Single and competitive adsorption of OMPₛ by carbon nanotubes – mechanism and fitting models

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Abstract. The adsorption of three organic micropollutants (diclofenac – DFN, pentachlorophenol – PCP and octylphenol – OP) on two kinds of carbon nanotubes (single walled carbon nanotubes – SWCNT and single walled carbon nanotubes with amine group – SWCNT-NH$_2$) was investigated, in single and bicomponent solution at pH 5. SWCNT-NH$_2$ had three times lower specific surface area than SWCNT. Significant differences were observed in sorption capacity of SWCNT and SWCNT-NH$_2$ for given chemicals. The sorption uptake changes in the following order: OP > PCP > DFN for SWCNT and DFN > PCP > OP for SWCNT-NH$_2$. A few times higher adsorption of OP on SWCNT came from low OP solubility in water in comparison to PCP and DFN. While, higher adsorption of DFN and PCP on SWCNT-NH$_2$ was a result of electrostatic attraction between dissociated form of these chemicals and positively charged SWCNT-NH$_2$ at pH 5. In adsorption from bicomponent solution, significant competition was observed between PCP and DFN due to similar adsorption mechanism on SWCNT-NH$_2$. Opposite tendency was observed for SWCNT, DFN did not greatly affect adsorption of PCP and OP since they were very easily absorbable by sigma-sigma interaction.

1 Introduction

Organic micropollutants (OMPs) such as endocrine disrupting compounds, pharmacuticlas, pesticides, polycyclic aromatic hydrocarbons, surfactants usually enter into wastewater after their industrial and domestic application [1–3]. Therefore, they occur in effluents, since the technologies used at conventional wastewater treatment plant does not allow their complete elimination [4, 5]. This is due to many of these contaminates are highly hydrophobic like PAHs, hardly soluble in water and toxic, like pesticides. A consequence of these properties is OMPs' bioaccumulation in environment, for example in animal's tissues and some environmental parts like sediments, soils [6, 7].

Last years many efforts have been made to find the most favourable process for micropollutants removal from different aqueous media. Among many methods to remove these contaminants, membrane filtration, advanced oxidation processes and adsorption have been widely proposed [8–11]. Although advanced oxidation and membrane filtration are very

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effective for the elimination of OMPs, these methods led to the generation of highly concentrated retentate and formation of undesirable for water oxidation by-products [12, 13].

Therefore, adsorption is considered as superb process, since the high-quality effluent is produced. As an alternative for well-known activated carbon, carbon nanotubes are considered as highly effective adsorbent for OMPs removal. This is due to much faster adsorption of contaminants on carbon nanotubes than on activated carbon [14]. Most of the adsorption studies were conducted for single adsorbate to describe adsorption mechanism or adsorbent potential. This approach does not bring useful information about real adsorption behaviour, for example in environmental water matrix containing a few different contaminates. In that conditions, we can observe cooperative or competitive behaviour, depending on affinity of coadsorbates to the adsorbent surface [15].
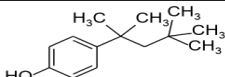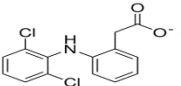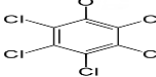
The aim of this study was to better understand the competition behaviour between OMPs with different properties (diclofenac, pentachlorophenol, octylphenol) during adsorption on carbon nanotubes. For that purpose, two kinds of experiments were conducted: (1) adsorption of OMPs from single solution, (2) adsorption of OMPs from bicomponent solution.

2 Materials and methods

2.1 Materials

Selected OMPs i.e. 4-octylphenol (OP), diclofenac sodium salt (DFN) and pentachlorophenol (PCP) were purchased from Sigma-Aldrich (Poland) in analytical purity grade. Their physico-chemical properties are presented in Table 1. The stock solution of OMPs was prepared with methanol (1 g/L). The adsorbate feed solutions (single and bicomponent) were prepared by diluting the stock solution with pure water. pH of feed solution was adjusted to 5 using 0.5 M NaOH.

Table 1. Selected properties of micropollutants.

Compound	Chemical structure at pH 5	Molecular mass[1] (g/mol)	log K_{ow}[1] (-)	Solubility in water 20°C [1] (mg/L)	pKa[1] (-)	Equivalent width[2] (nm)	Molar volume (cm³/g)
4-tert-octylphenol (OP)		206.32	4.12	7	10.38	0.56	214.96
Diclofenac sodium salt (DFN)		296.15	4.51	50	4.15	0.48	493.58
Pentachloro phenol (PCP)		266.34	4.40	10	4.70	0.28	134.34

1 – https://pubchem.ncbi.nlm.nih.gov/compound/2336 2 – calculated with ChemBio3D Ultra 12.0

2.2 Carbon nanotubes and their characterization

Two different types of carbon nanotubes (CNTs): single walled carbon nanotubes (SWCNT) and single walled carbon nanotubes with amine group (SWCNT-NH₂) were used. CNTs were purchased from Chengdu Organic Chemistry Ltd. Characteristic of the nanotubes as provided by the manufacturer is shown in Table 2. Nitrogen adsorption-desorption isotherms of CNTs were estimated at 77 K by means of a volumetric adsorption analyzer ASAP 2010

(Micrometrics USA) and on this basis the BET surface area and porous structure parameters were calculated. Streaming potential of SWCNT was studied using electrokinetic analyser SurPASS[TM] 3 and then zeta potential was calculated from the Smoluchowski equation.

2.3 Adsorption isotherms experiments

The adsorption isotherms of PCP, DFN and OP were determined at 20°C in single and bicomponent solution system at pH 5. Two concentration levels of OMPs were used i.e. 0.1 and 0.5 mg/L. Experimentally, an adequate amount of a sorbent (from about 10 to 100 mg) was added into stoppered flasks containing 50 mL of single or bicomponent OMPs solution and shaked until equilibrium was reached. Then a sorbent was separated from the solution using PTFE syringe filter with a pore size of 0.45 μm and the resulting filtrates were analyzed for micropollutants concentration. The analytical procedure included solid phase extraction and chromatographic determination with HPLC. The amount of studied OMPs adsorbed on the nanotubes was determined by the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot v}{m}$$ (1)

where: q_e (mg/g) is adsorbed amount of the adsorbate, C_0 and C_e (mg/L) are initial and equilibrium concentrations of the adsorbate, respectively, m (g) is weight of the sorbent, v (L) is a volume in which the adsorption was performed.

2.4 Data analysis

In this study, three common adsorption isotherm models including: (1) Langmuir model, (2) Freundlich model, and (3) Dubinin-Radushkevich model were used to fit experimental data. Each of the model is briefly described below.

The Langmuir equation assumes monolayer adsorption, where molecules interact only with the surface of sorbent. The form of the Langmuir isotherm is represented by the following equation:

$$q_e = \frac{a_L \cdot b \cdot C_e}{1 + b \cdot C_e}$$ (2)

where: a_L (mg/g) is the maximum adsorption capacity, and b (L/mg) is the Langmuir fitting parameter.

The Freundlich model is empirical and well describes adsorption on heterogeneous surface energy system. The model has significant importance for chemisorption and some cases of physisorption and can be written as:

$$q_e = K_f \cdot C_e^{\frac{1}{n}}$$ (3)

where: K_f ((mg/g) (L/mg)[n]) is the Freundlich adsorption coefficient, n is the number describing surface heterogeneity and sorption intensity.

The Dubinin-Radushkevich model, which was originally proposed as an empirical adaptation of the Polanyi adsorption potential theory, has been the fundamental equation to quantitatively describe the adsorption of gases and vapours by microporous sorbents. The equation, based on the postulate that the mechanism for adsorption in micropores is that of pore-filling rather than layer-by-layer surface coverage, generally applies well to adsorption systems involving only Van der Waals forces and is especially useful to describe adsorption

on microporous adsorbent. The Dubinin-Radushkevich equation is given in the following form:

$$\ln q_e = \ln a_{DR} - E^{-2} \cdot \varepsilon^2 \tag{4}$$

where: a_{DR} (mg/g) is the amount of adsorbate that can be adsorbed in micropores, can be obtained by plotting lnq_e as a function of ε^2, E (kJ/mol) is the adsorption energy, can be read from the slope of the line, ε is adsorption potential, is defined as:

$$\varepsilon = R \cdot T \cdot \ln\frac{C_s}{C_e} \tag{5}$$

where: R (8.314 J·mol^{-1}·K^{-1}) is the ideal gas constant, T (K) is temperature, C_s (mg/L) is the solubility in water.

The models were fitted to the experimental data using the Microsoft Excel spreadsheet with the Solver add-in. The least-squares method was used to determine the constants of the equations.

In order to compare competition strength between coadsorbates in bicomponent solutions following equation was used:

$$A = \frac{(K_{dA} - K_{dC})}{K_{dA}} \cdot 100\% \tag{6}$$

where: A (%) is competition strength K_{dA} and K_{dC} (L/g) are adsorption distribution coefficient for studied OMPs without and with coadsorbate, respectively, calculated for selected equilibrium concentration, obtained from equation:

$$K_d = \frac{q_e}{C_e} \tag{7}$$

3 Results

3.1 Morphology and texture of CNT

The pore size distribution (PSD) of the SWCNT and SWCNT-NH$_2$ are shown in Fig. 1 and their physical structure properties are listed in Table 2. SWCNT have three times larger surface area than SWCNT-NH$_2$ that suggests better sorption potential of SWCNT. From PSD, SWCNT are dominated with micropores, while the SWCNT-NH$_2$ structure is bidispersive, in large part consists of micropores and average fraction of mesopores.

The zeta potential versus pH is presented in Fig. 2. The charge of both kinds of nanotubes was positive at pH around 4 and negative at pH around 7. What is more important, the SWCNT-NH$_2$ have higher electric charge than SWCNT, which is attributed to dissociated form of amine group (NH$_3^+$) on their surface. The isoelectric point was found at pH 4.5 and 6.3 for SWCNT and SWCNT-NH$_2$, respectively.

Table 2. Textural characteristic of studied carbon nanotubes.

Name	Outer diameter [1] (nm)	Length [1] (µm)	Purity [1] (wt%)	Specific Surface Area (m²/g)	Total Pore Volume (cm³/g)	Total Area in Pores (m²/g)
SWCNT	< 2	5–30	95	1124.26	0.88	945.56
SWCNT-NH$_2$	< 2	5–30	90	410.63	0.60	257.52

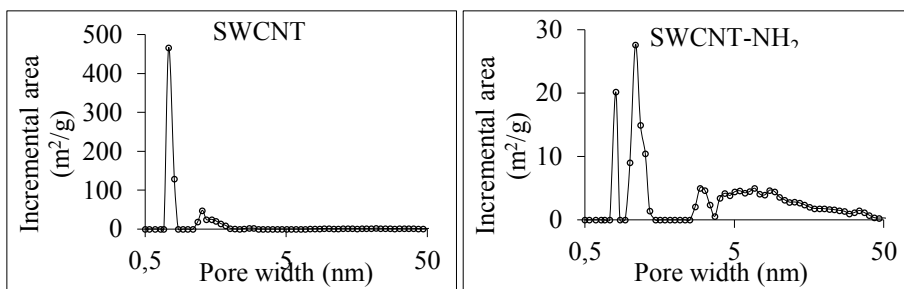1 – Data provided by manufacturer

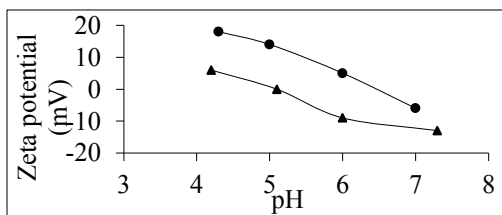**Fig. 1.** Pore size distribution of SWCNT and SWCNT-NH$_2$.

Fig. 2. Zeta potential curves of SWCNT (triangles) and SWCNT-NH$_2$ (circles).

3.2 Single adsorption of OMPs from water – isotherms and mechanism

The adsorption isotherms yield the most important information about the distribution of the adsorbate molecules between the liquid and the solid phase when the adsorption process reaches equilibrium. Fig. 3 shows the isotherms of DFN, PCP, and OP on SWCNT and SWCNT-NH$_2$. The sorption of some OMPs on SWCNT occurs in different manners than on SWCNT-NH$_2$. According to, the Giles classification, OP adsorption isotherms correspond to the L1 and L2 type for SWCNT and SWCNT-NH$_2$ respectively. This type of isotherm is typical for microporous adsorbents [16], that is consistent with structural properties of SWCNT and SWCNT-NH$_2$ obtained from nitrogen sorption desorption measurements. The initial curvature in the L type isotherm shows that as more sites in the adsorbent are filled it becomes increasingly difficult for a bombarding adsorbate molecule to find an empty site available. This implies that molecules are adsorbed non-vertically or there is lack of strong competition from the solvent. The shapes of the DFN and PCP isotherm curves resembles the L2 type and the H2 type for SWCNT and SWCNT-NH$_2$. The H type isotherm is a special case of the L curve, in which the solute has high affinity for the adsorbent surface because of ion-ion attraction [17, 18]. Thus, we can notice that adsorption mechanism of given OMPs was similar for SWCNT (due to L – shape of isotherm), while for SWCNT-NH$_2$ two different sorption behaviours occurred, first when OP is an adsorbate, the second for PCP and DFN.

Significant differences were observed in sorption capacity of SWCNT and SWCNT-NH$_2$ for given OMPs. The sorption uptake changes in the following order: OP > PCP > DFN for SWCNT and DFN > PCP > OP for SWCNT-NH$_2$, respectively. In order to elucidate the factors controlling adsorption mechanism and sorption affinity of OMPs we should consider their hydrophobicity, molecular weight, ionic form and solubility. A few times higher adsorption of OP on SWCNT in comparison to the two other adsorbates can be ascribed to the different solubility in water, which is 7, 10, 50 mg/L for OP, PCP and DFN, respectively. Affinity of the adsorbate to sorption is larger when solubility is low [19], therefore it explains very high sorption uptake of OP and very low uptake of DFN by SWCNT. Effect of molecular weight and log K_{ow} of studied OMPs seems to be negligible because these properties were similar (Table 1). For SWCNT-NH$_2$, PCP and DFN were found as easily absorbable compounds, while OP as hardly. It can be explained by chemical nature of these compounds at pH 5. When solution pH is around 4.5, both PCP and DFN are dissociated, in contrast to OP (Table 1). When we consider that surface charge of SWCNT- NH$_2$ is positive at pH 5, we can assume that sorption of PCP and DFN was enhanced by ionic attraction. Mechanism does not occur for SWCNT due to neutral form at pH 5.
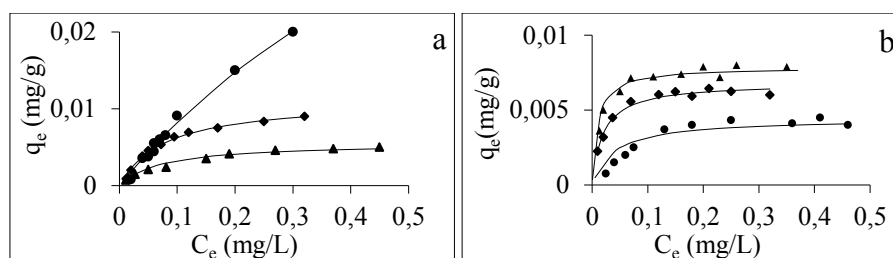

Fig. 3. Adsorption of PCP (diamonds), OP (circles) and DFN (triangles) by SWCNT (a) and SWCNT-NH$_2$ (b) from single adsorbate solution.

The Langmuir, Freundlich and Dubinin-Radushkevich models were used to describe the experimental data, and the relevant parameters derived from these models are presented in Table 3. The fitting degree (based on correlation factors R^2) decreases in the following order: Langmuir, Dubinin-Raduskevich and Freundlich. Therefore, the subsequent discussion will be mostly concentrated on the parameters obtained from Langmuir and Dubinin-Radushkevich computations. The values of adsorption energy for both SWCNT and SWCNT-NH$_2$ lie in the range of physical adsorption, apart from OP adsorption on SWCNT. Higher values of energy for SWCNT-NH$_2$ can suggest that this sorbent mainly induces the adsorption of OMPs coming from strong electrostatic interactions [20].

From the value of maximum adsorption capacity derived from Langmuir and Dubinin-Radushkevich was found that OP and PCP were better adsorbed by SWCNT than SWCNT-NH$_2$. Maximum adsorption capacity of PCP was 0.011 mg/g and 0.0068 mg/g on SWCNT and SWCNT-NH$_2$, respectively, and for OP: 0.074 mg/g (SWCNT) and 0.0044 mg/g (SWCNT-NH$_2$). On the one hand, it can be a consequence of the differences in structural properties of the adsorbents. As many authors suggest higher sorption capacity is found for the adsorbents with high specific surface area [14, 21]. Specific surface area (SSA) of SWCNT is around three times higher than SWCNT-NH$_2$, thus both OP and PCP were better adsorbed by SWCNT than SWCNT-NH$_2$. An interesting exception is noticed for DFN adsorption, because higher maximum sorption capacity was observed for SWCNT-NH$_2$. This suggests that sorption behaviour, when DFN is adsorbate, is different for SWCNT and SWCNT- NH$_2$. This fact was also revealed by isotherm type, discussed above. In the other words, normal dependence of SSA and sorption capacity does not apply for DFN adsorption

6

by SWCNT-NH$_2$, suggesting the presence of specific interactions between adsorbate and adsorbent, like for an example ionic interactions and Van der Walls forces.

Table 3. Parameters of Langmuir, Freundlich and Dubinin - Radushkevich equations and correlation coefficients for the adsorption of OMPs on carbon nanotubes from single solution.

Model		Langmuir			Freundlich			Dubinin-Radushkevich		
Adsorbent	Adsorbate	a_L (mg/g)	b (L/mg)	R^2 (-)	K_f ((mg/g) L/mg)^n)	n (-)	R^2 (-)	a_{DR} (mg/g)	E (kJ/mol)	R^2 (-)
SWCNT	DFN	0.0054	14.99	0.974	0.0079	2.15	0.9715	0.0126	12.9	0.9907
	PCP	0.011	12.61	0.993	0.0160	2.23	0.937	0.0237	10.0	0.9445
	OP	0.074	1.25	0.992	0.0579	1.16	0.986	0.0817	7.0	0.9700
SWCNT- NH$_2$	DFN	0.0082	68.99	0.963	0.0087	8.99	0.867	0.0126	18.3	0.8891
	PCP	0.0068	50.00	0.975	0.089	4.34	0.849	0.0098	14.1	0.9278
	OP	0.0044	25.00	0.965	0.0039	9.99	0.893	0.0084	15.8	0.9063

3.3 Competetive adsorption of OMPs

Fig. 4 presents adsorption isotherms of DFN, PCP and OP from bicomponent adsorbate solution. Shape of these isotherms, both for SWCNT and SWCNT-NH$_2$ was similar to the single adsorption system. It means that second adsorbate in the solution did not cause significant change in adsorption mechanism of given OMPs. On the contrast, adsorption magnitude changed greatly as an effect of competition between some adsorbates. It was observed that the Langmuir and Dubinin-Radushkevich equations described the adsorption of OMPs with better correlation coefficient (Table 4), meaning that heterogeneous surface or porous structure played an important role in their adsorption and different binding sites with several adsorption energies were involved. Excluding adsorption of OP on SWCNT, adsorption energy of studied OMPs is higher than 8 kJ·mol^{-1}, indicating physical sorption. Comparing the values of adsorption energy for single and bicomponent solutions we can notice that adsorption energy was slightly lower for competitive adsorption. Take, for an example, adsorption of DFN by SWCNT-NH$_2$, energy is 18.3 kJ·mol^{-1}; 11.2 kJ·mol^{-1}; 14.1 kJ·mol^{-1} for single solution and for bicomponent solutions with PCP and OP, respectively. Similarly, from Langmuir and Freundlich models, the constants b and n, describing the affinity of binding sites and adsorption intensity, are lower for bicomponent system than for single, independently from adsorbent.

Table 4. Parameters of Langmuir, Freundlich and Dubinin - Radushkevich equations and correlation coefficients for the adsorption of DFN, PCP and OP on carbon nanotubes from single and bicomponent solutions.

| Adsorbent	Adsorbate solution system	Langmuir			Freundlich			Dubinin-Raduskevich		
		a_L (mg/g)	b (L/mg)	R^2 (-)	K_f ((mg/g) L/mg)^n)	n (-)	R^2 (-)	a_{DR} (mg/g)	E (kJ/mol)	R^2 (-)
SWCNT	DFN	0.0055	14.00	0.978	0.0078	2.15	0.9715	0.0126	12.9	0.9907
	DFN&PCP	0.0045	8.50	0.995	0.0057	2.08	0.946	0.0123	11.2	0.973
	DFN&OP	0.0029	6.98	0.965	0.0034	2.00	0.938	0.0072	10.05	0.9769
SWCNT - NH$_2$	DFN	0.0079	102.00	0.967	0.0087	8.99	0.867	0.0126	18.3	0.8891
	DFN&PCP	0.0031	20.50	0.951	0.0042	2.50	0.9095	0.0088	11.2	0.9463
	DFN&OP	0.0062	43.00	0.979	0.0083	3.48	0.865	0.0134	14.1	0.942
SWCNT	PCP	0.0112	12.61	0.993	0.016	2.23	0.937	0.0237	10.0	0.9445
	PCP&OP	0.0080	5.00	0.992	0.01	1.419	0.973	0.0125	7.0	0.9832
	PCP&DFN	0.153	5.63	0.997	0.02	1.64	0.9803	0.0237	10.0	0.9897
SWCNT - NH$_2$	PCP	0.0068	50.00	0.975	0.0087	8.99	0.8831	0.0097	14.1	0.9278
	PCP&OP	0.0055	30.00	0.940	0.007	3.34	0.8255	0.0093	11.2	0.7829
	PCP&DFN	0.0024	18.00	0.984	0.002	3.47	0.936	0.0032	12.0	0.9504
SWCNT	OP	0.0752	1.22	0.992	0.0579	1.16	0.987	0.0817	7.0	0.970
	OP&PCP	0.088	5.00	0.993	0.0108	1.43	0.972	0.0146	7.0	0.984
	OP&DFN	0.0347	2.34	0.988	0.036	1.32	0.975	0.0361	7.0	0.9868
SWCNT - NH$_2$	OP	0.0047	25.0	0.965	0.0392	9.99	0.893	0.0084	10.0	0.906
	OP&PCP	0.0031	17.0	0.974	0.0044	2.50	0.899	0.0052	10.0	0.955
	OP&DFN	0.0023	18.0	0.983	0.0019	8.99	0.955	0.0031	12.0	0.949
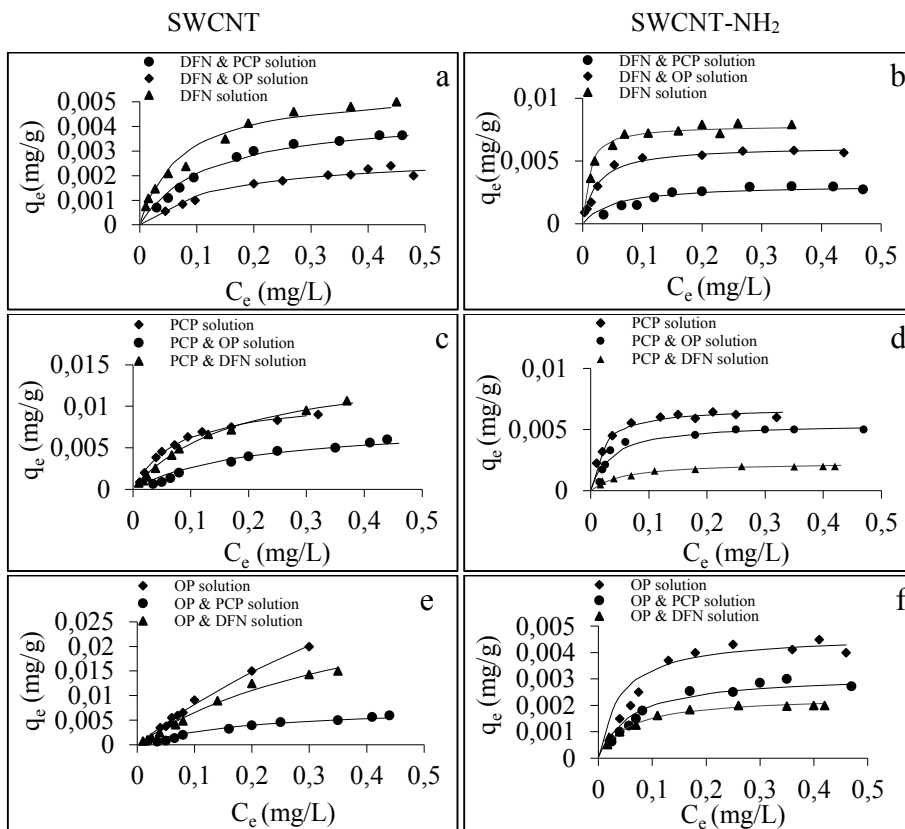
Fig. 4. Adsorption isotherms of DFN (a, b), PCP (c, d) and OP (e, f) by SWCNT and SWCNT-NH$_2$ from single solution and two bicomponent solutions. The solid lines represent Langmuir model fit.

It was found that between some of OMPs intense competition occurred, expressed as competition strength (Table 5). More specifically, for SWCNT stronger competition was observed between DFN and OP with competition strength of 61.7% than between the DFN and PCP with competition strength of 31%, while for SWCNT- NH$_2$, opposite tendency was observed i.e. competition strength was 69% and 42% between DFN and PCP and between DFN and OP respectively (Fig. 4a, 4b). Similar results were obtained for PCP adsorption on SWCNT-NH$_2$ in the presence of DFN and OP (Fig. 4d). In that case, competition strength was at the level of 70% and 23% for DFN and OP as coadsorbates, respectively. Interesting exception was observed for PCP adsorption on SWCNT, in the presence of DFN. Competition strength was 4.4% suggesting negligible impact of DFN on PCP adsorption. These results can be explained when we compare adsorption mechanism of given coadsorbates. Adsorption of DFN, in the presence of OP and PCP, on SWCNT was very low. Lower solubility of OP and its undissociated form (when pH<pKa) resulted in more preferential adsorption of OP than DFN on SWNCT. Similarly, DFN adsorption was inhibited by PCP as coadsorbate. Probably due to a role of ∏-∏ electron-donor-acceptor interaction and hydrogen bonds in PCP adsorption [22]. Strong competition between DFN and PCP on SWCNT-NH$_2$ was a result of the same mechanism of their adsorption, which was mainly electrostatic attraction. As was documented in the first part of this study, DFN was hardly adsorbable on SWCNT and easily on SWCNT-NH$_2$, mainly due to its high solubility in water and dissociated form at pH 5. Therefore, dominant adsorption strength of DFN is ionic attraction, that occurs only for SWCNT-NH$_2$ due to its positive charge at given

solution pH. The same adsorption mechanism was documented for PCP and therefore strong competition between these adsorbates was observed.

Separate discussion has to be done for OP adsorption with its coadsorbates (Fig. 4e and 4f). As was mentioned, OP was very easily adsorbable by SWCNT from single solution system. Moreover, competition between OP and DFN in bicomponent solution, was relatively low with competition strength at the level of 3%. This effect relates to negligible adsorption of DFN on SWCNT. Higher competition about sorption sites was observed between OP and PCP. Due to both sorbates can be adsorbed by hydrogen bonding and $\prod$-$\prod$ interactions. Similar adsorption mechanism of PCP and DFN induces mutually competition. On the one hand, OP should be more preferentially adsorbed on SWCNT, on the other hand for two coadsorbates with different size, the smaller one can access the porosity in greater amount [23]. Thus, PCP with smaller size than DFN (expressed as equivalent width and molar volume – Table 1) inhibits DFN uptake. Surprisingly, coadsorbate size did not affect adsorption of OP on SWCNT-NH_2. A careful observation of Fig. 4f shows that competition was higher with coadsorbate molecules with higher size (DFN) than with smaller size (PCP). In other words, considering size of coadsorbates (PCP and DFN) we could have expected that higher competition will occur with PCP due to its lower steric hindrance. In fact, competition effect on SWCNT-NH_2 was clearly controlled by ionic attraction, that was stronger for DFN.

Table 5. Competition strength (calculated for selected equilibrium concentration) between coadsorbates in bicomponent solution.

Bicomponent solution	SWCNT	SWCNT- NH_2
DFN&PCP	31.0%	69.8%
DFN&OP	61.7%	42.4%
OP&PCP	73.7%	32.8%
OP&DFN	3.0%	51.5%
PCP&DFN	4.4%	70.0%
PCP&OP	56.0%	22.8%

4 Conclusions

The adsorption behavior of OMPs in single and bicomponent solution was evaluated. Adsorption of three OMPs by SWCNT and SWCNT-NH_2 were compared with each other. From the shape of isotherms, similar adsorption mechanism of OMPs was observed for SWCNT and two different behaviors for SWCNT-NH_2 – first for OP, the second for PCP and DFN. In addition, the loadings of OMPs on adsorbents decreased in the following sequence: OP > PCP > DFN for SWCNT and DFN > PCP > OP for SWCNT-NH_2. Favorable adsorption of OP and PCP by SWCNT was an effect of their low solubility in water and sigma-sigma interactions. Easy adsorption of DFN and PCP by SWCNT-NH_2 was assigned to electrostatic attraction between dissociated form of PCP and DFN and positively charged sorbent surface at pH 5.

It was found that the values of adsorption energy for both sorbents indicated physical adsorption, apart from OP adsorption on SWCNT. Higher values of energy for SWCNT-NH_2 can suggest that this sorbent mainly induces the adsorption of OMPs coming from strong electrostatic interactions.

From results obtained in bicomponent solution, different competitive effects were observed. Take, for an example adsorption of DFN with its coadsorbates PCP and DFN by SWCNT, OP inhibited DFN adsorption much stronger than PCP. For comparison, when DFN

was adsorbed by SWCNT-NH$_2$, opposite tendency was observed, stronger inhibition of DFN adsorption was caused by PCP. This is due to control of PCP and DFN adsorption on SWCNT-NH$_2$ by electrostatic attraction. on the other hand, between some coadsorbate, a lack or negligible competition was observed, like for OP and PCP adsorption on SWCNT with DFN as coadsorbate. Comparing the values of adsorption energy for single and bicomponent solutions we can notice that adsorption energy was slightly lower for competitive adsorption.

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