



Eidgenössische Technische Hochschule Zürich  
Swiss Federal Institute of Technology Zurich

# Sorption of Organic Pollutants by Carbon Nanoparticles

TERM PAPER

BY

DANIELE VERGARI

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TUTOR:

DR. MARTIN KRAUSS

EAWAG AQUATIC RESEARCH, DUEBENDORF  
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## 1 Abstract

Nanoparticles are widely distributed in different applications and also released into the environment. The aim of this paper is to discuss whether mathematical models are useful for adsorption prediction and to evaluate applications of fullerene and carbon nanotubes adsorbing organic pollutants. In the papers there were two methods applied to collect the data, batch and flow experiments which are presented here. The mathematical models used to fit the obtained data were mainly the Freundlich model, the Polanyi-Manes model and the Dubinin-Ashtakhov model. At a given equilibrium concentration of organic substance the adsorbed concentration per weight was highest on single walled nanotubes followed by multi walled nanotubes and then fullerene and increased with decreasing molecular size of the sorbate. Fullerenes showed irreversible adsorption-desorption hysteresis whereas nanotubes did

not. Competitive sorption was only relevant if the concentrations of the competitors were high and the concentration of the primary solute low. For this experiments, the Polanyi-Manes model was a good fitting model. In the reviewed paper, fullerene were found to be bad adsorbent for analytical application in contrast to convenience adsorbents. Carbon nanotubes instead are good adsorbents for resorcinol for example and could be used as a removal tool from wastewater as it was showed by an other paper. There is evidence, that nanoparticles affect the fate of organic pollutants, hence there is more research needed to understand the processes of adsorption and desorption on organic matter better.

## 2 Introduction and Motivation

The increasing application of engineered nanoparticles, among them carbon based structures like fullerenes and carbon nanotubes (CNT), will probably result in their release into the environment in the future. An indication for an environmental problem due to nanoparticles is one estimate for the production of engineered nanomaterials. It was 2000 tons in 2004, expected to increase to 58000 tons in 2011-2020 [1]. Due to their new physical characteristics as a material the application of nanoparticles are found in many different areas, such as in households, electronics, biomedicine, cosmetics and many more materials and engineering [1]. This paper discusses the potential of sorption of organic pollutants on these nanoparticles and the possible co-transport. Several studies exist, which address to the toxicity of organic pollutants and the toxicity of nanoparticles. To date, only few studies exist which combine the interaction between nanoparticles and organic pollutants. Most of the studies deal with carbon nanoparticles as sorbent for solid-phase extraction under lab conditions (e.g. Ballesteros et al. [4]). However, there were some studies which addressed to the adsorption and desorption of organic pollutants, namely polycyclic aromatic hydrocarbons (PAH) to carbon nanoparticles in an environmental scale (i.e. Yang et al. [6], [5], [7]).

In the large family of fullerenes the Buckminster fullerene ( $C_{60}$ ) is the most investigated [1]. Buckminster fullerene have a spherical structure and consist of 60 carbon atoms. They have a molar weight of 720 g/mol and a diameter of approximately 1nm [5]. Carbon nanotubes differ much more in diameter, length and therefore number of atoms and molar weight. Carbon nanotubes can either be single walled (SWCNT) or multi walled (MWCNT) and the end can be closed or open. Figure 1 shows the structure of a buckminster fullerene and of carbon nanotubes.

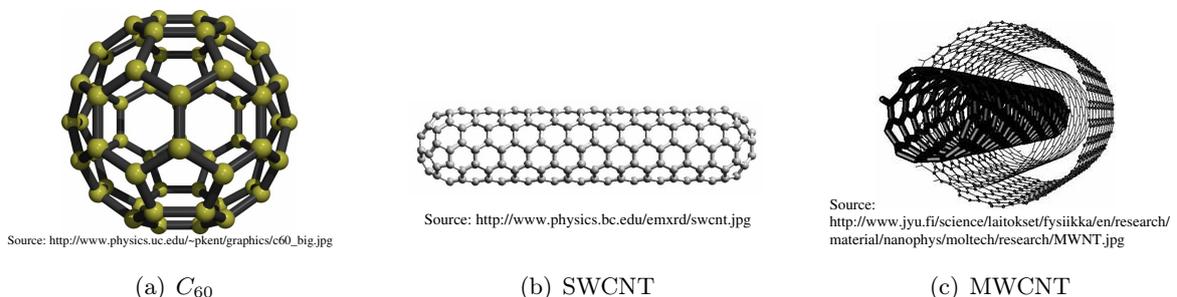


Figure 1: the buckminster fullerene (a) is a spherical structure made out of 60 carbon atoms. Carbon nanotubes can either be single walled (SWCNT (b)) or multi walled (MWCNT (c)) and can differ in length, diameter and be closed or open ended.

Most organic pollutants (e.g. dioxin, PAH's) are sterically detained to enter the inner space of fullerenes and therefore the only place for interaction is the surface of the fullerene. CNT can vary in diameter, hence the interaction with organic pollutants might occur in the inner cavity and between the walls if the tubes are open and on the surface (see figure 1).

Figure 2 shows possible behavior of organic pollutants in the presence of carbon nanoparticles. Figure 2a.) indicates a possible ecotoxicological problem; organic pollutants, which are normally hindered to pass the cells membrane may use nanoparticles as carrier, as it is known that nanoparticles are able to pass the membrane [1]. Figure 2b.) demonstrates a possible positive impact of nanoparticles; some organic pollutants adsorb very strongly on nanoparticles (see Liao [3]) and therefore can be used as a removal tool for example in waste water treatment. The organic-pollutant-nanoparticle complex settles down and might be no longer mobile and bioavailable [1]. On the contrary, figure 2c.) shows the opposite, strong sorption of pollutant to nanoparticle may result in a higher mobility of a pollutant which is normally immobile.

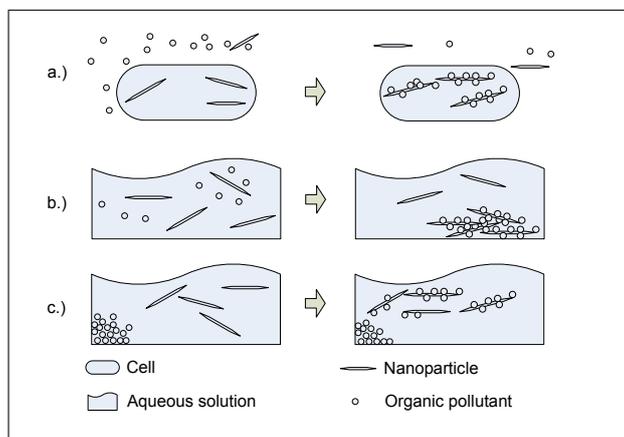


Figure 2: a.) transport into the cell, b.) sedimentation, c.) co-transport.

## 2.1 Fundamentals of the Adsorption Theory

Adsorption is a phenomenon that occurs on the surface or pores of a solid (sorber), is characterized by the available surface area and is a function of the partial pressure (or concentration in aqueous solutions) of a chemical species (solute) [2]. Adsorption occurs if the attractive force between the solute and adsorbent is greater than the cohesive energy of the substance itself. To maintain a favorable free-energy driving process (i.e. a negative  $\Delta G$ ), the  $\Delta H$  must be greater in magnitude than the  $\Delta ST$ , because adsorption leads to a loss of entropy ( $\Delta S$ ). When a solute adsorbs on a surface the available space for further adsorption becomes smaller. Due to the heterogeneity of the surface, the energy which is released during adsorption is also decreasing during the process. First, the places with the highest energy release are occupied then the next, and so on. Adsorption is typically nonlinear due to the energy heterogeneity and the available sites for adsorption.

Table 1 is made by Yang et al. [6] but modified and gives an overview of five widespread models which describe adsorption. As said above, adsorption is typically nonlinear and therefore the models which describe adsorption at best are neither.

Table 1: five different adsorption models, table by Yang et al. [6], modified.  $q_e$  = equilibrium sorbed concentration,  $K_f$  = Freundlich affinity coefficient,  $C_e$  = equilibrium solution phase concentration,  $C_s$  = maximum concentration due to solubility,  $1/n$  = Freundlich exponential coefficient,  $B$  = BET constant,  $Q^0$  = sorbed capacity,  $K_d$  = affinity coefficient,  $\epsilon_{sw}$ ,  $\epsilon$  effective adsorption potential,  $E$  = correlating divisor,  $a$  and  $b$  = fitting parameters

name	equation	linear form
Freundlich (FM)	$q_e = K_f C_e^{1/n}$	$\log q_e = \frac{1}{n} C_e + \log K_f$
Langmuir (LM)	$q_e = \frac{Q^0 C_e}{K_d + C_e}$	$\frac{1}{q_e} = \frac{1}{C_e Q^0} + \frac{K_d}{Q^0}$
Brunauer-Emmett-Teller (BET)	$q_e = \frac{B Q^0 C_e}{[(C_s - C_e)^{1+(B-1)(C_e/C_s)}]}$	$\frac{C_e}{q_e(C_s - C_e)} = \frac{B-1}{B Q^0} \frac{C_e}{C_s} + \frac{1}{B Q^0}$
Polanyi-Manes (PMM)	$\log q_e = \log Q^0 + a(\epsilon_{sw})^b$	nonlinear
Dubinin-Ashtakhov (DA)	$\log q_e = \log Q^0 - (\epsilon/E)^b$	nonlinear

In this paper only a very short overview of the different models is given. The *Freundlich Model* does not approach mathematically the linearity of adsorption in low concentrations nor the saturation at high concentrations. But in general, the Freundlich Model offers a simple mathematical tool to describe the adsorption in a small concentration range [2]. The *Langmuir Model* considers saturation by the assumption of a well defined number of identical active sites on the surface. The model shows a rather linear band at low relative concentrations and a saturation behavior at relative high concentrations. Relative concentration means the concentration in solution divided by the solubility concentration. A advancement of the Langmuir Model is the *Brunauer-Emmett-Teller Model* (BET), which considers sublayer to multilayer adsorption. But the theory contends a infinite growth of layers, which does not proceed in reality. The most used model in this paper is the *Polanyi-Manes Model* (PMM), developed from Manes in 1998 based on the Polanyi theories from 1916 [2]. The Polanyi theories introduce a potential  $\epsilon$ , and the larger this potential is the more likely adsorption occurs, at  $\epsilon = 0$  the adsorption space is saturated at the given concentration. The highest potential is found in the finest pores. For further information of the models, please see: C. T. Chiou, Partition and Adsorption of Organic Contaminants in Environmental Systems, [2]. The Dubinin-Ashtakov Model (DA) is a derivative of the PMM.

## 2.2 Approaches to Determine Sorption Phenomenons on Nanoparticles

As said above, carbon nanomaterials can be fullerenes or carbon nanotubes. There is one study of Ballesteros et al. [4] made in 2000 which discussed the analytical potential of  $C_{60}$  fullerene as a sorbent for organic and organometallic compounds from aqueous solutions for the first time. In this paper only the sorption of organic compounds to the fullerenes will be looked at. They examined the sorption efficiency of a column filled with  $C_{60}$  fullerene. The experimental setup of these experiments is described in section 3. *Methods*.

A new article by Liao et al. addresses to the adsorption of resorcinol (1-3-benzenediol, as a representative for phenolic derivatives) on multi walled carbon nanotubes [3]. In his study, it was the first time that MWCNT adsorbing phenolic derivatives was investigated.

Yang et al. discussed in their studies adsorption [6], desorption [5] and the competitive sorption [7] of mainly polycyclic aromatic hydrocarbons (PAH) to carbon nanomaterials. They chose PAH because of their high hydrophobic behavior and high toxicity [6]. Yang et al. focused on the modeling part and used some sorption theories (described above) which were used to describe sorption on surfaces in general or on charcoal and tried to adapt them to carbon nanomaterials.

The goal of this paper is reviewing the work which has been done in the field of sorption of organic compounds on nanoparticles including the applied sorption models.

## 3 Methods

### 3.1 Batch Experiments

To determine the amount of sorbed organic pollutants one can use different experimental setups. Liao et al. [3] made batch experiments with untreated and with  $HNO_3$  treated MWCNT. They prepared the acid-treated MWCNT with concentrated nitric acid then filtered and washed the nanotubes and dried them again. The acidification of MWCNT changes their surface significantly, which will be discussed later. Subsequently they mended the MWCNT with distilled water containing different concentration of different phenolic derivatives and mixed them after 20min of sonication for 10 more hours. After that, they measured the concentration of phenolic derivatives in the solution and calculated the adsorbed amount with equation (1).

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

In this equation  $q_e$  is the adsorbed amount by MWCNT in mg/g after equilibrium,  $C_0$  the initial concentration in mg/ml,  $C_e$  the equilibrium concentration (mg/ml),  $V$  the solution volume in ml and  $m$  the amount of added MWCNT in g. They made the same experiments with untreated and treated MWCNT.

A similar experiment to the one presented above was conducted by Yang et al. [6]. The adsorption isotherms were obtained using a batch equilibrium technique. They used screw cap vials for the experiments which they filled with either fullerenes or CNT's and a background solution (pH7) containing a biocide ( $NaN_3$ ) to avoid biological effects. Following that they injected  $^{14}C$ -labeled organic compounds (i.e. phenantrene, pyrene or naphthalene) into the vials and let the solution equilibrate for 5 days. After centrifugation they mixed 1ml of the supernatant with a Scintiverse cocktail and analyzed the concentration by liquid scintillation counting. The adsorbed solute by the nanomaterials was simply calculated by mass difference. They assumed that the difference of what they put in and what they got out is sorbed on the nanoparticle.

For the desorption experiments Yang et al. [5] proceeded the same way but took more of the supernatant as in the previous experiment and refilled the vials with background solution. After additional equilibration (5days), they measured the activity of the supernatant with the same method and calculated the sorbed amount again.

The competition experiments by Yang et al. [7] were carried out the same way as the adsorption experiments except for the following: mixtures of  $^{14}C$ -labeled and unlabeled primary solute as well as unlabeled competing solutes were mended into the suspensions [7]. So the only labeled compound was the primary solute, and this was measured as free concentration. If there is more of this primary compound in solution than in a single solute system, some of the available places must have been occupied by a competitor.

### 3.2 Flow Experiments

Ballesteros and his colleagues [4], used the setup shown in figure 3.

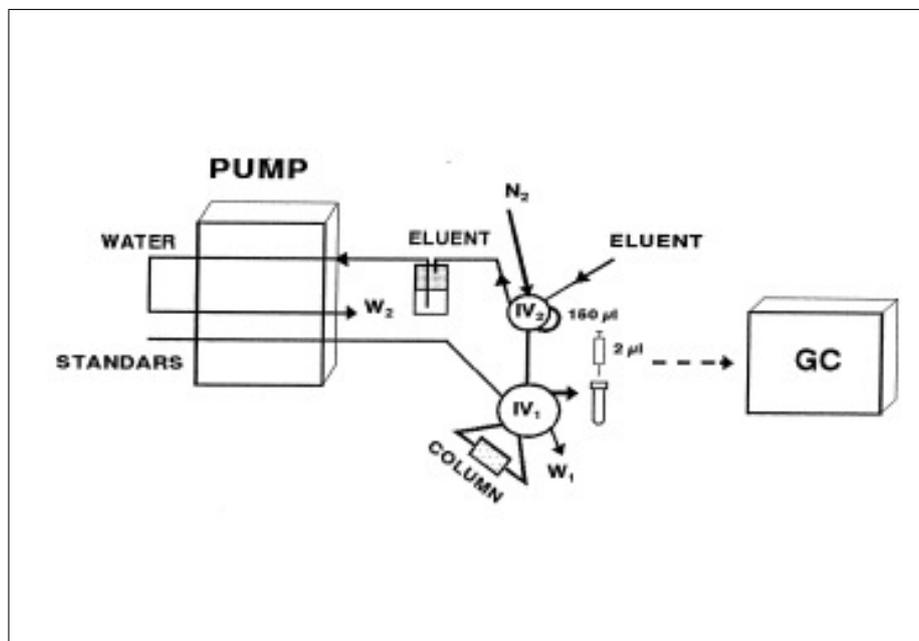


Figure 3: Flow injection manifolds for on-line adsorption of organic compounds. IV = injection valve, W = waste, GC = gas chromatograph with flame ionization detection. Figure by Ballesteros et al. [4]

The experiment was carried out in three steps. In the first step they let pass the standard aqueous solution containing the pollutant at different concentrations (i.e. N-methylcarbamates, phenols, polycyclic aromatic hydrocarbons, amines) through the sorbent column (located in the loop of IV<sub>1</sub>). In a second step they dried the column with nitrogen coming from valve 2 (IV<sub>2</sub>) and filled at the same time the loop of IV<sub>2</sub> with the eluent (ethyl acetate or toluene). In the last step, valve 2 was switched and the eluent passed with a stream of nitrogen through the column to elute the retained analytes. Subsequently the eluate was collected and injected manually to the gas chromatograph (GC).

## 4 Results

Fullerenes and Carbon nanotubes have different geometries as described in the introduction part and shown in figure 1 and therefore also different spaces for adsorption. Theoretically, all of the surface of a fullerene is available for adsorption, but in the experiments there was found to be less (Yang et al. [6]).

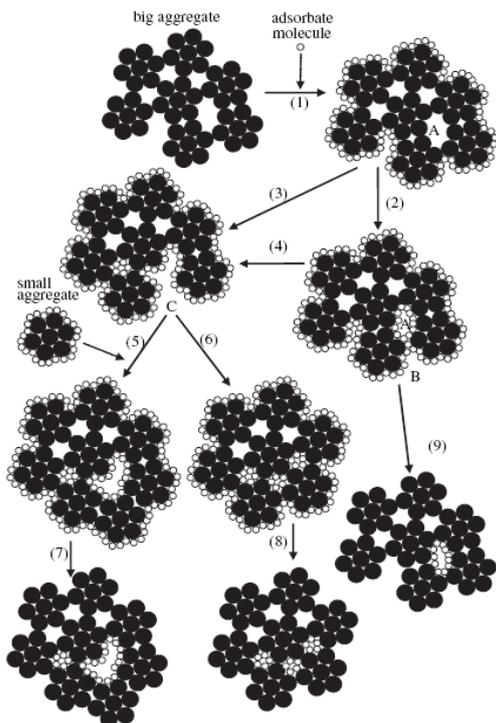


Figure 4: Adsorption-desorption scheme of PAHs for fullerene. Step (1): adsorption; step (2): penetration into space A; step (3): rearrangement leading to opening of space A; step (4): deformation at site B leading to opening of space A; step (5): rearrangement at site C by combining with another small aggregate; step (6): rearrangement at site C; steps (7), (8) and (9): desorption, showing entrapment of organic molecules in the closed interstitial spaces. Figure and description by Yang et al. [5]

Yang et al. [5] found only the outer surface of CNT to be available space for adsorption, neither the inner cavities nor the inter wall space (see later). They also observed a spontaneous aggregation of nanoparticles under lab conditions and suggested the same in the environment. Hence the maximum space available for adsorption of organic molecules is smaller than the calculated surface of the particles. Forming aggregates will give place for intra-aggregates space. Fullerenes aggregation (figure 4) may result in closed interstitial spaces in small aggregates and the small aggregates can form bigger ones with space between the small ones. Cylindrical nanoparticles like the nanotubes cannot form interstitial spaces due to their shape, i.e. their length. Figure 4 shows the possible pathway for organic pollutants to adsorb on fullerenes and aggregates.

The results of the adsorption batch experiments conducted by Yang et al. [6] are shown in figure 5. At a given equilibrium concentration ( $C_e$ , figure 5A), adsorbed concentrations ( $q_e$ ) on multi walled carbon nanotubes (MWCNT15, the 15 stands for their length in  $nm$ ) increased from naphthalene to phenanthrene and pyrene, consistent with their hydrophobicity and their molecular weights [6]. The solid lines are fitted by the Polanyi-Manes-Model and the dashed lines represent linear isotherms. Figure 5B shows the sorption of phenanthrene on SWCNT, MWCNT of different length and fullerene. At a given equilibrium concentration, SWCNT adsorb the most phenanthrene, followed by all the MWCNT and then (about two orders of magnitude lower) fullerene.

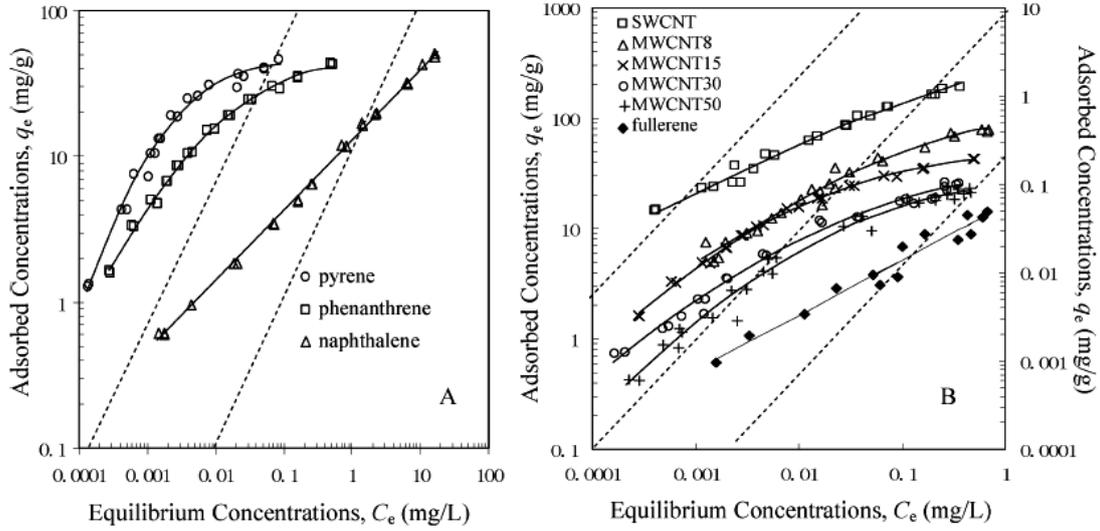


Figure 5: Adsorption isotherms of PAHs onto carbon nanomaterials: (A) pyrene, phenanthrene and naphthalene onto MWCNT15; (B) phenanthrene onto SWCNT, MWCNTs and fullerene. Solid lines are the isotherms fitted by Polanyi-Manes-Model. Dashed lines with a slope of 1 on log scale represent linear isotherms. Figure and description by Yang et al. [6]

They investigated further the desorption of pyrene, phenanthrene and naphthalene from fullerenes, SWCNT and MWCNT [5]. They found irreversible adsorption-desorption hysteresis for fullerenes but there was no observed hysteresis for CNT's (data not shown).

As it could become relevant for environmental scale, Yang et al. [7] investigated the competition for adsorption on nanomaterials and found only competition at low concentrations of primary solute and high concentrations of competitors (figure 6).

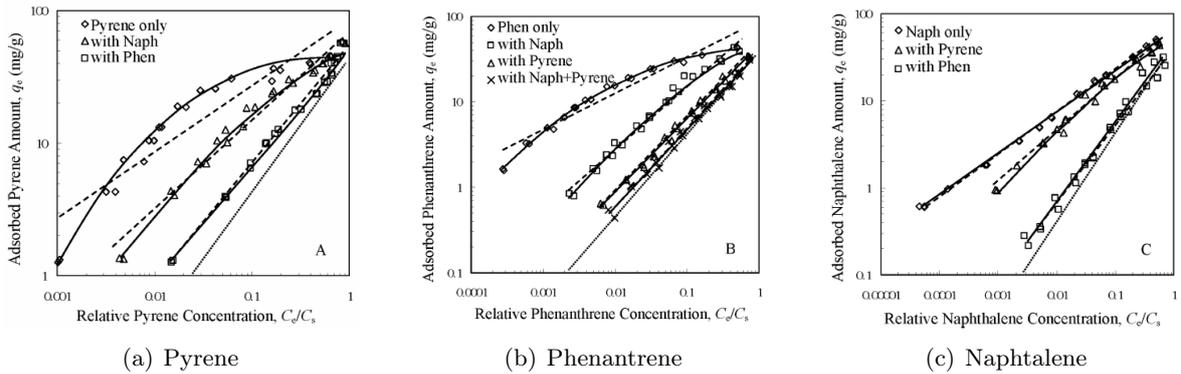


Figure 6: Sorption isotherms of PAH's on MWCNT15 without or with competitors at  $C_e/C_s = 1$ : (A) pyrene alone and with naphthalene or phenanthrene as competitor; (B) phenanthrene alone and with naphthalene, pyrene, or their mixture as competitors; and (C) naphthalene alone and with pyrene or phenanthrene as competitor. All isotherms were normalized by the primary solute solubility. Solid lines the isotherms fitted by DA model; long dashed lines, the isotherms fitted by Freundlich model. Short dashed lines represent the limits of competition, computed using DA model with  $E = 5.71$  kJ/mol,  $b=1$ , and  $Q^0$  of single-solute isotherms. Phen and Naph represent phenanthrene and naphthalene, respectively. Figure and description by Yang et al. [7]

The dashed lines in figure 6 represent the isotherms fitted by the Freundlich model (see table 1) and are not fitting the data well at the single solute system but become better as competition occurs. The solid lines are the isotherms fitted by the Dubinin-Askathov model and fit all of the data better. As expected, at low relative concentration the adsorbed amount of organic compound is also low but increases with increasing  $C_e/C_s$  ratio. The isotherms of the single compound start below than the isotherms of the competition experiments but they all end at the same point, at high  $C_e/C_s$  ratios an high adsorbed amount. The isotherms of the competition experiments are much steeper and more linear than the ones which were conducted with only one organic compound.

There is evidence shown above that organic pollutants sorb to nanoparticles. Ballesteros et al. [4] analyzed a possible application of this occurring adsorption of organic pollutants to carbon nanoparticles namely fullerenes. They found, that their High-Performance-Liquid-Chromatography-like column filled with fullerene never sorbed more than 63% of the total amount of organic compound which was added to the solution. For the phenolic compounds they investigated the sorption capacities over a wide pH range from 1-10 as shown in figure 7 and compared the sorption capacity of fullerene to the sorption capacity of a conventional sorbent (i.e. XAD-2). It can be seen, that the pH range for maximum adsorption of the fullerenes is much wider than the one of XAD-2. However all dashed lines (XAD-2, except with phenol) have higher chromatographic areas than the areas of the solid lines (nanomaterial) [4]. The sorption efficiency never exceeded 63%, whereas XAD-2 showed values over 90%. The

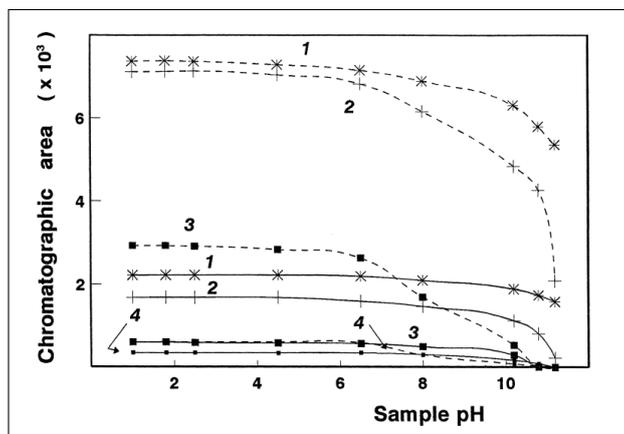


Figure 7: Influence of the sample pH on the adsorption of phenols on XAD-2 (dashed line) and C fullerene (solid line) using the flow system 60 of figure 3: 1=2-tert.-butylphenol; 2=3,4-dimethylphenol; 3=4-chlorophenol; 4=phenol. Sample=10 ml of aqueous solution containing 100 ng/ml of each phenol compound. Figure and description by Ballesteros et al. [4]

PAH showed no pH effects as it is assumed due to lack of acid protons. A further compound class investigated by Ballesteros et al. [4] were amines and had even a much weaker tendency to sorb on fullerenes (30%) than the compounds described above.

On the contrary to fullerenes, phenols and their derivatives (i.e. dichlorophenol or dinitrophenol) are relatively strong adsorbed by multi walled carbon nanotubes as it is shown by Liao et al. [3]. They showed, that about 60% of the total amount of adsorbed species in equilibrium adsorb in the first minute after contact of the solute and the sorbent. They also confirmed the available space for adsorption to be the cylindrical outer surface of the nanotubes and not the inner cavities nor the space between the walls. The effect of the pH

for uptake of resorcinol was rather negligible in the tested pH range (4-8). Above the pH of 8 resorcinol would oxidize in the basic condition. Below the pH of 6, the uptake of resorcinol slightly increases due to the better solubility of the compound. Figure 8 shows the difference between the acid-treated and the untreated MWCNTs. In general, the figure shows higher

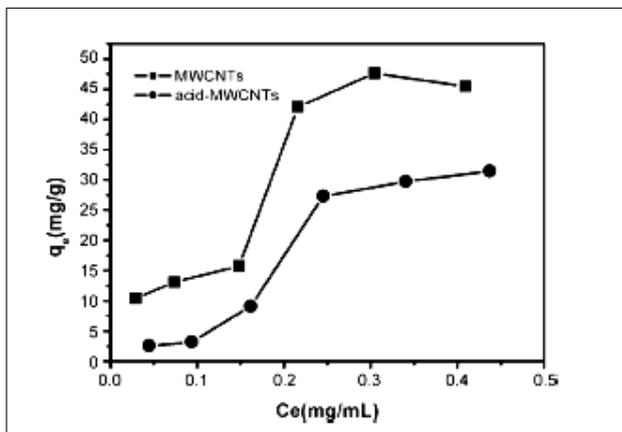


Figure 8: Adsorption isotherms of resorcinol onto MWCNTs and acid-treated MWCNTs. Figure by Liao et al. [3]

adsorbed amount by MWCNT after equilibrium ( $q_e$ ) with a higher equilibrium concentration ( $C_e$ ). The untreated multi walled carbon nanotubes show a higher adsorption capacity than the acid-treated tubes. Although the shape of the curve is quite the same but shifted along the y-axis.

## 5 Discussion

### 5.1 Sorption Models and Extent of Sorption and Desorption

Looking at figure 5, it is obvious that adsorption is a non-linear process by comparing the dashed lines with the solid curves. Hence, Yang et al. [6] tested nonlinear isotherm models like the Freundlich model, the Langmuir model, the BET model or the PM model like it is presented in table 1 for all the different experiments (Fullerenes, MWCNT, SWCNT and the different organic compounds) and the PMM was found to be the best fitting model, as shown in figure 5. This evaluation was due to the lowest mean weighted square error (MWSE) of the data attained by the PMM. But is the Polanyi-Manes-Model also a good fitting model for the adsorption process on carbon nanomaterials in general? As said in the introduction, the Polanyi theories introduce a potential  $\epsilon$  which describes the energy needed to remove a molecule from the attractive force of the sorbent, this is the first assumption. A second assumption is that this potential is temperature independent and the third assumption is that the adsorbed liquid has similar properties to the bulk liquid. Out of these three assumptions one can plot a temperature invariant curve, plotting the sorbed volume ( $q_e$ ) against the adsorption potential ( $\epsilon$ ). This curve is called the *characteristic curve*. Yang et al. [6] plotted this curve with data from experiments carried out at different temperatures and saw that the characteristic curve was congruent for every temperature. This is a indication that the PMM is feasible to describe the adsorption of PAH's by carbon nanomaterials. Further, the PMM consists of three parameters, namely adsorbed capacity ( $Q^0$ ) and the fitting parameters  $a$  and  $b$ . The

mass capacity  $Q^0$  could be transformed to the adsorbed volume capacity by calculating with the density of the solid phases of the solute. They found a negative correlation of the volume capacity to the molecular size. This is somehow logical, regarding that a molecule cannot enter a pore which is smaller than the molecule itself. Therefore, the available space for adsorption becomes smaller with increasing molecular size of the sorbate. Their conclusion out of these experiments is that adsorption is related to the molecular size.

In the desorption experiments (Yang et al. [5]), they found no adsorption-desorption hysteresis for CNT's but irreversible hysteresis for fullerenes. Desorption hysteresis can be true or just an experimental artifact. As experimental artifacts one can understand volatilization of the compound or not enough time to equilibrate. But they conducted all their experiments under quite identical conditions and found still significant hysteresis for fullerene but there was not any hysteresis observed for CNT's. This is an indication for true hysteresis. They suggested pore deformation to explain the hysteresis effect and in figure 4 one can see the pathway for possible hysteresis by pore deformation. Molecules cover the surface of an aggregate of fullerenes and the aggregate deforms itself and encloses some of the molecules, which are not able to desorb at later time anymore. So the reason for hysteresis is, according Yang et al. [5], the fact of building interstitial spaces. They pronounce as a direct evidence that the theoretical surface area of fullerene is 3-4 orders of magnitude higher than the experimental one. But this is rather a indirect evidence of forming interstitial spaces, the direct evidence following the surface fact is forming aggregates.

The data from the competition experiments shown in figure 6 (Yang et al. [7]) are fitted with the Freundlich model and the DA model, which is a derivative from the PMM. The DA model fitted well for all different experiments, as reported by low MWSE values. The Freundlich model fitted only for multi solute systems well. Since the Freundlich model is a special form of the DA model ( $b=1$ , Yang et al. [7]) it is also feasible for some cases. The curves of the single solute systems are so called *typical Polanyi isotherms* due to their non-linearity. Further the more similar two compounds are the greater is their competition as it is expected. Similarity in this case means physicochemical properties and molecular structure have only small differences. For example phenantrene has its physicochemical properties (e.g. water solubility) between pyrene and naphthalene, hence the competition between phenantrene and pyrene is greater than between pyrene and naphthalene. The good fits of the DA model indicates that the Polanyi theories are feasible for the description of single and multi solute sorption. The total volume of sorbate adsorbed in a tri-solute system was calculated like above and is much higher than in a bi-solute or single solute system and even higher than the total micro pore volume of MWCNT15. How can this be? This indicates, that micro pore filling alone cannot be the dominant mechanism. But the Polanyi theories are also applicable for surface adsorption with following assumptions: (a.) the potential energy of a uncoated MWCNT is more heterogeneous and higher than the potential of a coated one; (b.) sorbed solute is attractive for a other solute and let other solutes adsorb; (c.) the maximum adsorption capacity is determined by the available space on the adsorbent (Yang et al. [7]). Therefore it is possible to form multiple layers of different solutes on a MWCNT, and a higher adsorption volume can be attained in multi-solute systems than it would be assumed by only a single solute system. They conclude therefore, that sorption for a single solute is a mono layer and it is a multilayer for multi solute systems (the number of layers equals the number of solutes). As said above the non-linearity of the isotherms is because of the inhomogeneous surface and therefore the changing potential  $\epsilon$ . Looking at the more homogeneous surface of a coated MWCNT the adsorption isotherms of the competition experiments become more linear

than the isotherms in the single solute systems (Yang et al. [7]).

## 5.2 Discussion of the Application Experiments

Ballesteros et al. [4] found less than 63% of the total amount (2-Isopropoxyphenol) sorbed to the fullerene. The aim of their study was to describe the analytical potential of fullerenes. As they found this little recovery they pronounced the  $C_{60}$  fullerene as a bad adsorbent for organic compounds in general. A possible explanation might be the fact, that they passed the solution at a higher time rate than Yang et al ([6], [5], [7]) and therefore, there was not enough time for equilibration. Yang et al. let the solution equilibrate within 5 days, Ballesteros et al. about 10 minutes. Regarding the application of fullerene Ballesteros wanted to show, they are right when they pronounce fullerene as bad adsorbents for organic compounds. A sorbent designed for an analytical application should adsorb more than 63% and in a shorter time scale like XAD-2 for example. But regarding environmental scale: organic pollutants do adsorb on fullerene and they do it in very short time (less than 10 minutes) so one has to concern about the environment. Even though naphthalene as the weakest compound sorbed within 10 minutes over 20 %. The sorbed amount of naphthalene to CNT would be much more as showed by Yang et al. [6]. Looking on a environmental scale one has to consider, that fullerenes will form aggregates but are generally in solution and not packed in a column. Therefore the available space for adsorption (i.e. the surface) would be much more than in his experiments. A other very important issue found by Ballesteros et al. [4] was the fact, that the adsorption efficiency decreased with increasing polarity of the solute.

The second application which was presented above is the removal of resorcinol from water using carbon nanotubes. This study by Liao et al. [3] discussed the sorption capacity of pristine and acid-treated multi walled CNT's. As reported by Liao et al. [3], acid-treated MWCNT become more hydrophilic and have more active moieties on the surface (mostly carboxylic groups). These functional groups make the surface negatively charged and hinder also negatively charged organic pollutants (i.e. resorcinol,  $C_6H_4O_2^{2-}$ ,  $pK_a = 9.32$ ) to adsorb on the particle. A second effect of the acid treatment is the deformation of the surface of the nanotube. The pore size distribution and the specific surface will change significantly. They reported the micro pore volume decreased over 95% after acid treatment. But as seen before (Yang et al. [7]), the adsorption on MWCNT is not determined by the micro porous structure of the sorbent. The weaker ability to be a sorbent is due to the negatively charged surface. They concluded that pristine multi walled carbon nanotubes are a powerful sorbent for resorcinol and other phenolic derivatives. However they assumed, that they could release everything with the eluent they let through the column but they did not test if that was true. It is possible, that a systematic error in the experimental setup let some of the compounds disappear and therefore pretend to be more adsorbed. But the data is supported by the work of Yang et al. [6] which also describe the high affinity of organic pollutants to MWCNT's.

## 6 Conclusion and Outlook

Is the PMM feasible for describing adsorption processes on carbon nanoparticles? Yang et al. [6] suggest yes, but only three chemicals were tested and all of them were PAH's in their study. So further investigation is needed, with more chemicals, with different properties (e.g. polar compounds). But so long the PMM shows reliable results and could be interesting for future modeling of the fate of organic pollutants.

The adsorption of a single solute to nanoparticles can be modeled with different mathematical approaches (i.e. DA-Model or the PM-Model as shown by Yang et al. [6], [5]) but in the environment one has to consider much more interaction of pollutants, nanoparticles and other compounds (e.g. humic acids, inorganic compounds, etc.). Yang et al. [7] described the competitive sorption of three PAH on MWCNT and found only competition at high concentrations. For environmental aspects, these concentrations are way too high and competition would not occur in such dimensions under natural conditions. For this case competitive sorption experiments are important and should be conducted with realistic environmental occurring concentrations of the different species and not just different PAH's. But as we saw above, competition occurs only if the relative concentrations are high enough.

For analytical application Ballesteros et al. [4] found the fullerene as bad adsorbents, but they measured only the remaining concentration of pollutant in the eluate. As we know from above, fullerenes are forming aggregates and show irreversible adsorption-desorption-hysteresis [5]. It could be that Ballesteros did not release everything which was trapped in his column due to deformation of the aggregates and enclosure of some of the organic pollutant. But also Yang et al. [6] showed in their work similar behavior of adsorption to fullerene, namely their limited adsorption capacity compared to the one of CNT's. A better sorbent for analytical application may be SWCNT's, they sorb high amounts of organic chemicals ([3], [6]) and show now hysteresis ([5]).

Liao et al. [3] pronounced pristine MWCNT as a tool to remove resorcinol and other phenolic derivatives from aqueous solutions. It is no doubt that the sorption of resorcinol to MWCNT is successful but the concentration in wastewater treatment plants are very low in contrast to the concentrations applied in these experiments. The application of MWCNT would be very expensive and laborious. The remaining and polluted CNT's have to be filtered out after the treatment step.

It is widely described, that nanoparticles and especially carbon nanoparticles become more interesting for different applications in the future. I summarized the key findings of some studies which deal with the interaction of those nanoparticles with persistent organic pollutants (POP), namely polycyclic aromatic hydrocarbons which are ecotoxicological of high interest. It has been shown, that adsorption and desorption occurs. In combination with the nanoparticles the additionally gained mobility of POP's make them even more problematic. Further research is needed to discuss whether nanoparticles carry POP's and other dangerous pollutants into the cell and release them there and lead to an accumulation which is in a higher magnitude than without the presence of nanoparticles.

Nanoparticles are ubiquitous and the amount of engineered particles is growing. There are strong interactions with organic pollutants and they affect the fate, transport and mobility of those compounds. One has to consider their future importance and possible effects on the environment.

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