

where k_i is the intraparticle diffusion rate constant (mg/g·min$^{-0.5}$), and C_i is the thickness of the boundary layer.

Table 3
Chemical composition (wt.%) of the multi-walled carbon nanotubes obtained by SEM-EDX analysis

Carbon nanotubes	C	O	N	Ni	Si	S
			wt.%			
CNT	96.8	2.6	0.3	0.2	0.1	–
CNT-OH	92.0	7.8	–	0.1	–	0.1
CNT-COOH	90.6	9.1	0.2	0.1	–	–

The intraparticle diffusion model assumes that when the plot q_t vs. $t^{0.5}$ is straight-line in the whole range and the curve passes through the origin, then adsorption is controlled only by intraparticle diffusion. In contrast,

Table 4
Kinetic modeling data for adsorption of ibuprofen and paracetamol on the multi-walled carbon nanotubes

Parameter	Adsorbent		
	CNT	CNT-OH	CNT-COOH
Ibuprofen			
$q_{e(exp)}$ (mg/g)	23.67	12.23	30.58
Pseudo-first-order			
k_1 (min^{-1})	0.0611	0.0617	0.0463
$q_{e(cal)}$ (mg/g)	12.98	6.989	15.98
R^2	0.969	0.950	0.937
Pseudo-second-order			
k_2 (g/mg·min)	0.0125	0.0221	0.0092
$q_{e(cal)}$ (mg/g)	24.39	12.64	31.40
R^2	0.998	0.999	0.999
Paracetamol			
$q_{e(exp)}$ (mg/g)	9.81	5.87	12.21
Pseudo-first-order			
k_1 (min^{-1})	0.0447	0.0352	0.0508
$q_{e(cal)}$ (mg/g)	6.69	4.05	5.43
R^2	0.939	0.944	0.902
Pseudo-second-order			
k_2 (g/mg·min)	0.0102	0.0149	0.0201
$q_{e(cal)}$ (mg/g)	10.64	6.061	12.67
R^2	0.997	0.998	0.999

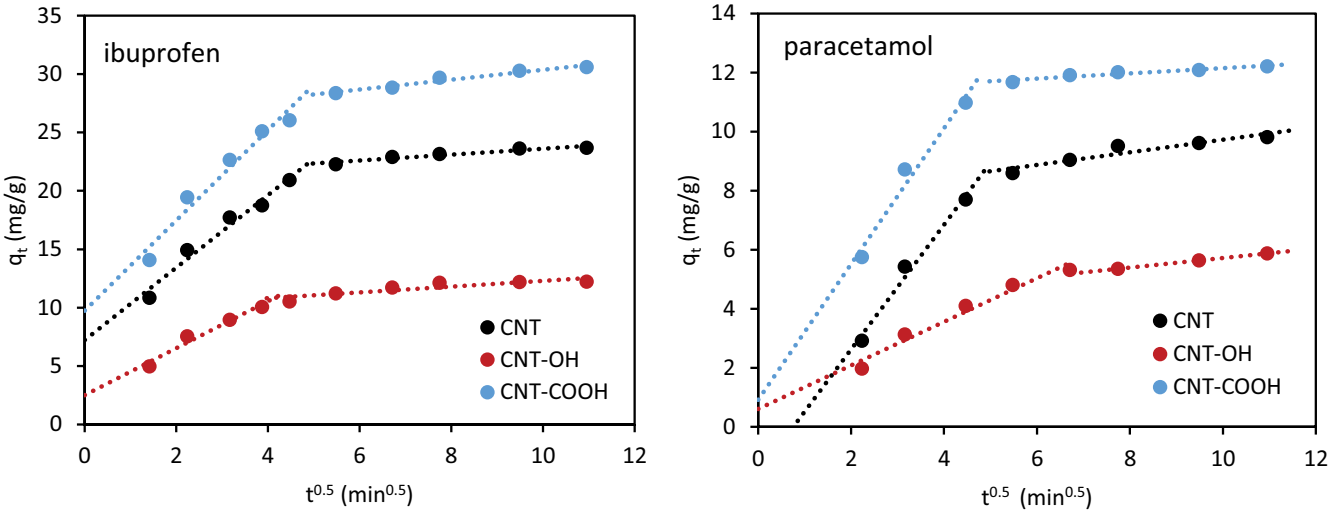


Fig. 3. Intraparticle diffusion model plots for adsorption of ibuprofen and paracetamol on the multi-walled carbon nanotubes.

when the plot $q_t = f(t^{0.5})$ is not straight-line and the curve does not pass through the origin then several processes are involved in adsorption (not just intraparticle diffusion). The model of intraparticle diffusion is shown in Fig. 3. As can be seen, none of the curves passes through the origin, moreover, in each case, the dependence of q_t on $t^{0.5}$ is not linear. All this suggests that intraparticle diffusion is not the only step limiting the adsorption rate of ibuprofen and paracetamol on CNTs.

Boyd's kinetic model was applied using Eq. (6):

$$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2}\sum_{1}^{\infty}\left(\frac{1}{n^2}\right)\exp\left(-n^2 B_T\right) \tag{6}$$

where B_T is a mathematical function of q_t/q_e.

This equation can be rearranged into the following modified forms:

$$B_T = \pi\left(1 - \sqrt{1 - \frac{\pi}{3}\frac{q_t}{q_e}}\right)^2 \tag{7}$$

$$B_T = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \tag{8}$$

Eq. (7) is used when $q_t/q_e < 0.85$ while Eq. (8) applies for $q_t/q_e > 0.85$.

The Boyd kinetic model implies that when the plot B_T vs. t is a straight line and passes through the origin, adsorption is limited by intraparticle diffusion. In contrast, when the plot $B_T = f(t)$ is linear (or non-linear) but does not pass through the origin, the rate of adsorption is controlled by film diffusion. Boyd model plots for the adsorption of ibuprofen and paracetamol onto CNTs are shown in Fig. 4. As can be seen, all curves are straight-line in the whole time range ($R^2 \geq 0.984$) and do not pass through the origin.

Based on these findings, it can be concluded that for the adsorption of both the ibuprofen and paracetamol on all the carbon nanotubes the film diffusion is a rate-determining step.

3.3. Adsorption isotherms

The adsorption isotherms of ibuprofen and paracetamol on CNTs are shown in Fig. 5. Three theoretical isotherm models including Freundlich (9), Langmuir (10), and Sips (11) [39] were used to describe the experimental data. The equations of these isotherms can be expressed as follows:

$$q_e = K_F C_e^{1/n} \tag{9}$$

$$q_e = \frac{q_{mL} b_L C_e}{1 + b_L C_e} \tag{10}$$

$$q_e = \frac{q_{mS} b_S C_e^m}{1 + b_S C_e^m} \tag{11}$$

where q_{mL} and b_L are the maximum adsorption capacity (mg/g) and the Langmuir constant (L/mg), K_F ((mg/g)(L/mg)$^{1/n}$) and n are the Freundlich constants, q_{mS} is the Sips maximum adsorption capacity (mg/g), and b_S (L/mg)^m and m are the Sips model constants.

All model parameters were evaluated by nonlinear regression using OriginPro 8.0 software and the calculated values, as well as the determination coefficients, are presented in Table 5.

In general, all three isotherm models used described the adsorption of ibuprofen and paracetamol on CNTs quite well. However, taking the highest value of the correlation coefficient R^2 as the fitting criterion, it can be concluded that the adsorption of both adsorbates was best described by the Langmuir isotherm model ($R^2 \geq 0.996$). The good correlation with the Langmuir isotherm model suggests monolayer adsorption with no interactions between the adsorbate molecules as well as the homogeneous nature of the CNTs surface.

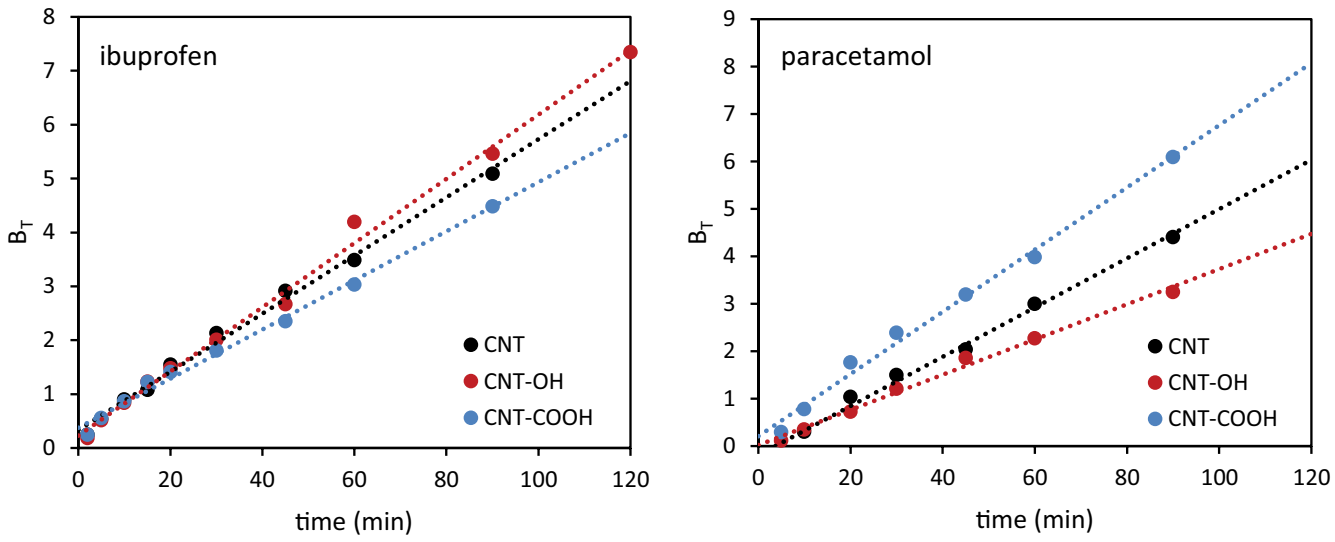


Fig. 4. Boyd kinetic model plots for adsorption of ibuprofen and paracetamol on the multi-walled carbon nanotubes.

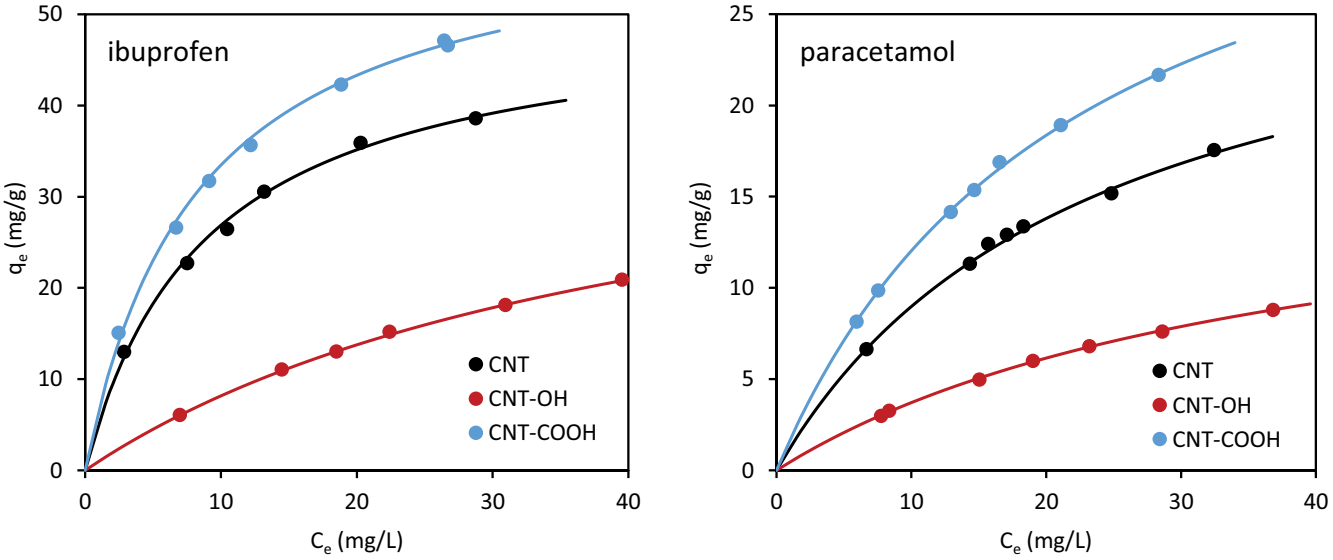


Fig. 5. Adsorption isotherms of ibuprofen and paracetamol on the multi-walled carbon nanotubes (line – fitting of Langmuir isotherm).

Comparing the adsorption of both drugs on individual carbon nanotubes, it can be seen that in each case ibuprofen adsorbed significantly better than paracetamol. A similar relationship – better adsorption of ibuprofen than paracetamol – was reported for the adsorption of these drugs on pristine multi-walled carbon nanotubes [28], CNT-COOH/MnO_2/Fe_3O_4 nanocomposite [29], commercial activated carbon [40], activated carbon prepared from oak acorn [41] as well as chitin modified with kraft lignin [42].

The better adsorption of ibuprofen, also observed in this paper, can probably be attributed to its weaker solubility in water (0.021 g/L) compared to paracetamol (14 g/L). The poorly soluble ibuprofen molecule, which is more hydrophobic, exhibits greater affinity for the hydrophobic surface of the adsorbent which promotes adsorption. However, it should be noted that this is not a general rule and the adsorption affinity of ibuprofen and paracetamol to the surface of the adsorbate depends on its individual and unique physico-chemical properties. Thus, Kollarahithlu and Balakrishnan [5] observed almost the same adsorption of ibuprofen (59 mg/g) and paracetamol (58 mg/g) on amine-functionalized superparamagnetic silica nanocomposite, while Streit et al. [43] reported better adsorption of paracetamol (145 mg/g) than ibuprofen (105 mg/g) on sludge-derived activated carbons.

Considering the adsorption isotherms (Fig. 5) and the values of the calculated isotherm parameters (Table 5), it can be seen that the adsorption capacities of CNTs concerning both drugs increase in the order CNT-OH < CNT < CNT-COOH.

It is well known that adsorption depends on both the adsorbent and the adsorbate properties. In the case of an adsorbent, its adsorption capacity is determined by its physical (surface area, porous structure, pore size distribution) and chemical (surface functional groups) properties. Thus, it is clear that modification of the adsorbent, for example, by introducing some functional groups on its surface, will affect the adsorption process [28,30,31]. In theory, surface functional groups can modify the wettability of CNTs' surfaces, and consequently make CNTs more suitable for the adsorption of relatively polar compounds [30]. In practice, however, the matter is not so obvious as evidenced by several papers that show different, often dissimilar results. This is due, among other things, to the complex mechanism of adsorption of organic compounds on CNTs. And so, adsorption can occur *via* electrostatic interaction between the adsorbate molecule and positively or negatively charged adsorbent surface, hydrophobic or π–π type interactions, and hydrogen-bonding interactions [31,32,43].

The effect of surface modification of various carbonaceous adsorbents on ibuprofen and paracetamol adsorption has been described in several papers [28,30,31,33].

Cho et al. [30] studied the adsorption of ibuprofen on single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT), and oxidized MWCNT (O-MWCNT). They found that the adsorption was dependent upon the specific surface area and surface oxygen content of CNTs, and that SWCNTs have greater adsorption capacity than pristine MWCNTs due to greater specific surface area, while oxidized MWCNTs showed lower adsorption capacity than unmodified MWCNTs due to higher oxygen content on the surface.

On the other hand, several works describe the opposite relationship – increasing the adsorption of ibuprofen or paracetamol on the surface of adsorbents containing oxygen groups.

Yanyan et al. [31] described the adsorption of paracetamol on MWCNTs modified with NaOH, HNO_3/H_2SO_4, ozone, and chitosan. Ozone-treated CNTs had the highest paracetamol adsorption efficiency and as-received (pristine) MWCNTs had the lowest. The adsorption capacities of the adsorbents used increased in the order: pristine MWCNT < NaOH-treated MWCNT < acid-treated MWCNT < chitosan-coated MWCNT < ozonated MWCNT. The authors postulate that paracetamol adsorption occurs mainly *via* electron

Table 5
Freundlich, Langmuir and Sips isotherm constants for adsorption of ibuprofen and paracetamol on the multi-walled carbon nanotubes

Parameter	Adsorbent		
	CNT	CNT-OH	CNT-COOH
Ibuprofen			
Freundlich			
K_F ((mg/g)(L/mg)$^{1/n}$)	8.237	1.576	10.53
$1/n$	0.485	0.715	0.469
R^2	0.979	0.982	0.983
Langmuir			
q_{mL} (mg/g)	50.76	43.67	61.35
b_L (L/mg)	0.1125	0.023	0.120
R^2	0.997	0.997	0.998
Sips			
q_{mS} (mg/g)	55.39	42.02	71.59
b_S (L/mg)^m	0.115	0.023	0.124
m	0.904	1.017	0.831
R^2	0.980	0.990	0.991
Paracetamol			
Freundlich			
K_F ((mg/g)(L/mg)$^{1/n}$)	2.169	0.733	2.718
$1/n$	0.615	0.699	0.636
R^2	0.981	0.952	0.991
Langmuir			
q_{mL} (mg/g)	29.85	17.98	38.76
b_L (L/mg)	0.043	0.026	0.045
R^2	0.996	0.997	0.998
Sips			
q_{mS} (mg/g)	27.69	18.11	36.77
b_S (L/mg)^m	0.042	0.026	0.045
m	1.059	0.997	1.035
R^2	0.988	0.989	0.990

donor-acceptor complex formation due to π–π dispersive forces between the surface carbonyl group and the aromatic ring of the adsorbate molecule.

Removal of ibuprofen and paracetamol *via* dynamic filtration onto multi-walled carbon nanotubes with selected properties, including pristine MWCNT, hydroxylated MWCNT, thin-walled MWCNT, and aminated MWCNT, was also reported [28]. The adsorption capacities of these materials for paracetamol were 5.3, 8.8, 4.6, and 5.3 mg/g, respectively. The removal of paracetamol by the carbon nanotubes containing hydroxyl functional groups was significantly greater than that by the pristine MWCNTs which was probably due to the existence of H-bonding.

The effectiveness of pristine and carboxylated CNTs for the filtration of ibuprofen from aqueous solutions was studied by Bakr and Rahaman [33]. The results showed enhanced performance of carboxylated CNTs for the removal of ibuprofen in comparison to pristine carbon nanotubes. Under acidic conditions, the increased efficiency of ibuprofen removal was due to hydrogen bond formation between the protonated carboxyl groups of ibuprofen and those of the CNT-COOH, along with strong π–π and hydrophobic interactions.

All of these presented examples show that the adsorption of ibuprofen and/or paracetamol on surface-modified adsorbents is very complex and requires further in-depth research.

The best adsorbent for both ibuprofen and paracetamol was found to be carboxylated multi-walled carbon nanotubes, while the weakest were carbon nanotubes with hydroxyl groups (CNT-COOH > CNT > CNT-OH). As mentioned earlier, the adsorption process depends on both the physical (textural) and chemical properties of the adsorbent. The specific surface areas of CNT, CNT-OH, and CNT-COOH are 182, 160, and 155 m^2/g, respectively (Table 2). Assuming that the porous structure is the most important factor affecting adsorption, the best adsorbent theoretically should be un-modified carbon nanotubes with the highest surface area (182 m^2/g); and the adsorption capacities of CNT-OH and CNT-COOH should be comparable. However, this is not the case. The nanotubes with –COOH groups had the highest adsorption capacity, despite their significantly lower specific surface area (155 m^2/g). Interestingly, carbon nanotubes with hydroxyl groups with about the same BET surface area (160 m^2/g) had a much lower adsorption capacity than CNT-COOH. This proves that the adsorption process of both drugs on these carbon nanotubes depends on their chemical properties (the presence of functional groups on their surface) rather than on their porous structure. However, there is a question of why CNT-COOH and CNT-OH differ so significantly in their adsorption capacities despite having comparable textural properties. The only difference between them is the presence of an additional carbonyl group on the surface of CNT-COOH, which, as our results suggest, plays a crucial role in the adsorption process. Adsorption occurs most efficiently on the surface of the CNT-COOH possibly as a result of hydrogen bond formation between the H atom from the hydroxyl group and/or carbonyl group of paracetamol and the carboxyl group located on the surface of the adsorbent as well as *via* hydrogen bond formation between the carboxyl groups of ibuprofen and those of the CNT-COOH, along with hydrophobic and π–π type interactions as suggested by Bakr and Rahaman [33]. A schematic illustration of the possible interactions between the pharmaceuticals and carboxylated CNTs is presented in Fig. 6.

3.4. Effects of solution pH and ionic strength

In addition to the properties of the adsorbent and adsorbate, the chemical properties of the solution, mainly its pH and ionic strength, also have a great influence on the adsorption process. Changing the pH and/or ionic strength of the solution affects the degree of ionization of the adsorbate molecule and determines the charge present on the adsorbent surface. The effect of solution pH on adsorption

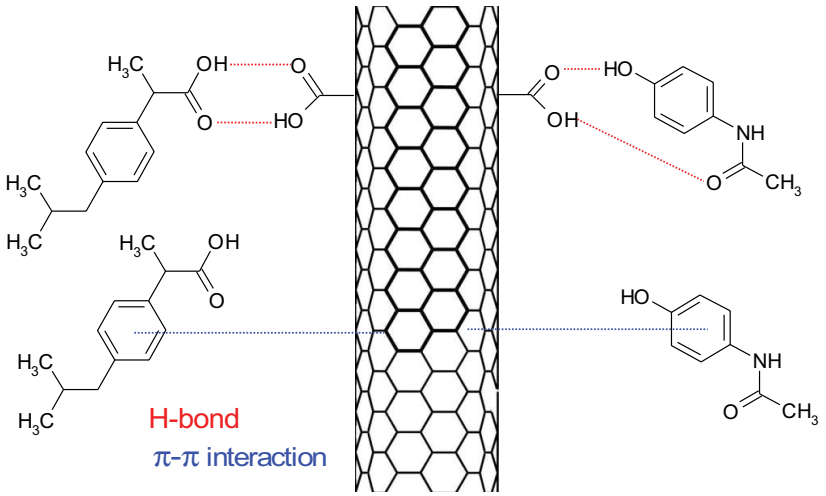


Fig. 6. Schematic illustration of the possible interactions between the pharmaceuticals and CNT-COOH.

was studied in the pH range from 2.3 to 11 and the results are shown in Fig. 7.

Adsorption of ibuprofen was best in acidic media and decreased successively with increasing pH. With an increase in pH from 2.3 to 11, the percent removal decreased from 75.4% to 17.6% for CNT, from 44.0% to 6.8% for CNT-OH, and from 97.1% to 21.6% for CNT-COOH. Adsorption of paracetamol was less sensitive to changes in environmental pH. Adsorption over a wide range of pH (from 2.3 to about 8) stayed more or less constant and decreased sharply in alkaline environments (at pH above 9). This phenomenon can be attributed to the much higher pKa value of paracetamol (9.4) compared to ibuprofen (4.9).

For both adsorbates, the sensitivity to pH changes was comparable for each type of carbon nanotubes. Such relationships observed for both ibuprofen and paracetamol could be explained using the pH_{PZC} concept. The point of zero charge of the adsorbent is defined as the pH value for which the surface charge of the adsorbent is equal to zero. The experimentally determined pH_{PZC} values for CNT, CNT-OH, and CNT-COOH were 6.40, 5.50, and 5.60, respectively. This means that at pH below these values ($pH < pH_{PZC}$) the surface of CNTs has a positive charge, while at pH above ($pH < pH_{PZC}$) it has a negative charge. Adsorption of both drugs was best in acidic environments (below pH_{PZC} and pKa) when the adsorbate molecules were present in a protonated form and the surface of the CNTs had a positive charge. Thus, it can be seen that the non-dissociated forms of the drugs were preferred by the positively charged CNTs surface. Such interactions between the non-dissociated drug molecules and the positively charged surface of the adsorbent promoted adsorption. Increasing the pH of the solution affects the degree of dissociation of the adsorbates. Thus, at pH above pKa, molecules of ibuprofen (pKa = 4.9) and paracetamol (pKa = 9.4) dissociate and appear in the solution as negatively charged ions. In an alkaline environment (above pH_{PZC}), a negative charge accumulates on the surface of the adsorbent. As a consequence, the electrostatic repulsion between negatively charged adsorbent surface and dissociated ibuprofen and paracetamol molecules results in a significant decrease in adsorption efficiency.

Similar effects of pH on adsorption have been reported by other authors, for example, for the adsorption of paracetamol on various MWCNTs [31], for the adsorption of ibuprofen on activated carbons [44], or adsorption of both compounds on activated carbon derived from oak acorn [41] and biosorbent based on chitin and lignin [42].

The effect of the ionic strength of the solution on adsorption was also investigated. Experiments were conducted for pure water (control sample) and four different concentrations of sodium sulfate (0.01, 0.05, 0.1, and 0.2 mol/L). The results are presented in Fig. 8. As can be seen, the increase in ionic strength from 0 to 0.2 mol/L Na_2SO_4 resulted in a slight change in the amount of ibuprofen and paracetamol adsorbed on all of the CNTs. Thus, it can be concluded that the ionic strength does not affect the adsorption of both drugs on the CNTs. A similar trend was reported by Cho et al. [30] and Nourmoradi et al. [41]. The addition of an inorganic salt to the solution reduces the solubility of individual adsorbates. The decrease in solubility with increasing Na_2SO_4 concentration in solution should, in theory, promote adsorption. Meanwhile, the results in Fig. 8 show no significant change. An explanation for this occurrence may be the phenomenon of aggregation of nanotubes in the presence of the electrolyte, which reduces their size while increasing their density and thus adversely affects the adsorption of organic compounds [45,46].

4. Conclusions

In this study, the adsorption of two popular drugs such as ibuprofen and paracetamol on multi-walled carbon nanotubes with different physico-chemical properties – pristine (CNT), hydroxylated (CNT-OH), and carboxylated (CNT-COOH) was investigated. Adsorption of both drugs on all carbon nanotubes was strongly pH-dependent while the ionic strength of the solution did not affect the adsorption efficiency. Adsorption equilibrium was reached after about 30 min. The kinetics followed a pseudo-second-order kinetic model and was limited by the film diffusion. The adsorption isotherms of ibuprofen and paracetamol on CNTs were

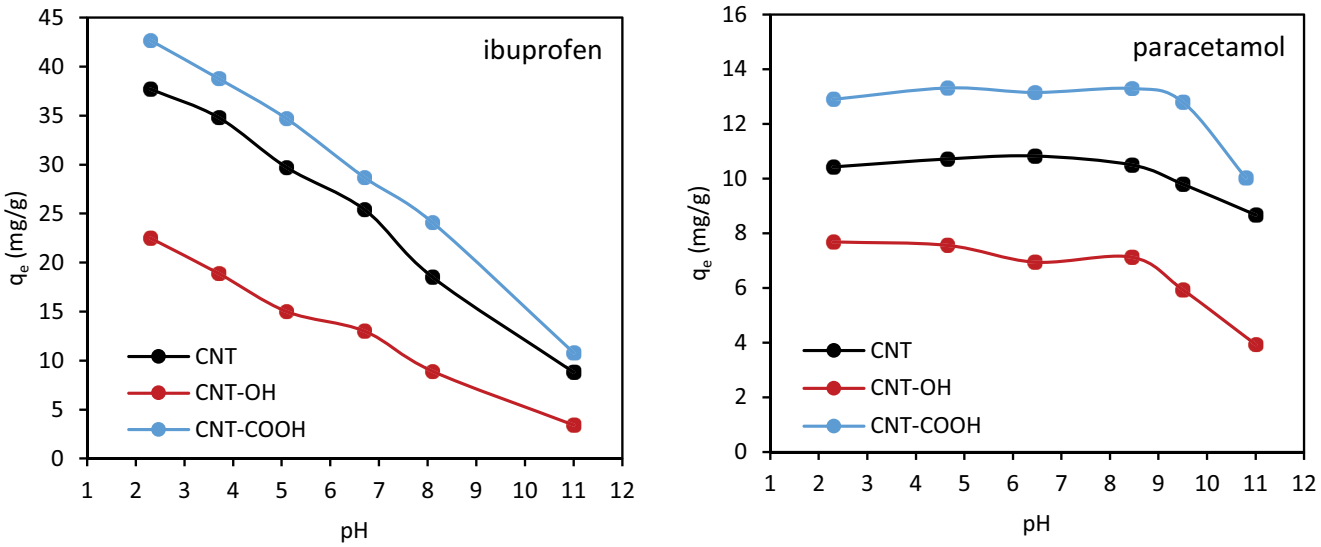


Fig. 7. Effect of initial pH on the adsorption of ibuprofen and paracetamol on the multi-walled carbon nanotubes.

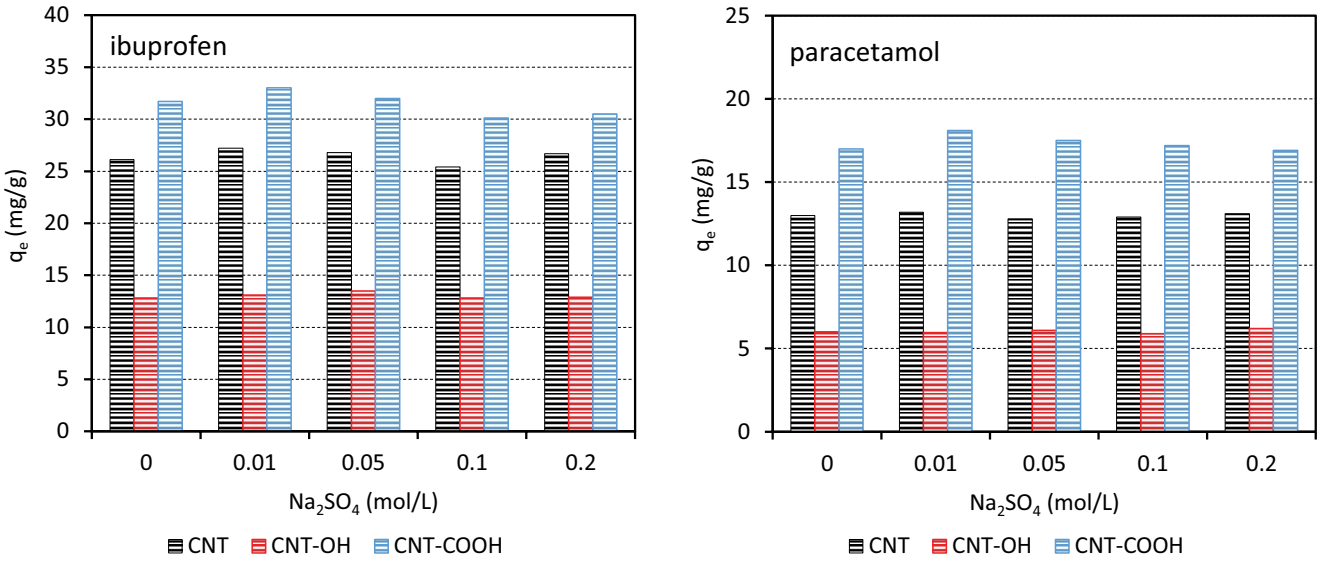


Fig. 8. Influence of solution ionic strength on the adsorption of ibuprofen and paracetamol on the multi-walled carbon nanotubes.

best described by the Langmuir equation. It was found that the adsorption process of both drugs on the carbon nanotubes depended on their chemical properties (presence of functional groups on their surface) rather than on their porous structure. The adsorbed amounts of ibuprofen and paracetamol were the highest on the carboxylated CNTs, followed by non-modified CNTs and hydroxylated CNTs (CNT-COOH > CNT > CNT-OH).

The results showed that carbon nanotubes have interesting adsorption properties. They have a relatively high adsorption capacity and excellent kinetic properties and can be used as adsorbents of pharmaceuticals present in water like ibuprofen and paracetamol. Of course, due to the relatively high price of CNTs compared to commercial activated carbons, they are unlikely to be used widely (on a large scale) for water purification. They seem to be much more useful in more specialized applications where their high adsorption capacity and ability to rapidly uptake contaminants found in water will be a major advantage. Analyzing the potential use of carbon nanotubes as sorbents, an important future area of use for CNTs could be their application in chemical analysis for the determination of pharmaceuticals in water, mainly using solid-phase extraction (SPE) as a method of analyte concentration.

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