Sorption of Bisphenol A (BPA) in Aqueous Solutions on Fullerene C60

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The important applications of engineered carbon nanomaterials in the last years represent the cause of their presence in the aquatic environment. The properties and on the composition of the aqueous solutions, will influence the distribution and the availability of fullerene (nC60) as a sorbent, in different aqueous environmental media. In this study, the adsorption of bisphenol A (BPA) from aqueous solutions on fullerene C60 was investigated in batch experiments. The kinetic, the isotherm and the thermodynamic of the reactions were determined. According to the Langmuir model, the maximum sorption capacity of BPA by the fullerene C60 in the studied systems was of 74.44 mg/g, at 20 ^{0}C, being observed that it varies by the temperature. The kinetic data were better described by the intra-particle diffusion model in the optimum range of pH values between 7 and 9.

Keywords: fullerene C60, sorption, bisphenol A, environment

Nanotechnologies are extensively applied in the last years in the environmental removal of organic and inorganic contaminants, potential applications of carbon based nanomaterials to remove environmental organic pollutants from water matrices being found in the literature [1, 2]. Among carbon based nanomaterials, fullerenes were only recently considered as potential environmental sorbents, because of safety concerns [3], often contradictory and of their tendency to aggregate in several solvents [4]. Carbon fullerene C60 consists of 60 carbons arranged in symmetrical structures with nano dimensions. These enclosed cage structures present sp^3 bonding character and several reactive carbon sites [5], their chemical behavior lying between aromatic molecules and straight chain alkenes. Buckminster fullerene C60 is highly insoluble in water, but in aqueous solutions it can form stable colloidal aggregates [6]. Due to the wide range of conditions to disperse C60 in water, nC60 becomes readily available in natural systems [7]. These nanoparticles have several applications [8], being released in the environment as hydrophobic aggregates, with characteristics depending on the natural water constituents [9].

Bisphenol A (BPA), used to improve the strength and the flexibility of polycarbonates and epoxy resins is considered an environmental pollutant [10], as an endocrine disrupting chemical. The BPA tolerable daily intake TDI was determined as 0.05 mg of BPA per kg of body weight per day [11]. Even if it presents a medium hydrophobicity (water solubility 120-130 mg/L), the octanol-water partition coefficient (K_{OW}) influences its solubility function of temperature, pH and salinity of the aqueous media [12].

This study was designed to describe the adsorption kinetics and thermodynamics of an endocrine disruptor, bisphenol A (BPA) on nC60 systems. Due to the complexity of nC60 systems in various experimental conditions, the nC60 aggregates were characterized at temperatures of 20 - 30 ^{0}C, at pH values of 6-7 and in ~10 mM NaCl aqueous solutions. The hydrophobic surface of C60 causes interactions with organic pollutants, their behavior being modified. In the above mentioned conditions, a value of 3.47 for log Kow of BPA was considered.

The resulted impregnated nC60 aggregates might present a Trojan horse effect, but this effect was still not proved. Its toxicity necessitates further study in order to obtain and to model significant data.

Experimental part

Materials and methods

Fullerene C60 (purity > 99 %) was obtained from Aldrich Chemical Co. Bisphenol A (minimum purity 99 %) was provided by Fluka, Germany. Methanol, used as solvent was purchased from VWR Chemicals, France. The concentrated BPA stock solution was prepared in methanol, solvent of chromatographic purity. The standard solutions were prepared by dilution from the stock one, using HPLC grade water.

Preparation and analysis of the working solutions

The 100 mg/L BPA concentrated stock solution was prepared in methanol, solvent of chromatographic purity and stored at in the refrigerator, up to one week. The working solutions were prepared by dilution, with ultrapure water and stored for maximum 24 h before experiments.

HPLC determinations using an external standard calibration method was used for the quantification of BPA. All the analysis were done by an Agilent 1100 Series HPLC instrument and described elsewhere, in [13].

Quantitative Concentration Analysis of C60

The standard working solutions of 2, 4, 6 and 8 mg C60/L were obtained by diluting the appropriate volumes of the stock solution in 100 mL ~10 mM aqueous solution of NaCl, based on a modified method from the literature [14]. The suspensions were continuously mixed with a magnetic stirrer for 24 h. Aliquots were sampled after 0.5, 1, 2, 12 and 24 h, filtered through 0.45 μm filters (Fisher Scientific Denver CO) to remove the undispersed material. The concentration of C60 aggregates was spectro-photometric determined [15]. The concentration of nC60 in water was estimated by UV absorption at 347 nm using a UV-Vis CINTRA 202 spectrophotometer, the UV-Vis absorbance spectra of the nC60 suspensions showing a characteristic absorbance peak of solvated C60, located at this

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wavelength. Broad band absorption between 400 and 550 nm might indicate the presence of aggregated forms of C60. The concentration of C60 aggregates was determined by fitting the measured spectrum to calibration reference spectra.

Batch adsorption experiments

The experiments using different concentrations of BPA in the initial solutions were developed. Each concentration of the solutions from the experimental set was obtained by dilution of the standard stock solution of 100 mg/L BPA with ~10 mM aqueous solutions of NaCl. 100 mL volumes of the prepared solutions were added in 100 mL glass sorption vials with stoppers that contained 1 mg of adsorbent, precisely weighed, in each. The mixtures were placed in a water bath and shaken at 150 rpm. The solutions were filtered on 0.45 μm PTFE syringe filters and the BPA concentration was chromatographically analyzed. Several influences such as the effect of the contact time at different concentrations of carbon nanomaterials and of BPA, the effect of different temperatures, the effect of *p*H were studied.

The BPA rate (%) and adsorption capacity (mg/g) calculates as:

$$q = \frac{C_0 - C_x}{m} \times V$$

where q (mg/g) is the BPA adsorption capacity, C_0 (mg/L) and C_x (mg/L) are the initial and equilibrium BPA concentrations in the solution, V (L) the solution volume, and M (g) the mass of adsorbent.

Characterization of the nanosorbents

BET specific surface areas and pore size distribution

The Brunauer-Emmet-Teller (BET) specific surface area of the nano sorbent was obtained from the nitrogen adsorption/desorption isotherms, using a Quantachrome NOVA 2200e instrument [13]. The specific surface area was calculated according to the BET equation. The total pore volume was estimated from the amount of gas adsorbed at $p/p_o = 0.99$. Pore size distribution was calculated from the isotherm using Barrett-Joyner-Halenda (BJH) method [16].

Transmission electron microscopy (TEM)

Electron micrographs were obtained by Philips 120 transmission electron microscopy. TEM specimens were homogeneously dispersed by placing thin layers of fullerene suspension on conductive copper carbon grid surfaces and drying overnight at room temperature.

Fourier Transformed Infrared spectrometry (FTIR)

The sorbents before and after the sorption process were analyzed by FTIR spectrometer Vertex 70 Brucker, for solids, using a pressed disc method. FTIR spectra were recorded between 4000-400 cm^{-1} with a resolution of 4 cm^{-1} and compared with the spectrum pure KBr.

Differential scanning calorimetric analysis (DSC)

Thermal analyses, TG-DSC, of the compounds were carried out with a Netzsch 449C STA Jupiter. Samples were placed in covered Al crucibles and heated with 5 $K \cdot min^{-1}$ from room temperature to 550 °C under a flow of 50 $mL \cdot min^{-1}$ Ar. An empty Al crucible was used as reference[13].

Results and discussions

Characterization of the nanosorbents

The molecular interactions, sorption and partition coefficients governing the behavior of fullerenes are based on electrostatic, hydrophobicity, Hansen solubility parameters and also the already mentioned DLVO model of colloidal stability. The hydrophobic C60 molecules interact less favorably with water and better with hydrophobic solute molecules, based on their solubility in water matrices. The characterization of the fullerene C 60 used as nanosorbent in this study was done before and after the adsorption process, the results being further compared.

BET analysis

The textural characteristics of the studied carbon nanostructures (table 1) such as: specific surface area, pore volume and pore diameter were determined by N_2 adsorption at 273 K, showing small pore volume with small surface area, suggesting that C60 present micropore constrictions, which hinder the N_2 adsorption. The specific surface area and the total pore volume were determined and the data are presented in table 1.

TEM

The morphology of the studied C60, simple and impregnated with BPA is presented in figure 1 observing that C60 show a homogeneous distribution of the spheres. TEM images show circular shape of C60 aggregates, with averaged diameters between 20-50 nm. Study of the simple and impregnated C60 with BPA by transmission electron microscopy indicated the presence of a compact layer that covers the surface with BPA. BPA molecule can interact through hydrogen bonds with the surface of the nanotubes with only one hydroxyl group and ð-ð interaction, or it may interact through two hydrogen bonds with both hydroxyl groups, but without π-π interaction. In the case in which a hydroxyl group remains available, it can form hydrogen bonds with the spherical surface of another molecule of BPA, forming a compact impregnation layer.

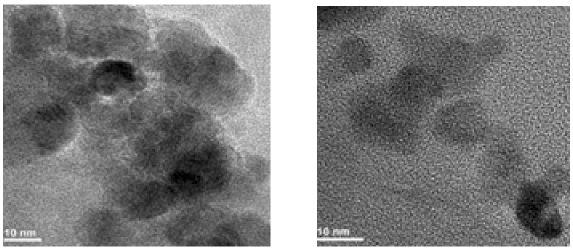


Fig. 1 TEM images of nC60 before and after impregnation with BPA: 1 - C60 without BPA; 2-C60 with BPA

FTIR analysis

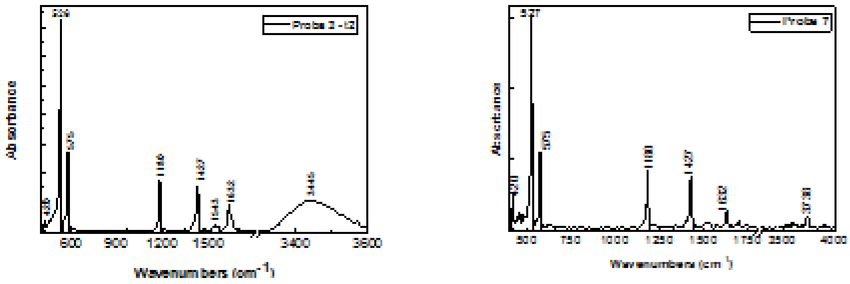
FTIR spectra of the nanosorbents before and after the sorption of BPA (fig. 2) confirm the presence of BPA molecules on the surface of C 60. The peaks at 1622, at 1633 and 1523 cm^{-1} are assigned to the skeleton vibration of C = C double bonds from the aromatic rings.

In the FTIR spectra of C60 the peak, which appear around 1445 cm^{-1} can be attributed to the carbon double bond from the benzene molecule. This peak can be also

Table 1

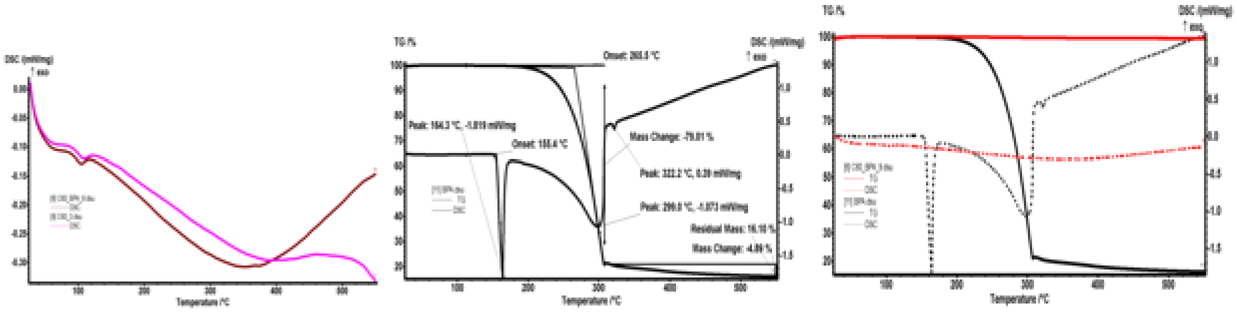
TEXTURAL CHARACTERISTICS OF FULLERENE C60 USED IN THE EXPERIMENTS

Nanomaterial	Purity, %	Structural parameters	Specific surface area, m^2/g	Pore volume, cm^3/g	Pore diameter, nm
C60	99 %	720.4 g/mol	4.26	0.016	9.17



C60 BPA-C60

Fig. 2 FTIR spectra of C60 before and after sorption of BPA



(1) (2) (3)

Fig. 3 DSC analysis for nC60 before and after sorption of BPA (1) and TGA termograms of pure BPA (2) and impregnated nC60 with BPA (3)

observed in the FTIR spectra of BPA. The skeleton vibration peaks of carbon double bond from the aromatic rings are found at 1633 and 1523 cm^{-1}. After the BPA adsorption, new peaks appear in the spectra, indicating presence of oxygen containing groups: at 1200 cm^{-1} the C-OH stretching, at 1700 and 3600 cm^{-1} the O-H stretching. The peak corresponding to the skeleton vibration of the carbon double bond from the aromatic molecules is thinner and shifted at 1630 cm^{-1}. This is a possible indication of the π-π interactions between the benzene rings from the BPA molecule and the benzene rings from the C60.

Differential scanning calorimetry (DSC) analysis

The samples were tested with scanning rates between 0.25 and 2 ^{0}C min^{-1}, in a range of temperatures 30-600 ^{0}C. It can be noticed (fig. 3) that the mass loss of impregnated C60 with BPA is very small, in this case probably the interactions between the organic molecule and the nanomaterial leading to more volatile compounds. The thermal stability of nC60 can be attributed to the bonds from aromatic rings and it might be affected by the nature of the catalyst used in their synthesis, and the presence of defects in the material. Fullerenes C60 impregnated with BPA present a very small mass loss at 300 ^{o}C.

BPA suffers a melting process at 155.4 ^{o}C and a further decomposing at 265.5^{o}C. The decomposing process presents an endothermal effect, with a mass loss of 79 %. The resulted carbonic mass slowly decomposes with a supplementary mass loss of 4.89 % till 550 ^{o}C, the final residue representing 16.1 % of the initial mass. The number of the oxidation temperature peaks observed in the figures above is an indicator of the presence of BPA molecules at the surface of nC60. The mass loss can be observed at 450 ^{o}C for the not impregnated fullerene and between 400-450 ^{o}C for the impregnated one, this indicating the formation of chemical bonds between the surface of the fullerene and the hydroxylic groups of the BPA molecules.

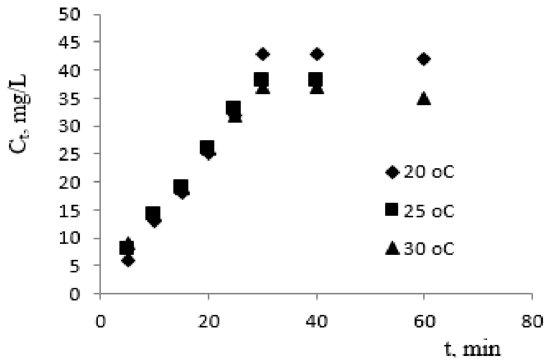


Fig. 4 Adsorption kinetics of BPA on C60 at three temperatures: 20, 25 and 30 ^{0}C

Kinetic analyses of BPA adsorption on C60 aggregates

The adsorption kinetic study (fig. 4) was done using an initial BPA concentration of 10 mg/L, *p*H =6.5, at a temperature of 20 ^{0}C. The BPA concentrations were measured at different adsorption times, between 5 and 80 min. Pseudo-first, pseudo-second and intra-particle diffusion models (fig. 5) were applied to the experimental data [17].

Among the mechanisms that govern the kinetics of the sorption process, the most limiting are the diffusion mechanisms, such as external diffusion, boundary layer diffusion and intra-particle diffusion.

The values of the kinetic parameters for the removal of BPA by fullerene C60 are presented in table 2.

BPA adsorption isotherms

In order to describe the equilibrium adsorption of BPA on C60 aggregates (fig. 6), non-linear Langmuir and

Table 2
KINETIC PARAMETERS FOR THE ADSORPTION OF BPA BY C60

Sorbent	Pseudo-first model				Intra-particle diffusion model			Pseudo-second model		
	q_e,exp, mg/g	k_1, L/min	$q_e$calc, mg/g	R^2	C	k_1, mg/g/min	R^2	$q_e$calc, mg/g	K_2, L/min	R^2
C60	43	0.0568	30.42	0.9266	15.75	99.21	0.9799	89.28	0.00014	0.8882

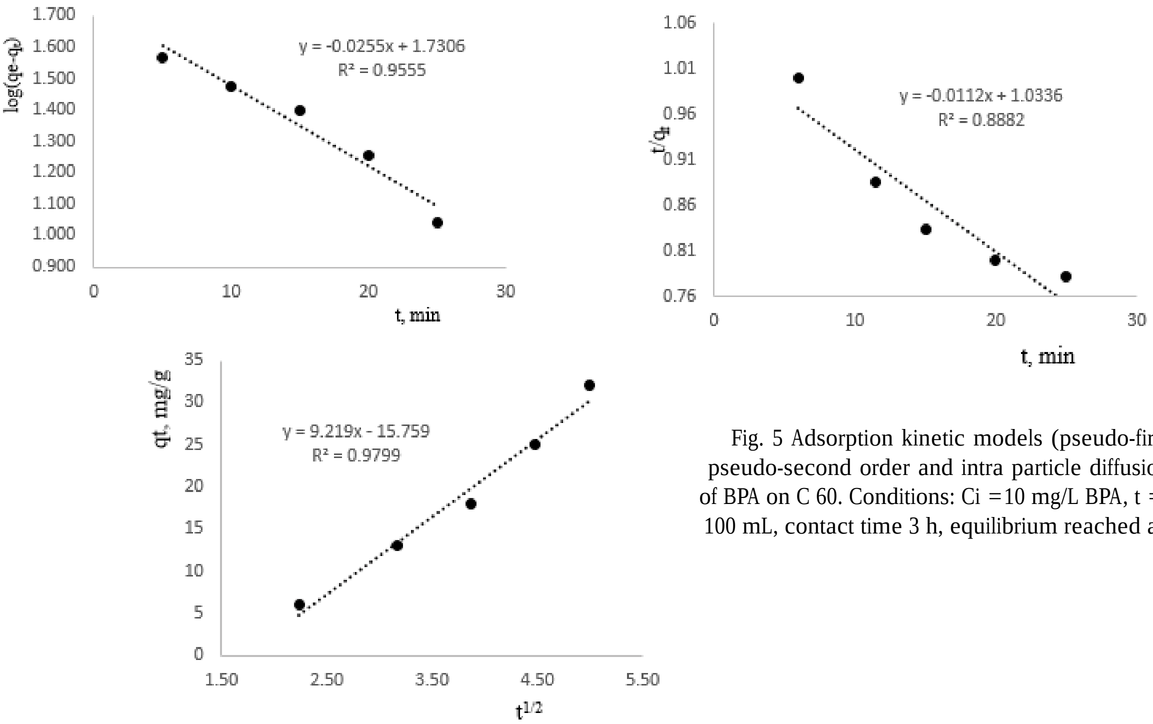


Fig. 5 Adsorption kinetic models (pseudo-first order, pseudo-second order and intra particle diffusion models) of BPA on C 60. Conditions: Ci =10 mg/L BPA, t = 20 ^{0}C, V = 100 mL, contact time 3 h, equilibrium reached after 30 min

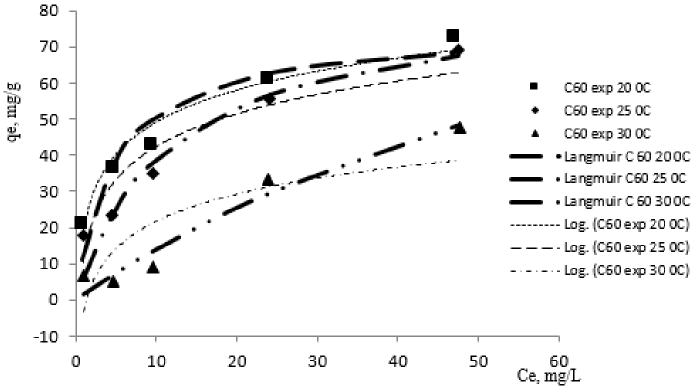


Fig. 6 Langmuir 4 and Freundlich non-linear adsorption isotherms of BPA on C 60; Conditions: Ci =10 mg/L BPA, t = 20, 25, 30 ^{0}C, V = 100 mL, contact time 3 h, equilibrium reached after 30 min

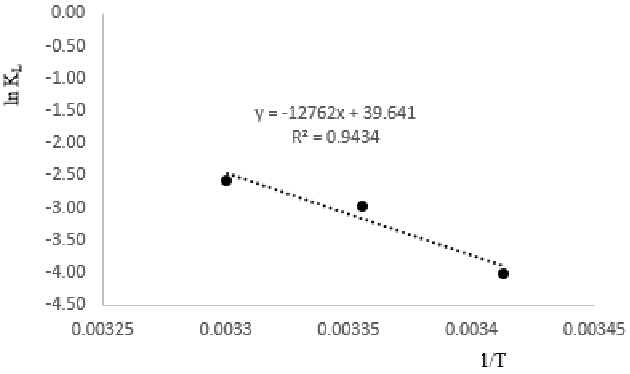


Fig. 7 Plot of Gibbs free energy change vs. temperature for the adsorption of BPA on C60

Table 3

ISOTHERM PARAMETERS FOR THE ADSORPTION OF BPA ON C60 AT DIFFERENT TEMPERATURES

Sorbent	Langmuir			Freundlich		
	q_m, mg/g	K_L, L/mg	R^2	K_F	n	R^2
C 60 20 ^{0}C	74.44	0.0180	0.9174	27.68	2.12	0.9628
C 60 25 ^{0}C	20.07	0.0860	0.9781	20.74	1.36	0.8803
C 60 30 ^{0}C	10.09	0.0507	0.9990	9.45	1.87	0.7237

Freundlich isotherms were used [18]. The interrupted lines represent the fitting curves using Freundlich and Langmuir models at the three studied temperatures. The values of the Freundlich and Langmuir adsorption parameters are listed in table 3.

Thermodynamic studies

The values of the thermodynamic parameters indicate changes associated with the adsorption process. The values of the enthalpy ΔH^0 and entropy ΔS^0 of adsorption were calculated (fig. 7) in order to establish if the adsorption is endothermic or exothermic. The thermodynamic parameters were calculated from the equation:

$$\Delta H^0 - \Delta S^0 T = -RT \ln K_L$$

where, K_L is the Langmuir equilibrium constant (l/mol); R is the gas constant (8.314×10^{-3} kJ/mol K); T is the absolute temperature (K). ΔH^0 and ΔS^0 were determined from the slope and the intercept of the van't Hoff dependence of $\ln(K_L)$ vs. 1/T.

The value of ΔH^0 of - 106.93 (kJ mol^{-1}) defines a physical sorption. The negative value of ΔH^0 indicates that the adsorption of BPA on C 60 is exothermic (table 4). Moreover, the positive ΔS^0, (J mol^{-1}K^{-1}) reveals an increasing number of degrees of freedom at the solid-liquid interface by the adsorption of BPA on C 60. All the values of ΔG^0, (kJ mol^{-1})

Table 4

THERMODYNAMIC PARAMETERS FOR ADSORPTION OF BPA ON C60

Thermodynamic parameter	ΔH^0, (kJ mol^{-1})	ΔS^0, (J mol^{-1}K^{-1})	ΔG^0, (kJ mol^{-1})		
			293	298	303
C60	- 106.03	32.95	- 9.54	- 7.89	- 6.24

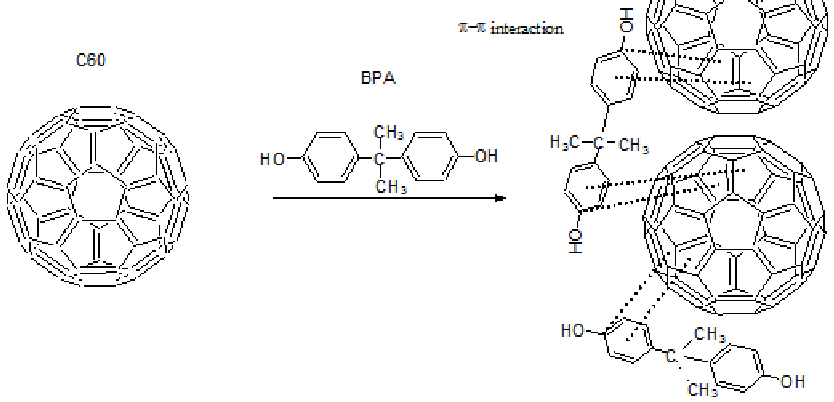


Fig. 8 Adsorption mechanism of BPA on fullerene C 60

Table 5
ADSORPTION CAPACITY OF BPA BY C60 IN COMPARISON TO OTHER LITERATURE VALUES

Adsorbent	T (^{0}C)	Sorbent/ solution (w/v) ratios	Contact time	pH	C_s (mg/g)	Reference
C60	20	1 mg/100 mL	24 h	7	$5.76x10^2$	[25]
C60	25	1 mg/100 mL	7 days	6	2.40	[26]
C60	20	-	60 min.	7	43	[27]

based on the equation: $\Delta G^0 = \Delta H^0 - T\Delta S^0$ were negative, indicating a spontaneous adsorption.

Effect of pH

The variation of *p*H modifies the electrical surface charges of the adsorbent in the experimental solutions. The effect of *p*H refers to the type of the adsorbent and to the value of the dissociation constants of the sorbate (pKa of BPA = 9.6 -10.2). In aqueous solutions, BPA will be found in the molecular form (H_2BPA) at *p*H values lower than pKa and it will deprotonate at *p*H values above pKa. At *p*H values higher than 9, the BPA molecules are negatively charged, the anions ($HBPA^-$ and BPA^{2-}) being present in the experimental solutions. Electrostatic repulsion are induced with the negatively-charged adsorbent.

Adsorption mechanism

From the experimental results, it was supposed that the sorption of organic contaminants to the C 60 surface is influenced by the factors that influence sorption energies in conventional systems, such as: hydrophobicity, dispersion properties and weak polar forces [19]. The dominant interaction for the adsorption of aromatic organic chemicals on C 60 might be the π-π bond [20], stronger for electron-donor-acceptor systems (EDA), than that with pairs of donors or of acceptors [21]. The tendency of C60 to form stable crystalline nanoparticles with diameters between 25-500 nm in diameter is explained by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloidal stability [22] and also by molecular dynamic studies [23].

Physical sorption is the dominant mechanism of sorption for pristine C60 in the case of BPA (fig. 8), the adsorption study showing rapid equilibrium rates, high adsorption capacity and low sensitivity to variations of *p*H. Good fitting with Langmuir and Freundlich isotherm models of adsorption was also observed. In environmental applications, adsorptive capacity depends on several other factors, such as ionic strength, temperature and pH especially connected with the structure of the organic sorbate. The two benzene rings in BPA molecule attach to carbon atoms through a single bond, forming different angles. BPA molecule could also attach on the fullerene surface because of its small diameter and spherical surface. The π-π formed complex is a strong donor-acceptor system, the phenol group being a charge donor and the C60 an acceptor.

Molecular self-assemblies of the C60 aggregates are based on non-covalent van der Waals, electrostatic and hydrophobic interactions that explain the behavior of fullerene in aqueous solutions. Further solutions will be found for improving their solubility and reducing their agglomeration [24].

The adsorption capacity of BPA by C60 was already studied in the literature, the results being shown in the table 5.

In a previuos paper was studied the sorption of bisphenol A in a aqueous solutions on irradiated and as-grown multiwalled carbon nanotubes [28].

Conclusions

Several carbon nanomaterials were already found and characterized as good adsorbents for removing organic contaminants from water in environmental applications. This study offers a short characterization of the sorption process of BPA on fullerene C60 in aqueous solutions. It proved a short contact time and a significant influence of the variation of the working temperatures over the sorption process. The adsorption could be interpreted by the large number of available active sites and high driving force, both factors improving the transfer of BPA on the surface of CNTs. Another important factor that affects the adsorption kinetics is the initial concentration of the sorbate, this being explained by a larger interaction forces provided by the higher BPA concentration, which could defeat the mass transfer resistance in the aqueous solution.

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