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EFFECT OF IONIC STRENGTH AND NATURAL ORGANIC MATTER IN AQUEOUS SOLUTIONS OVER THE SORPTION OF ORGANIC CONTAMINANTS ON IRRADIATED AND PRISTINE CARBON NANOMATERIALS

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Carbon nanotubes may undergo transformation upon interaction with different environmental factors, like ionic strength and natural organic matter (NOM), which lead to a change in its sorption capacity and also to a change in the stability of the MWCNTs suspension. This study proposes the use of multi-walled carbon nanotubes (MWCNTs) pristine and irradiated as nanosorbents for bisphenol A (BPA), as a moderate hydrophobic organic contaminant in saline solutions in the presence of NOM. Several types of sediment with different compositions from a saline lake have been used to perform the competitive sorption experiments between the BPA and the NOM at the active sites of the MWCNTs. It was found that the increase of Na^+ concentration could reduce the electrostatic energy barrier, leading to fast aggregation in reaction-controlled regime, till the critical coagulation concentration (CCC).

Keywords: multi-walled carbon nanotubes, adsorption, bisphenol A, ionic strength, natural organic matter.

1. Introduction

Among emerging organic contaminants, personal care products have gained more attention, because they are frequently released in the environment and might raise potential risks to surface and drinking waters [1]. As environmental nanosorbents, carbon nanotubes were tested for the removal of several organics, such as tetracyclines [2], triclosan [3], bisphenol A and 17α-ethynyl estradiol from aqueous matrices [4]. Adsorption on carbon nanotubes, as

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well as on other types of carbon nanosorbents might be affected by the chemical composition of the aqueous solution [5, 6]. Inorganic cations, such as Na^+ or Ca^{2+} present a salting-out effect on the adsorption of several hydrophobic compounds [7] and natural organic matter may also decrease or increase the adsorption process, based on competitive effects [8] and pore blockage [9], or better dispersion [10]. These studies showed that the interactions between the different types of MWCNTs and several organic contaminants [11, 12, 13] are very important in real aqueous solutions for further environmental applications [14].

In the present study, there was systematically investigated the adsorption mechanism of bisphenol A (BPA) to multi-walled carbon nanotubes (MWCNTs) pristine and aged by irradiation (irradiated MWCNTs), in synthetic aqueous solutions. There were further studied the conditions of the chemical solutions (pH, ionic strength and natural organic matter) on the adsorption of BPA on these types of carbon nanosorbents. Preliminary studies were done in real aqueous solutions and these will be continued in future environmental applications.

2. Materials and methods

2.1 Materials and solutions

Multi-walled carbon nanotubes (MWCNTs) are provided by Baywatch, Germany. Irradiated MWCNTs were prepared by irradiation during 2160 hours at 65 W/m^2 in the laboratories from RWTH Aachen, Germany. Bisphenol A (minimum purity 99 %) was the sorbate selected for this study and it was obtained from Fluka/Sigma-Aldrich Chemical, Germany. HPLC grade methanol was purchased from VWR Chemicals, France. Stock reference solutions were individually prepared in methanol and kept in the refrigerator for three months. All working reference solutions were prepared prior to use. Aqueous solutions were prepared using HPLC grade water. The preparation of working solutions was described in [15].

2.2 HPLC analytical conditions

HPLC determinations were performed using an Agilent 1100 Series HPLC BPA concentrations were determined using high-performance liquid chromatography (HPLC, Agilent 1100 Series). The separation of BPA was accomplished with a C18 column (Zorbax Eclipse Plus-Agilent), 3.5 μm, 100 × 4.6 mm i.d. The mobile phase was 0.5 mL/min of 80% methanol and 20% HPLC grade water. A sample volume of 10 μL was injected in the chromatograph at a column temperature of 25 °C. The elution times of BPA was 8 min. DAD detector operated at 280 nm [16].

2.3 Batch adsorption experiments

For the first sorption experiments 1 mg of MWCNTs pristine respectively irradiated were added in a 100 mL synthetic aqueous solutions or natural water samples and treated with ultrasound for 30 minutes. Concentrated BPA was then added to obtain concentrations of 5, 10, 25, 50 mg/L in the analyzed samples and shaken mechanically for 48 hours at 25 °C, reading the BPA concentration at 30 minutes, 1 h, 24 h, and 48 h. Sorption experiments have also been carried out for mixtures of natural waters with different salinities and sediments, by adding 1 mg of sorbent and 1 mg of sediment in a 100 mL natural sample and treated for 30 minutes with ultrasound. The chemical characterization of the natural waters was done by using several methods [15, 16, 17], as well as the determination of the chemical composition of the sediments.

2.4 Characterization of the nanosorbents

The characterization of the studied nano-sorbents in synthetic and in real aqueous samples was done by BET specific surface areas and pore size distribution, scanning electron microscopy (SEM), Fourier Transformed Infrared spectrometry (FTIR) and differential scanning calorimetric analysis (DSC). All the methods were described in [15]. It was also evaluated the Zeta potential by electrophoretic mobility of colloidal particles of pristine and irradiated MWCNTs in aqueous suspensions with different pH values.

3. Results and discussion

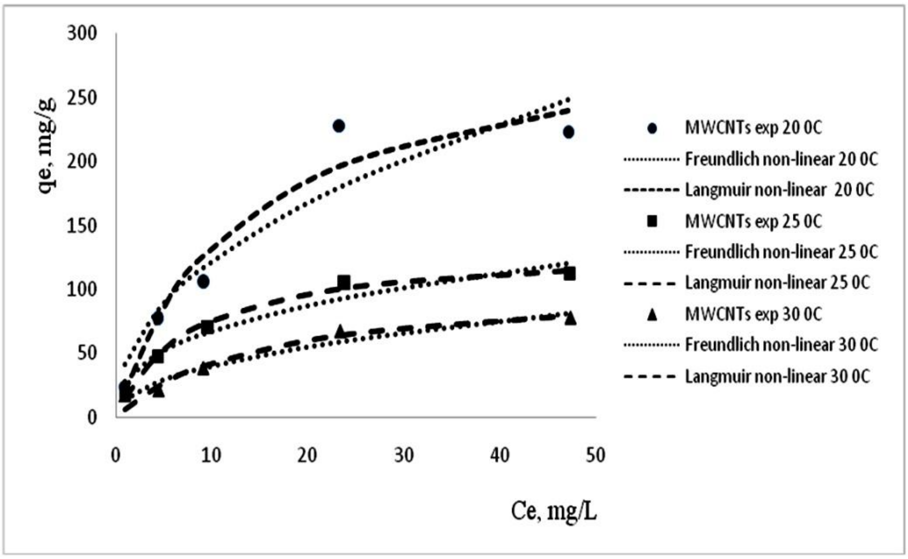
3.1 Characterization of the nanosorbents

The data regarding the characterization of MWCNTs pristine and weathered are presented in [16]. From the textural characteristics of the pristine and irradiated MWCNTs were observed that the irradiated one presents larger pore diameter, but the surface area is smaller, indicating the presence of micropore constrictions, which prevent the N_2 adsorption. From the SEM analysis of MWCNTs pristine and impregnated with BPA were observed that the distance between nanotubes are bigger for MWCNTs impregnated with BPA due to the presence of BPA on the surface of the nanostructure. In contrast with the pristine MWCNTs, the irradiated ones indicate the presence of fragments on external walls of the nanotubes, probably due to the oxygen containing fragments on the structure of nanotubes. FTIR spectra have highlighted the presence of new peaks in the case of impregnated MWCNTs due to the adsorption of BPA molecules on the surface of pristine and irradiated MWCNTs. DSC analysis indicates that MWCNTs do not have significant mass losses between 100-200 ^{0}C, meaning inclusion water molecules are absent from their crystalline lattice. The thermal stability of MWCNTs can be attributed to the bonds from aromatic rings.

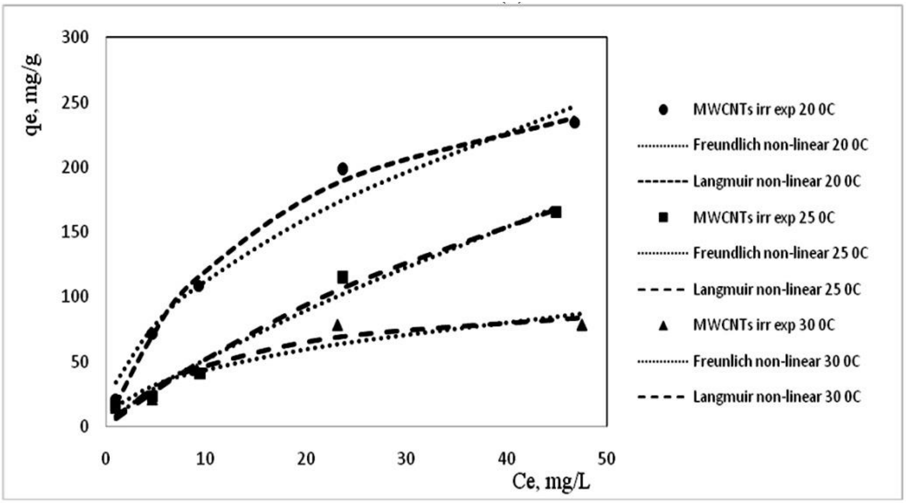
Zeta potential measurements indicated that at low pH, the particles of MWCNTs are positively charged and unstable colloidal nanostructures are formed. By increasing the pH, the particles are negatively charged and stable colloidal; At Zeta potential values higher than 30 mV (absolute value), electrostatic repulsions appear and the particles tend to remaind dispersed while at Zeta potential values smaller than 30 mV, the electrostatic repulsions are weaker.

3.2 BPA adsorption isotherms

There were used the Langmuir and Freundlich isotherms to describe the equilibrium adsorption. The Langmuir isotherm model presumes monolayer coverage of the surface, no interactions appearing between adsorbed molecules during the sorption process (Fig. 1). The Freundlich isotherm models the multilayer adsorption and the adsorption on heterogeneous surfaces.



(a)



(b)

Fig. 1 Adsorption isotherms of BPA on MWCNTs pristine (a) and irradiated (b); Conditions: Ci =10 – 50 mg/L BPA, T = 25, 20, 35 ^{0}C, V = 100 mL, contact time 3 hours, equilibrium reached after 30 minutes, in water [15].

It can be observed from Fig. 1 that the adsorption capacities increased by increasing BPA concentration, the maximum adsorption capacities of pristine MWCNTs being smaller than of the irradiated ones at the same temperature and decreasing by increasing the temperature (Table 1).

Table 1

Isotherm parameters for the adsorption of BPA by MWCNTs pristine and irradiated at different temperatures, in aqueous solutions [15]

Sorption conditions	Langmuir constants			Freundlich constants		
	q_m, mg/g	K_L, L/mg	R^2	K_F	n	R^2
MWCNTs pristine 20 ^{0}C	305.36	0.077	0.9762	42.40	2.18	0.9907
MWCNTs pristine 25 ^{0}C	132.72	0.131	0.9581	28.26	2.65	0.9945
MWCNTs pristine 30 ^{0}C	103.37	0.069	0.9917	14.12	2.20	0.9704
MWCNTs irradiated 20^{0}C	353.80	0.013	0.9999	8.57	1.27	0.9720
MWCNTs irradiated 25^{0}C	321.58	0.060	0.9897	35.28	1.97	0.9714
MWCNTs irradiated 30 ^{0}C	205.85	0.081	0.9813	16.11	2.29	0.9758

Experimental data show that in NaCl aqueous solutions of concentrations between 0.01M (Figs. 2, 4) and 0.05 M (Figs. 3 and 5), the adsorption of organic contaminants increases, probably due to a better contact of the non-planar molecules of BPA with the carbon nanostructures. Distribution of the Na^+ and Cl^-

ions between the negatively charged MWCNTs increases the distance between the surfaces, facilitating the access at the surface of the organic molecules.

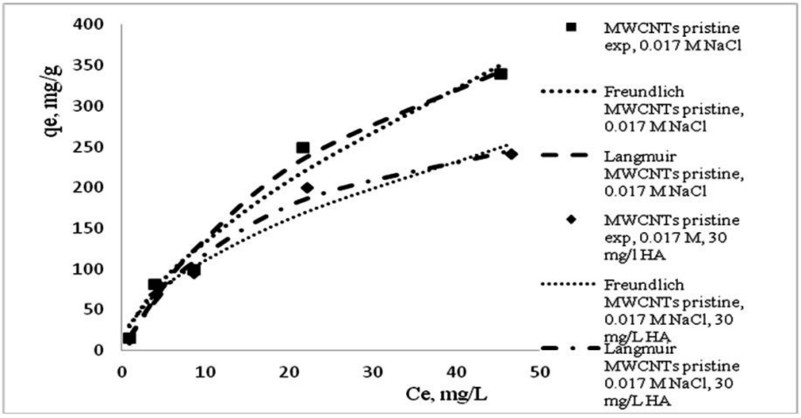
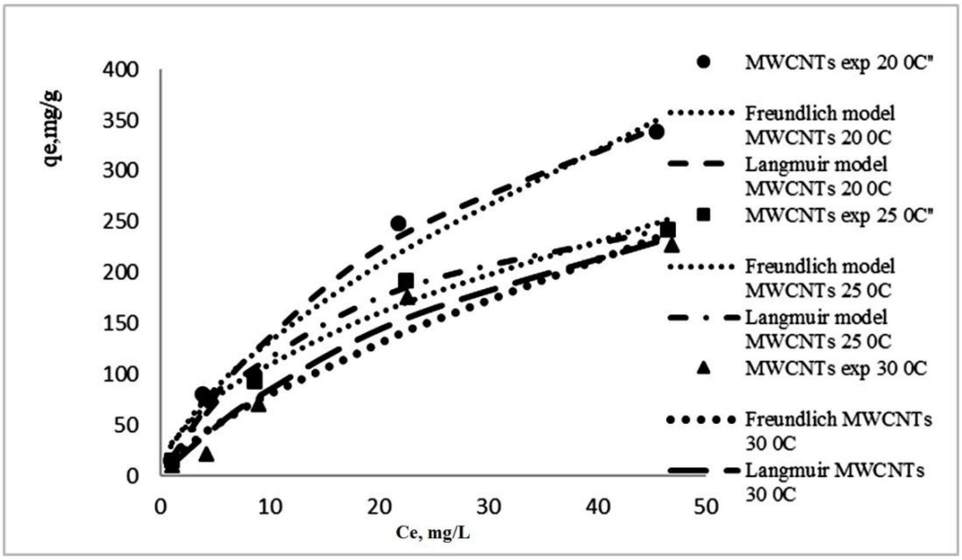
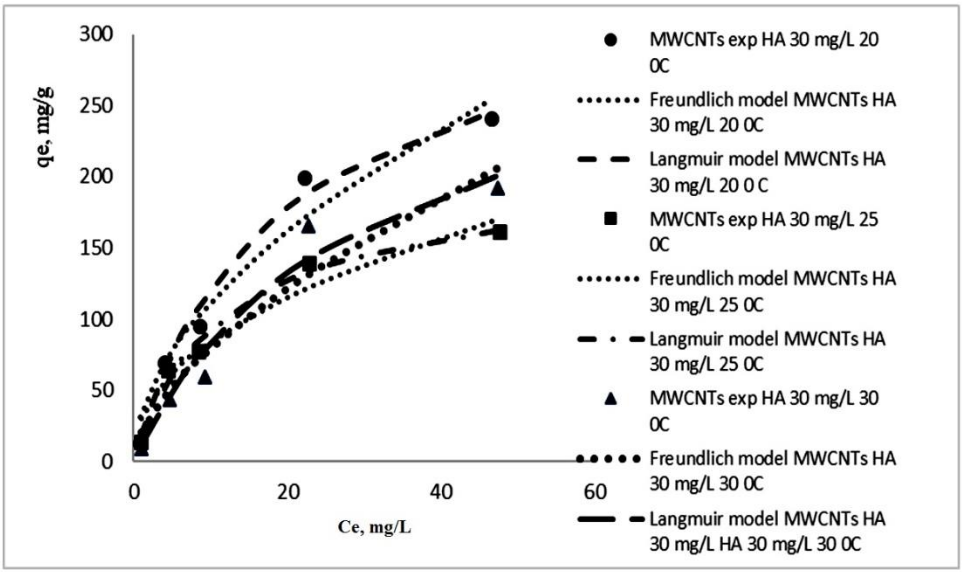


Fig. 2 Adsorption isotherms of BPA on MWCNTs pristine without and with HA 30 mg/L; Conditions: Ci =10 – 50 mg/L BPA, T = 20 ^{0}C, V = 100 mL, contact time 3 hours, equilibrium reached after 30 minutes, NaCl 0.01 M.

The presence of higher concentrations of NaCl (~ 0.1 M) in solution, decreases the solubility of BPA (120 mg/l la 25 ^{0}C, log Kow = 3.2 la 25 ^{0}C), facilitating its orientation to the hydrophobic surfaces of the carbon surface and increases also the dimensions of the aggregates by reducing the electrostatic energy barrier and leading to faster aggregation.



(a)



(b)

Fig. 3 Adsorption isotherms of BPA on MWCNTs pristine without (a) and with (b) HA 30 mg/L, NaCl 0.05 M; Conditions: Ci =10 – 50 mg/L BPA, T = 25, 20, 35 ^{0}C, V = 100 mL, contact time 3 hours, equilibrium reached after 30 minutes.

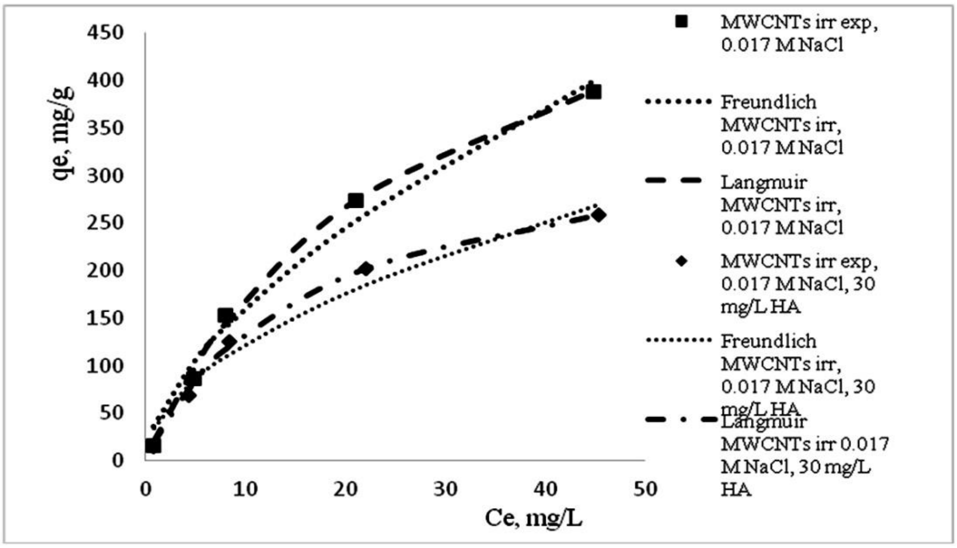
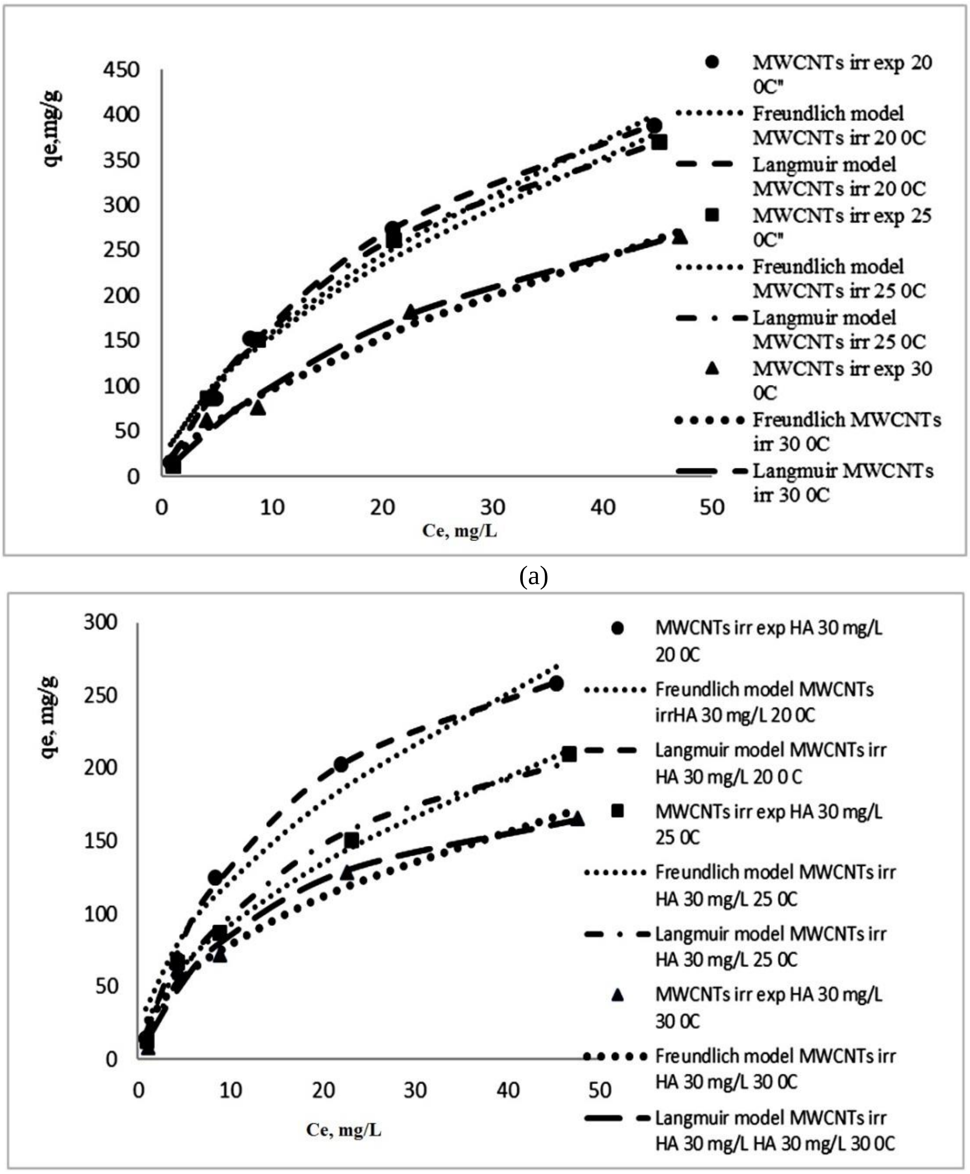


Fig. 4 Adsorption isotherms of BPA on MWCNTs irradiated without and with HA 30 mg/L; Conditions: Ci =10 – 50 mg/L BPA, T = 20 ^{0}C, V = 100 mL, contact time 3 hours, equilibrium reached after 30 minutes, NaCl 0.01 M.



(a)

(b)

Fig. 5 Adsorption isotherms of BPA on MWCNTs irradiated without (a) and with (b) HA 30 mg/L; Conditions: Ci =10 - 50 mg/L BPA, T = 25, 20, 35 ^{0}C, V = 100 mL, contact time 3 hours, equilibrium reached after 30 minutes, NaCl 0.05 M

The adsorption of BPA was nonlinear, and it fitted well the Langmuir model. The presence of HA suppresses the adsorption of BPA onto MWCNTs (Figs. 2-5) and the degree of inhibition increased by increasing the humic acid (HA) concentration (Tables 2 and 3). The results can be explained by the direct competition for the adsorption sites between HA and BPA, which made the adsorption of BPA onto the MWCNTs surface more difficult.

Table 2

Isotherm parameters for the adsorption of BPA by MWCNTs pristine and irradiated at different temperatures, in aqueous solutions 0.01 M NaCl, with HA 10 mg/L

Sorption conditions	Langmuir constants			Freundlich constants		
	q_m, mg/g	K_L, L/mg	R^2	K_F	n	R^2
MWCNTs pristine 20 ^{0}C	391.55	0.3030	0.9986	30.63	1.56	0.9141
MWCNTs pristine 25 ^{0}C	344.59	0.0520	0.9938	31.83	1.85	0.9566
MWCNTs pristine 30 ^{0}C	347.66	0.0234	0.9993	15.78	1.41	0.9037
MWCNTs irradiated 20^{0}C	571.46	0.0404	0.9937	39.41	1.68	0.9492
MWCNTs irradiated 25^{0}C	520.43	0.0375	0.9994	39.60	1.64	0.9189
MWCNTs irradiated 30 ^{0}C	485.46	0.0258	0.9898	221.30	1.51	0.9083

The presence of HA prevented the carbon nanostructures to form bigger aggregates as affected by NaCl. The aggregation rate decreased by increasing the HA concentration, consistent with the results of MWCNTs behavior in water samples. It might be supposed that the adsorption of HA molecules on MWCNTs increase electrosteric repulsions and improve their stabilization. The presence of NaCl at low concentrations, (< 0.1 M) in environmental solutions does not severely influence the sorption of BPA in the presence of 30 mg/l HA.

As can be seen from the Tables 2 and 3, as in the aqueous solutions without HA addition, sorption capacity decreases with increasing temperature for both MWCNTs pristine and irradiated and also decreases with increasing HA concentration probably due to the direct competition for the adsorption sites between HA and BPA, as already mentioned.

Table 3

Isotherm parameters for the adsorption of BPA by MWCNTs pristine and irradiated at different temperatures, in aqueous solutions 0.01 M NaCl, with HA 30 mg/L

Sorption conditions	Langmuir constants			Freundlich constants		
	q_m, mg/g	K_L, L/mg	R^2	K_F	n	R^2
MWCNTs pristine 20 ^{0}C	244.52	0.0533	0.9917	32.20	1.86	0.9461
MWCNTs pristine 25 ^{0}C	203.25	0.0845	0.9767	29.58	2.20	0.9772
MWCNTs pristine 30 ^{0}C	222.77	0.0345	0.9843	18.96	1.61	0.9880
MWCNTs irradiated 20 ^{0}C	387.04	0.0527	0.9776	26.97	1.86	0.9592
MWCNTs	352.50	0.0612	0.9866	36.95	1.92	0.9606

irradiated 25 ^{0}C						
MWCNTs irradiated 30 ^{0}C	316.16	0.0662	0.9636	24.99	2.00	0.9733

It has concluded that maximum sorption capacity was obtained for MWCNTs irradiated in solutions containing 10 mg/L humic acid at 20 ^{o}C.

3.3 Environmental implications

It is important to use real water samples, to apply the studied adsorbents for removing BPA. The preliminary study revealed that aqueous suspensions of MWCNTs pristine and irradiated are stable in real solutions of natural waters, at pH values between 4 and 10 and ionic strength between 0 and 0.05 M. These values are usual for to most environmental water media, the pH and salinity influencing the sorption of BPA to aqueous suspensions of MWCNTs in connection with the log Kow values. For medium hydrophobic organic compounds such as BPA (log Kow = 3.5), both parameters play an important role in the sorption process.

Ten natural water samples with different values of the salinity (in NaCl, g/L) and five sediments with different values of the total organic carbon TOC (%), indicated in Table 4 were collected from Dobrogea, Romania. The concentrations of BPA initially measured in the samples were lower than the detection limit of chromatographic method used in these experiments. In the sorption experiments, the natural samples, containing firstly only the saline waters and then the mixtures of saline waters and sediments were tested, by using the same experimental conditions: the chemical composition of the natural samples (salts and sediments) being correlated with the maximum sorption capacity of the studied sorbents obtained from the Langmuir model of the sorption isotherms obtained in the following conditions Ci = 10 – 50 mg/L BPA, t = 25 ^{0}C, V = 100 mL. The contact time was of 48 hours the equilibrium was reached after 30 minutes [16].

The values of the Langmuir parameters for the sorption of BPA on MWCNTs in natural aqueous systems were calculated in Table 4.

Table 4

Values of maximum sorption capacity, for MWCNT pristine and irradiated for BPA in the studied natural systems with 0.01 g / L sediment and 1 mg / 100 mL nanomaterial as compared to nanomaterial-free systems

Natural saline water with sediments	Pristine MWCNT +sediments			Irradiated MWCNT +sediments			Sediments without MWCNTs		
	Langmuir			Langmuir			Langmuir		
	q_m, mg/g	K_L, L/mg	R^2	q_m, mg/g	K_L, L/mg	R^2	q_m, mg/g	K_L, L/mg	R^2
0.129 g/L NaCl 1.29 % TOC	329.3	0.060	0.9921	362.8	0.051	0.9971	231,7	0,116	0,994

0.109 g/L NaCl 3.53 % TOC	395.1	0.039	0.9984	433.8	0.031	0.9861	294,9	0,069	0,998
0.113 g/L NaCl 5.80 % TOC	348.1	0.052	0.9973	350.6	0.061	0.9983	279,4	0,072	0,999
0.110 g/L NaCl 3.77 % TOC	362.1	0.050	0.9961	467.7	0.030	0.9866	293,6	0,078	0,998
0.098 g/L NaCl 3.74 % TOC	427.0	0.034	0.9902	472.0	0.029	0.9871	302,9	0,095	0,997
0.645 g/L NaCl 1.29 % TOC	322.3	0.056	0.9981	343.6	0.042	0.9948	213,1	0,083	0,998
0.543 g/L NaCl 3.53 % TOC	365.4	0.035	0.9911	402.0	0.028	0.9855	226,1	0,095	0,997
0.567 g/L NaCl 5.80 % TOC	339.0	0.051	0.9970	348.9	0.053	0.9978	215,7	0,132	0,992
0.549 g/L NaCl 3.77 % TOC	354.0	0.045	0.9952	442.7	0.028	0.9855	231,4	0,125	0,993
0.490 g/L NaCl 3.74 % TOC	356.9	0.056	0.9981	447.2	0.029	0.9871	254,3	0,099	0,997

It was observed that in the presence of small concentrations of sodium (34.5 mg/L), the maximum sorption capacity of both studied nanostructures present higher values in the order: irradiated MWCNTs and sediment; pristine MWCNTs and sediment and only sediment in comparison with the same studies in real aqueous solutions with higher concentrations of sodium (170 mg/L). The values of maximum sorption capacities do not agree with the additive model even though BPA presenting closer values of the sorption capacity on sediment only and pristine MWCNTs. Higher values of the maximum sorption capacity are observed on irradiated MWCNTs due to the presumed sorption mechanism which will presented. It was revealed in previous studies [17] that the ionic strength at or above 100 mM NaCl causes deposition of MWCNTs. In our study, the decrease of the sorption capacity appears for smaller concentrations, of 50 mM of NaCl in synthetic solutions.

3.4 Adsorption mechanism

Sorption of BPA to the surface of the multi-walled carbon nanotubes is governed by interactions based on hydrophobicity, dispersion and weak polar forces [15, 18]. A possible adsorption mechanism is presented in Fig. 6. The improved sorption on carbon based nanosorbents might be explained based on the π-π electron-donor-acceptor (EDA) interactions and on the absence of pore diffusion [19]. Capillarity contributes to the orientation of the sorbate molecules. For pristine MWCNTs the physical sorption can be considered the dominant mechanism of sorption, rapid equilibrium rates following the traditional Langmuir and Freundlich isotherms [20].

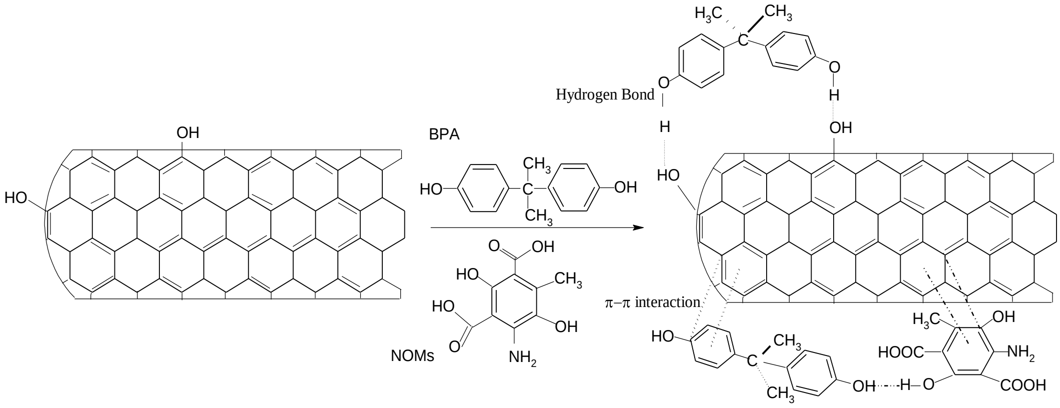


Fig 6. Mechanism of interaction between carbon nanotubes, NOMs and BPA

In the case of irradiated MWCNTs, van der Waals interactions appear at the ends of the nanotubes, MWCNTs increasingly oxidize by the UV irradiation [21, 22]. This type of MWCNTs agglomeration might hinder the dispersion even under sonication treatment [23]. The Van der Waals interactions between carbon nanotubes of 500 eV/µm contribute to their tendency of aggregation. Different models might be applied in order to understand the effect of each studied factor over the sorption process in natural aqueous systems [24].

4. Conclusions

The presence of natural organic matter in environmental systems influences the adsorption of organic contaminants on carbon-based nanomaterials. It was shown that HA suppresses the adsorption of BPA on MWCNTs in the studied conditions. This might be ascribed to competitive interactions between the two organic molecules on the surface of the studied carbon nanostructures. The degree of inhibition increased by increasing the HA concentration. Maximum sorption capacity was obtained for MWCNTs irradiated suspension with 10 mg/L HA at 20 ^{o}C.

In the presence of humic acid, by increasing the values of ionic strength, the sorption capacity for the studied organic contaminant was moderately reduced, because the surface-bond HA increases the surface electronegativity of the nanosorbents, mitigating the aggregation through electrosteric repulsions. On the other hand, the presence of HA prevented the carbon nanostructures to form bigger aggregates as affected by NaCl. It might be supposed that the adsorption of

HA molecules on MWCNTs increases electrosteric repulsions and improve their stabilization.

The maximum values of sorption capacity, in real natural waters, increase from sediment alone, sediment and pristine MWCNTs and sediment and irradiated MWCNTs. For equal amounts of sediment and both types of MWCNTs in the samples, the additive model was not obeyed, the total sorption capacity being not the sum of the sorption capacity for each studied sorbent. The maximum sorption capacities decrease in the presence of higher values of the ionic strength (170 mg/L Na^+) for both studied sorbents but maintaining the same increasing in the order: sediments containing between 0 and 1 mg/L TOC; sediments and pristine MWCNTs and sediments and irradiated MWCNTs.

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