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Adsorption of Pyrazolone[HPMSP],Calix[4]-arene, Cu(II) and Cs on Carbon Nanotube

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ABSTRACT

The adsorption of pyrazolone(HPMSP), Calix[4]-arene,Cu and Cs, on carbon nanotube(CNT) at room temperature has been investigated using spectroscopy.
Uv spectroscopy indicated that pyrazolone molecules adsorbed on carbon nanotube at room temperature in compared calix[4]- arene molecules adsorbed approximately same.The amount of pyrazolone(HPMSP) adsorb 3.8×10^{-5} mol/g and amount calix[4]-arene adsorbed 1.3×10^{-5}mol/g.The physisorption of such an organic molecules is an example of nano covalent functionalization involving π-□stacking interactions and corresponding to weak binding energy.The most favourable adsorption site is one type C-C bond. Atomic adsorption shown carbon nanotube has capability and a high adsorption efficiency for adsorption of Cu(II) and Cs from of water.

Keywords: Pyrazolone(HPMSP),Calix(4)-arene,Cu(NO3)2,CsNO3,Carbon nanotube

INTRODUCTION

After its discovery by Lijima (1) in 1991, reseach on carbon nanotube (CNT) reaches a critical mass in many areas of physics and chemistry. Synthesis methods have been rapidly improved,making it possible to produce.Larg amount of size-contrlled CNT for commercial applications (2).Carbon nanotube can adsorbed a number of atomic and molecular species,e.g,alkali metal[i.e,Li(3), K(4), Rb(5)and Cs(6)] and hydrogen(7), nitrogen(8), oxygen (9) and methane (10) gases. The adsorption properties provide the opportunities for applications such as hydrogen and other gases storage (11), sensor (12), catalyst (13) and Li-ion batteries (14). The chemistry of single-wall carbnon nanotubes (SWNTC) has been a subject of interest for several years (15) for recent reviews,see ref(16-18).In recent years,a great interest has been focused on electrochemical double layer capacitors because of their high energy density and long cycle life (19-22). The crystalline porous strcture and large surface area of the carbon nanotube make it an ideal adsorption for polymer.Usually,the adsorption of polymer on carbon nanotubes can be surveyed by some traditional techniques such as SEM,STM and Raman spectra.However,more valuable information on the modification of surface properties such as surface irregularities and defects can be monitored by the fractal analysis.Plenty of investigations have been carried out on the synthesis, purification, structure characterization and application of the carbon nanoparticles (23-35), few of which are related to the surface fractal analysis.Hennce,the surface fractal analysis maybe a feasible approach to explain some phenomena occurring at surface and interface of carbon

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nanotubes such as adsorption, surface modification and coating by some polymer (36). Chemical derivatization (or functionalization) is an efficient and widely used tool to modify the chemical and physical properties of carbon nanotubes (CNTs) and to expand in this way application areas of the latter.All the existing derivatization methods.Belong to one of two large groups,covalent and noncovalant derivatization (37-41). While covalent derivatization can be equally applied to both CNT tips and side wall, the nanocovalant technique relies essentially upon physisorption on CNTs (through hydrophobic, stacking interactions, ets) and therefore takes place predominantly on CNT-side walls. Both approaches have their advantages and draw backs, depending on the application area.The main “pro” of nanocovalent functionalization is that it does not alter the geometric and electronic stracure of CNTs and allows for the introduction of higher concentractions of modifying groups. With in short time, aromatic compounds have gained special attention as reagents for nano covalent CNT derivatization.Substituted pyrenes are first to be mentioned, which were primarily employed as molecular unchors (42-46) as well as for increasing CNT solubility (47-49). Interaction of other aromatic molecules with were anthracene derivative (50), and 1,2-dichlorobenzen (51)

EXPERIMENTAL SECTION

Reagents

1- The carbon nanotube were prepared at the ECPM laboratory of the University of ULP(France).
2- Pyrazolone and Calix[4]-arene were prepared at the ECPM laboratory of the University of ULP(France)
3- Copper and Cesium stock solutions were prepared from copper nitrate [$Cu(NO_3)_2.3H_2O$] and $CsNO_3.H_2O$ of Fluka (98٪) by dissolution in water.

Adsorption of HPMSP and Calix [4]-arene on CNT

Physisorption of pyrazolone and calyx [4]-arene on carbon nanotube studied by UV spectroscopy. Adsorption of HPMSP and calix[4]-arene measured at temperature room.

300mg of carbon nanotube as adsorbent was placed in a ballon with 10ml of HPMSP 0.001molar and 10mlCalix[4]-arene 0.001molar is stirred at temperature room for overnight (24h) to the adsorption equilibrium and filtered .The adsorption amount of HPMSP and Calix[4]-arene are calculated by Uv spectroscopy,results shown in table 1.

Adsorption of Cu and Cs on CNT

In experimental method amount Cu and Cs adsorbed on CNT calculated.300mg CNT as adsorbent was placed in a ballon with 10ml HPMSP 0.001molar stirred at temperature room for overnight(24h) to the adsorption equilibrium and filtered.CNT separated of HPMSP with 10ml Cu 200ppm contact and stirred at temperature room for 24h to the adsorption equilibrium and filtered.This process doing for Calix[4]-arene and Cs. Amounts of Cu and Cs

adsorbed determination with atomic adsorption spectrometer. The amounts of Cu(II) and Cs on CNT was calculated by substracting the equilibrium Cu and Cs content from the initial Cu and Cs conten Adsorption results shown in table 2.

Results and Discussion

Carbon nanotubes a new type of carbon material,show exceptional capability and a high adsorption efficiency for the removal of Cu(II) ions from water in compared with Cs ions from water(amount adsorption Cu(II) equal 6.76mg/g and for Cs equal 1.26mg/g).The largest adsorption capacity for CNT occurred at 24h.It is clear that the Cu(II) with HPMSP adsorption capacity of CNT is low and 3.38mg/g. While the adsorption capacity increase and reach 6.76mg/g with water .For Cs with Calix[4]-arene adsorption capacity of CNT is 1.26mg/g.While the adsorption capacity small increase and reache 1.30mg/g.This indicates that the functional groups introduced by oxidation improve the ion-exchange capabilities of the CNT and thus make Cu adsorption capacities increase correspondly.CNTs have attracted researchers interest as a new type of contaminants from water.Li et al ,found that acid-refluxed CNTs can be good adsorbents for Pb (II) ion and cd (II) ion (52-53).

As a preliminary study of the possibility of reversible modification of CNT sidewalls with metal complexes employing similar stacking phenomena, we studied the interaction of Cu (II) and Cs complexes of pyrazolon (HPMSP) and Calix[4]-arene with carbon nanotube.As a conclusion and further prospect,we believe that the adsorption of aromatic molecules having a bent shape,which increases the area of contact with nanotube sidewall,can be very useful in the chemical modification of CNT materials.being an alternative to covalent derivatization, it allows for the reversible attachment of modifying moisties.The latter stick strongly to the nanotube walls because of $\pi-\pi$ and hydrophobic interactions and remain stable in aqueous solutions (and probably in some other media), whereas they can be removed by washing with nonpolar,in particular, aromatic, solvents.

Conclusion

The specific surface area and pore specific volume of CNTs decrease after adsorption HPMSP

and calix[4]-arene,because after adsorption these compounds ,amount adsorption Cu and Cs decreased.Our study predicts that adsorption of HPMSP and Calix[4]-arene ligands on carbon nanotube is not noticeably influenced by the presence of aliphatic (methyl) or/and aromatic (benzo) substituents in the macrocyclic molecules.On the contrary,the adsorption dramatically increase in the case of metal(Cu,Cs) complexes,resulting in substantial changes in their geometry and electronic structure.The increase in negative electrostatic potential at the exposed macrocycle side might imply an enhanced reactivity toward electrophilic agents,which, along with the strong adsorption predicted,is an encouraging prerequisite for the preparation of new carbon nanotube based adsorbent.

Table 1. Results of adsorption Hpmsp and Calix[4-arene on CNT

Sample	**HPMSP intial Mol/l**	**HPMSPintial mol**	**HPMSP end mol**	**HPMSP in CNT mol**	**HPMSP in CNT mol/g**
	10^{-3}	10^{-5}	4.63×10^{-7}	9.54×10^{-6}	3.18×10^{-5}
Sample	Calix[4]arene intial mol/l	Calix[4]arene intial mol	Calix[4]arene end mol	Calix[4]arene in CNT mol	Calix[4]arene in CNT mol/g
	10^{-3}	10^{-5}	6.89×10^{-6}	3.101×10^{-6}	1.034×10^{-5}

Table 2. Results of adsorption Cu and Cs on CNT

Sample	**amout intial**	**amount adsorped in CNT**
Cu without HPMSP	10ml200ppm	1.04×10-4mol/g
Cu with HPMSP	10ml200ppm	5.2×10-5 mol/g
Cs without Calix[4]arene	10ml200ppm	9.5×10-6mol/g

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