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## ADSORPTION OF ENDOCRINE DISRUPTORS ON EXFOLIATED GRAPHENE NANOPATELETS

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### Abstract

Drinking water treatment using activated carbon (AC) decontamination offers effective methods for removing some organic compounds, tastes and odors, but it is not so efficient for metals, nitrates, microbial contaminants and other organic and inorganic contaminants. In the last years, nanotechnologies introduced several types of nanomaterials for organic, inorganic and biological removal of contaminants in drinking water, such as: sorption, filtrations and catalytic processes. In this work, exfoliated graphite nanoplatelets (xGnP) were used as bisphenol A (BPA) adsorbents, their potential of removing this endocrine disruptor being investigated. The effect of the following parameters such as: contact time, initial BPA concentration, temperature, ionic strength and pH over the sorption behavior of xGnP was studied. In these experiments, it was found that the maximum adsorption capacity of xGnP at 298.15 K is 850 mg/g and the adsorption process most closely fits to the Langmuir isotherm. The results also showed a decrease in the affinity of BPA molecule for the xGnP binding sites by increasing the temperature.

*Key words:* decontamination, endocrine disruptor, exfoliated graphite nanoplatelets, sorption

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### 1. Introduction

In water purification, high adsorption capacity of the adsorbents is mandatory. Based on this, the lifetime of the system was observed to be substantially improved (Pan et al., 2010). Carbon based nanomaterials can offer promising applications in drinking water treatment, extensive reviews on the adsorption of metal contaminants, organics and biological contaminants already existing in the literature.

Several studies present Carbon Nanotubes (CNTs) as adsorbents for organic chemicals in water treatment by comparison with activated carbon (Su and Lu, 2007; Wang et al., 2008), the understanding of organic chemical-CNT interactions providing important information on their possible applications

and environmental risks. Organizing individual nanotubes into hierarchical structures represents a new strategy to scale up nanomaterials for macroscopic engineering applications. These structures are more effectively separated from water using gravitational sedimentation, magnetic attraction, and membrane filtration while having the ability to perform adsorption, disinfection, and catalytic degradation of contaminants (Pyrzynska et al., 2007).

The researchers showed that these hierarchical structures are as good as CNTs for removing contaminants from water as adsorbents, disinfectants, and catalyst and they can be separated more effectively using common techniques such as gravitational sedimentation, magnetic attraction, and membrane filtration. For water purification, the

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challenge is how to connect these two worlds (nanotechnology and water chemistry) on the dimension ladder.

Since its discovery, graphene has become a spotlight nanomaterial. In the last few years, there are investigations focused on the applications of graphene, pristine, functionalized, or composites in removal different water pollutants (Wang et al., 2013), due to its flexibility in introducing functional groups and to its easy operation (Ji et al., 2009; Maliyekkal et al., 2013; Pavaghadi et al., 2013).

Endocrine disruptors as environmental contaminants can generate severe health risks (Shi et al., 2013). Among them, bisphenol A (BPA; 2, 2-bis(4-hydroxyphenyl)propane) is an organic compound present in food containers, industrially used in the production of polycarbonates. It can be discharged as a waste product into the water system, ground, surface and drinking water (Santhi et al., 2012). BPA is an endocrine disruptor, the risks of BPA pollution leading to obligatory control and detection of BPA in the environment (EU, 2011). It is an endocrine disruptor linked to prostate cancer, obesity and hypertension (Vandenberg et al., 2007).

Exfoliated graphite nanoplatelets (xGnP) represent a new effective adsorbent material with high adsorption capacity, good stability and fast adsorption, with thicknesses of the platelets in the nano range, but areas in the micrometer range (Ion et al., 2011a, 2011b). Additionally, xGnP can be easily obtained from cheap, natural graphite, in large quantities, without any need for dimensional increasing for their use in water purification. These materials are less expensive than CNTs, possible to be incorporated into water treatment processes and facile to remove or to regenerate after. There were several computational studies on the interaction energies of systems formed upon the adsorption of BPA on single-walled carbon nanotubes (SWCNTs) and graphene (Zaib et al., 2012).

Various models have been used to explain the adsorption of organic molecules on carbon based nanomaterials, such as Freundlich (Agnihotri et al., 2005; Liu et al., 2004; Pyszynka et al., 2007), Langmuir (Brichka et al., 2006; Lu et al., 2007) and Polanyi-Manes (Yang et al., 2006; Yan et al., 2008) models, all suggesting a heterogeneous adsorption. Multilayer adsorption occurs when organic chemicals are adsorbed on carbon based materials surfaces, the first layers interacting with the surface and other molecules interact with each other (Gotovac et al., 2006, 2007). These factors indicate distributed adsorption energy of adsorption sites and a possible

concentration - dependent thermodynamics in aqueous solutions (Agnihotri et al., 2008). Recently, Xu et al. (2012) used graphene for removing BPA from water, obtaining better adsorption capacities in comparison with modified carbon nanotubes and porous carbon.

Different mechanisms have been proposed to explain the interactions between organic chemicals and carbon-based nanomaterials, like  $\pi$ - $\pi$  interactions between the surface and organic molecules with C=C double bonds or benzene rings, hydrogen bonds and electrostatic interactions (Chen et al., 2008; Lin and Xing, 2008). It must be also emphasized that the change of environmental conditions affects the contribution of each individual mechanism over the overall adsorption of the organic chemicals. Several analyses led to the proposal of an adsorption mechanism for BPA on graphene involving  $\pi$ - $\pi$  electron coupling between the  $\pi$ -electrons of the benzene rings of BPA and graphene and the hydrogen bond interactions between the hydroxyl groups of BPA and the functional groups on the graphene surface.

In this work, exfoliated graphite nanoplatelets (xGnP) were used as BPA adsorbents, their potential of removing this endocrine disruptor being investigated. The effect of several parameters such as: contact time, initial BPA concentration, temperature, ionic strength and pH of the batch sorption solutions were studied, various isotherm equations being used to assess the best isotherm equation which represents the correlation of the experimental data.

## 2. Experimental

### 2.1. Chemicals

Commercial exfoliated graphite nanoplatelets (xGnP) were purchased as powder from XG Sciences, Inc, Michigan, US. xGnP (with average diameter of 15  $\mu$ m and average length < 0.01  $\mu$ m) were provided from XG Sciences, Inc. East Lansing, MI 48823. Detailed information on fabrication, geometrical and surface characteristics of this material can be found elsewhere (Kalaitzidou et al., 2007). Bisphenol A (BPA) >99.9% purity, was purchased from Sigma, Germany and was dissolved in methanol for the stock solution (1000 mg/L), being further diluted with large amount of water till the required concentrations (Table1). All other chemicals were analytical reagent grade.

**Table 1.** Graphene-based materials as adsorbents for the removal of pollutants in water

Materials	Adsorbate	Adsorption capacity (mg/g)	References
Graphene	Methylene blue	153.85	Liu et al. (2012)
Graphene	Bisphenol A	182	Xu et al. (2012)
Sulphonated graphene	1-Naphthol	-6.4	Zhao et al. (2011a)
Sulphonated graphene	Naphthalene	-297	Zhao et al. (2011b)

## 2.2. Methods

The chromatographic separation of bisphenol A was achieved at 25°C, using an Agilent 1100 series HPLC system with UV detection at variable wavelengths. A Kromasil 100-5C18 column 150 mm x 4.6 i.d., 5µm was used. BPA elution was carried out using a mobile phase consisting of 20% water and 80% methanol, using a flow rate of 0.5 mL/min. The column was equilibrated for 30 minutes before injection. The injected sample volume was 10 µL, and UV detection operates at 280 nm.

## 2.3. Adsorption procedure

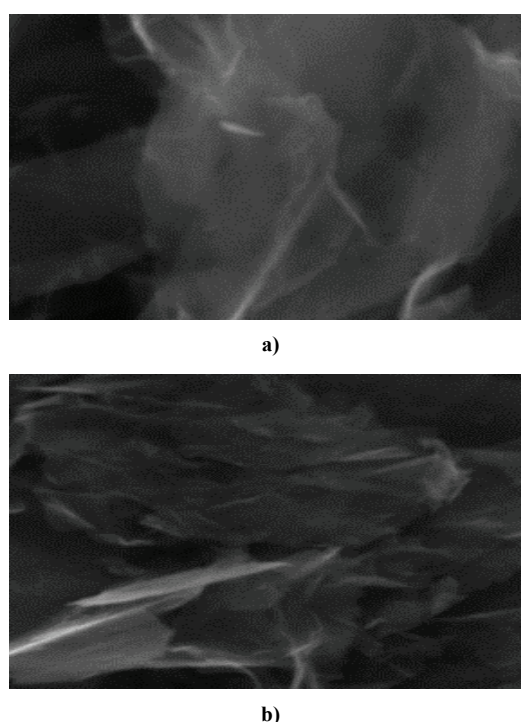
Adsorption experiments were performed in sealed 100 ml bottles in an ultrasound bath (Elma P-30H Ultrasonic) operated at a 37 Hz frequency at 25°C. Each bottle contained between 0.1 and 0.5 mg graphene and 100 ml of 1-10 mg/L BPA. The concentration of BPA was measured after 30 minutes. The adsorption kinetic study was carried out at 1 mg L<sup>-1</sup> initial BPA concentration at three different temperatures: 293.15 K, 298.15 K and 303.15 K, pH 5.5-6.15 in order to determine the minimum time required to reach the adsorption equilibrium. The concentrations of BPA were measured at different time intervals from 10 to 80 minutes. The influence of the pH over the adsorption of BPA was studied at an initial BPA concentration of 1 mg L<sup>-1</sup> in a pH range of 2 to 10 at 298.15 K, adjusted with appropriate volumes of 0.1 M HCl or 0.1 M NaOH. The influence of ionic strength on the adsorption of BPA was studied by adding by adding NaCl to a 1 mgL<sup>-1</sup> BPA solution in a concentration range from 0.01 to 0.375 M at 298.15 K and pH 6.

After adsorption experiments, the suspensions were filtered through 0.45 µm membrane filters. The concentration of BPA was determined by a high-performance liquid chromatography (HPLC, Agilent) system with a Kromasil C18 column (Agilent Technologies Inc.) and a UV absorbance detector operated at 280 nm. The mobile phase was 0.5 mL/min of 80% methanol and 20% deionized water.

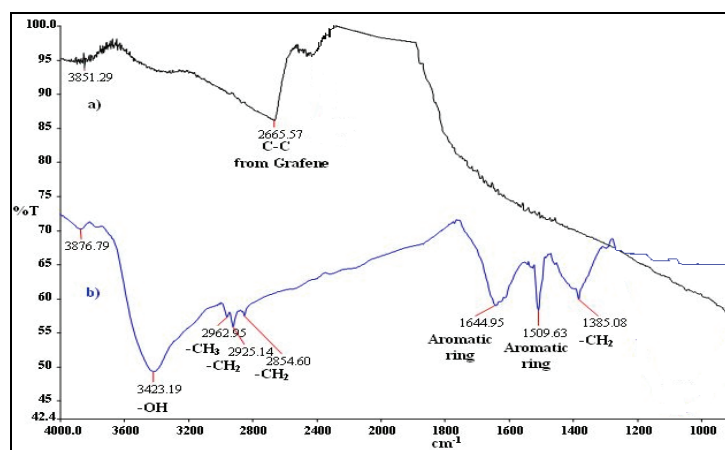
## 3. Results and discussion

### 3.1. Characterization of the nanomaterial

xGnP possesses the smallest particle size (X-Y dimension 2 micron, thickness 2 nm) and largest specific surface (720 m<sup>2</sup>/g), BET surface (771 m<sup>2</sup>/g), possibly due to dry powder aggregation. The particles are irregular in shape and planar with intermittent folds. Carbon sp<sup>2</sup> is the most abundant because of the conjugated π system, but carbon sp<sup>3</sup> also exists due to the C-C bonds with incomplete benzene structures. There can be also present rests of hydroxyl, ether, carbonyl and carboxyl groups (Figs. 1-2). The tested nanomaterials were fully characterized by Vandenberg et al. (2007).



**Fig. 1.** Scanning electron microscopy (SEM) images of xGnP; a) as grown before adsorption; b) after adsorption of BPA



**Fig. 2.** FT-IR spectra; a) xGnP; b) xGnP after adsorption of BPA

3.2. BPA sorption kinetics

Pseudo-first and second order models and intraparticle diffusion one were used to test the experimental data in order to understand the kinetics of the adsorption process. The equations of these kinetic models are presented in Table 2. There were three configurations found on the physisorption of BPA on pristine graphene (Cortes-Arriagada et al., 2013).

Table 2. The equations of several kinetic models

Kinetic Models	Functional Form
Lagergren model	$\frac{dq}{dt} = k(q_e - q_t)$ (1)
Kavitha and Namasivayam model	$q = k_i t^{1/2} + C$ (2)
Pseudo-second order model	$\frac{dq}{dt} = k(q_e - q_t)^2$ (3)
Variables in the kinetics equations: $q_e$ - amount of solute adsorbed at equilibrium, (mg/g) $q_t$ - amount of solute adsorbed at any given time $t$ , (mg/g) $C$ - concentration of sorbate in the solution at any given time $t$	

In the first one, BPA interacts with the graphene bulk at a distance of 2.36 Å, maximizing the π-π interactions with the phenol ring. In the second one the distance between the BPA and the graphene surface is of 2.76 Å, the phenol ring being perpendicular to the surface and van der Waals interactions are reduced. In the third one, the distance between the BPA and graphene surface is of 2.69 Å, while the angle between the phenols increased in comparison with the other two configurations. Here, the physisorption is increased, because it maximized the π-π stacking and the dispersion forces between adsorbent and adsorbate.

The effect of the contact time on the adsorption of BPA on xGnP is presented in Fig. 3. It was observed that the adsorption capacity increased in the first 30 minutes and then it decreased rapidly in the next 30 minutes.

Based on these results a contact time of 30 minutes was used in the experiments. The kinetic parameters are presented in Table 3. It can be observed that the experimental adsorption capacity  $q_e exp$  was in a better accordance with the calculated one based on the pseudo-second order model.

There are several mechanisms that govern the adsorption kinetics: external diffusion, boundary layer diffusion and intraparticle diffusion (Guibal et al., 2003), the last one being the most important limiting step of this process (Özkan and Özcan, 2005).

The lying-down configuration of BPA is conserved during the production step and it determines an increase in the adsorption energy, graphene being a strong electron acceptor, due to its large π system, favoring a configuration that allows the interaction with the negatively charged sites of BPA. In addition with to the van der Waals interactions, charged controlled interactions contribute to the physisorption of BPA on graphene, the chemisorption being less important on pristine xGnP.

3.3. BPA sorption isotherms

Equilibrium data are necessary in developing an equation that models the results in order to design adsorption systems. In this study, Langmuir, Freundlich, Harkin-Jura and Temkin isotherms were used to describe equilibrium adsorption and are presented in Table 4.

The adsorption isotherm models are used to indicate the interactions between the adsorbate and the adsorbent when the adsorption process reaches equilibrium. In Fig. 4, there are presented the adsorption isotherms of BPA on xGnP at different temperatures, 293.15, 298.15, 303.15.

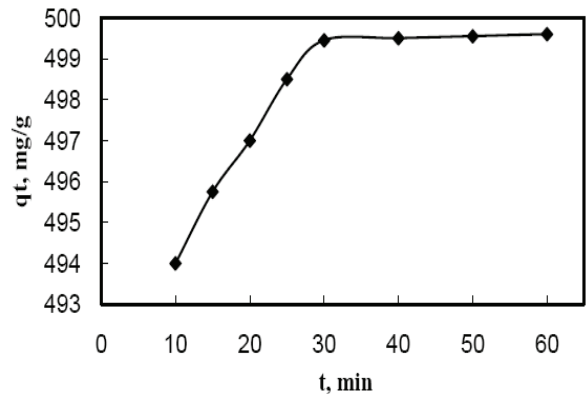
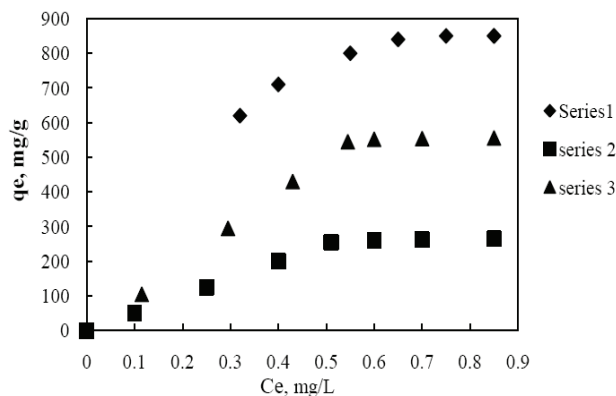


Fig. 3. Effect of contact time on the adsorption of BPA by xGnP (0.1 mg of xGnP and 50 mL of 1 mg/L BPA at 298.15 K, pH=5.5

Table 3. Kinetic parameters for adsorption of BPA onto xGnP (1, 5, 10 mg/L)

Model	Pseudo-first order	Pseudo-second order	Intra-particle diffusion
Equation	$\log(q_e - q_t) = \log q_e - (k_1/2.303)t$ (4)	$t/q_t = (1/k_2 q_e^2) + (t/q_e)$ (5)	$q = k_i t^{1/2} + C$ (6)
$q_e exp$ (mg/g)	850	850	850
$q_e$ (mg/g)	1071	725	C=7.25
$K, (g\ mg^{-1}\ min^{-1})$	0.049	0.024	10
$R^2$	0.9878	0.9824	1



**Fig. 4.** Adsorption isotherms of BPA by xGnP at three different temperatures (0.1 mg of xGnP and 50 mL of 1-10 mg/L BPA at 293.15 K (■), 298.15 K (▲), 303.15 K (◆), pH=5.5, contact time 30 minutes)

**Table 4.** Functional equations of different sorption models used in this study

Isotherm	Functional form
Freundlich	$q_e = K_F C_e^{1/n}$ (7)
Langmuir	$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e}$ (8)
Temkin	$q_e = \frac{RT}{b} \ln(a C_e)$ (9)
Harkin-Jura	$1/q_e^2 = (A/B) - (1/A) \log C_e$ (10)
Halsey	$q_e = \left(\frac{K_H}{C_e}\right)^{1/n_H}$ (11)

$C_e$  – equilibrium concentration;  $C_s$  – adsorbate solubility at a given temperature;  $E_0$  – solid characteristic energy towards a reference compound;  $q_e$  – adsorbed amount;  $q_{max}$  – saturated monolayer sorption capacity;  $K_F$  – Freundlich constant, mg/g;  $1/n$  – Freundlich constant indicating adsorption intensity;  $K_L$  – Langmuir constant, L/mg;  $a$  – Temkin constant, L/mg;  $b$  – Temkin constant related to adsorption heat;  $A, B$  – Harkins-Jura constants indicating the multilayer adsorption;  $K_H$  – Halsey constant.

It can be observed from Fig. 4, that the adsorption capacity of xGnP increased by increasing temperature and by increasing BPA concentration till the maximum value by reaching a plateau. In Table 5, the isotherm parameters of Langmuir, Freundlich, Temkin, Harkins-Jura and Halsey simulations for different temperatures are presented. The adsorption capacities increased by increasing the BPA concentration and reached almost constant final values, which represent the maximum adsorption capacity.

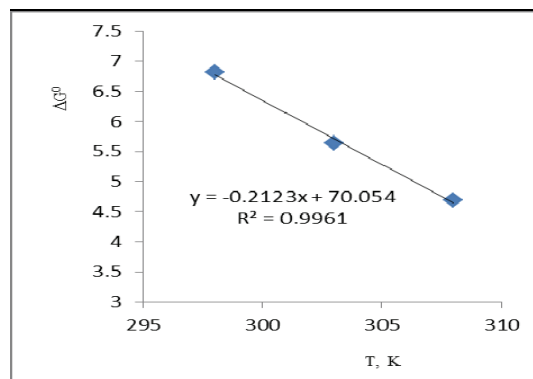
The maximum adsorption capacities of xGnP at 293.15 K, 298.15 K, 303.15 K are 250, 850 and 550 mg/g. Based on a comparison of the  $R^2$  values from the table, the adsorption of BPA on xGnP most closely fits to Langmuir isotherm, suggesting a monolayer adsorption system on the surface. The results showed a decrease of the affinity of BPA for the xGnP binding sites as temperature increases. The sub-unity value of  $R_L$  confirms a favorable adsorption.

### 3.4. Adsorption thermodynamic study

The thermodynamic parameters give indications about internal energy changes during the adsorption process and can be calculated using Eq. (18), where  $K_L$  is the Langmuir equilibrium constant (L/mol),  $R$  is the gas constant ( $8.314 \times 10^{-3}$  kJ/molK) and  $T$  is the absolute temperature (K).  $\Delta H^0$  and  $\Delta S^0$  were determined from the slope and the intercept of the van't Hoff plot of  $\ln(K)$  vs.  $1/T$  (Fig. 5). The calculated values are indicated in Table 6.

$$\Delta H^0 - \Delta T^0 = -RT \ln K_L \quad (18)$$

A positive value of the heat of adsorption indicates a chemisorption process together with the physisorption one at the surface of the exfoliated graphite nanoplatelets. The value of  $\Delta H^0$  (kJ mol<sup>-1</sup>) indicates an exothermic process, supported also by the decrease of the adsorption capacity by increasing the temperature. As it can be observed from Table 7, the negative standard free energy  $\Delta G^0$  indicates a spontaneous process (kJmol<sup>-1</sup>), the  $\Delta G^0$  value being more negative by increasing the temperature, a temperature of 298.15 K representing the optimum value for a facilitated adsorption process. The negative value of  $\Delta H^0$  (kJ mol<sup>-1</sup>) indicates an exothermic nature of the process. Similar observations were done before by Özcan and Özcan (2005).



**Fig. 5.** Van't Hoff plot for the adsorption of BPA onto xGnP

### 3.5. Effect of the solution pH and ionic strength

The effect of solution pH over BPA removal was investigated over the entire pH range. When the value of pH is below 4, due to protonation of the negative charge of xGnP surface, it was observed that the adsorption of BPA decreases (Gong et al., 2007). Above a 10 value of the pH, the hydrophobic interactions between the  $\pi$  electrons of the graphite surface and the  $\pi$  electrons of the C=C double bonds of BPA decrease because of the deprotonation of BPA and the adsorption of BPA on the xGnP surface decreases in consequence.

**Table 5.** Langmuir, Freundlich, Temkin, Harkin-Jura and Halsey isotherm parameters for BPA removal by xGnP

Equation	Parameter			
Langmuir 1 $C_e/q_e = 1/Kq_m + C_e/q_m$ (12)	$q_m(\text{mg/g})=526.31$	$K_L(\text{L/mg})=0.015$	$R^2=0.9935$	$R_L=0.06$
Langmuir 2 $1/q_e = 1/q_m + 1/Kq_m C_e$ (13)	$q_m(\text{mg/g})=555.5$	$K_L(\text{L/mg})=0.016$	$R^2=0.9095$	
Freundlich $\ln q_e = \ln K_F + 1/n \ln C_e$ (14)	$K_F(\text{mg/g})=38$	$n=3.01$	$R^2=0.9761$	
Temkin $q_e = B \ln A + B \ln C_e$ (15)	$A=3.50$	$B=24.39$	$R^2=0.9863$	
Harkins-Jura $1/q_e = A/B - (1/A) \log C_e$ (16)	$A=9.89$	$B=0.03$	$R^2=0.9626$	
Halsey $\ln q_e = [(1/n) \ln K] - (1/n) \ln C_e$ (17)	$n=7.50$	$k=1.71$	$R^2=0.9761$	

**Table 6.** Adsorption capacity of BPA by graphene in comparison to other literature values

Adsorbent	pH	T (K)	$q_{max}$ (mg/g)	Reference
graphene	6.0	302.15	181.6	Xu et al. (2012)
porous carbon produced at 400°C from Moso bamboo	NA	296.15	2.1	Asada et al. (2004)
AC purchased from Wako	NA	296.15	56.5	Lin and Xing (2008)
carbonaceous material produced at 600°C from wood chips	NA	298.15	4.2-18.2	Chen et al. (2008)
as-grown CNTs	6.0	280.15	61.0	Kuo (2009)
modified CNTs	6.0	280.15	70.0	Chen et al. (2008)

NA=data not available;  $q_{max}$  = maximum adsorption capacity

**Table 7.** Thermodynamic parameters for adsorption of BPA onto xGnP

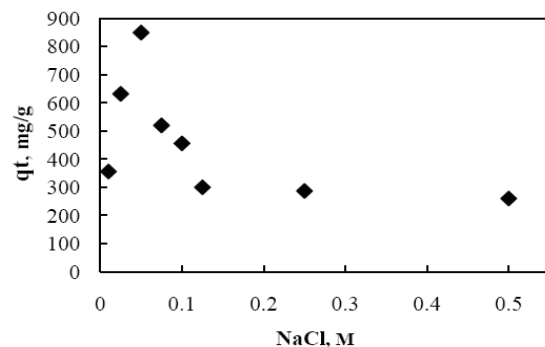
Thermodynamic parameter	$\Delta H^0$ (kJ mol <sup>-1</sup> )	$\Delta S^0$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^0$ (kJmol <sup>-1</sup> )		
BPA	-70.25	-212.3	-6.82 (293.15 K)	-5.64 (298.15 K)	-4.69 (303.15 K)

It was noticed that in the conditions of (0.1 mg of xGnP and 50 mL of 1-10 mg/L BPA at 298.15 K, pH = 5.5, contact time 30 minutes, by increasing pH from 3 to 7, the adsorption of BPA slightly increased, than it begins to decrease between 7 and 9. Based on these results, in the experiments pH values between 5.5 and 7 were maintained during investigating the effects of the studied sorption parameters.

The effect of ionic strength of the working solutions over removal of organic pollutants was also studied in previous papers (Guvén et al., 2012). The adsorption process of BPA on xGnP surface is improved in the presence of salts and natural organic matter.

In our experiment it was found that the optimum value of the concentration of NaCl in aqueous solution is 0.037 M (Fig. 6). Adsorption of BPA with nonplanar and flexible structure significantly increases at small concentrations of NaCl in solution and it begins to decrease at higher ones. This behavior might be explained by the distribution of the Na<sup>+</sup> and Cl<sup>-</sup> ions between the negatively charged graphite platelets, producing a screening effect and favoring the adsorption of BPA molecules. The presence of NaCl in solution decreases the solubility of BPA and enhances its adsorption on the xGnP. The “butterfly”, or lying-down configuration of BPA (Guvén et al., 2012) could facilitate the occupation of the more available

adsorption sites due to the presence of Na<sup>+</sup> and Cl<sup>-</sup> ions. This is more stable, in comparison with that one with one of the phenol rings oriented perpendicular to the surface and Van der Waals interactions are reduced. It was observed that at concentrations over 0.05 M, the adsorption capacity decreased, probably because of the competition between the species involved in the process.



**Fig. 6.** Effect of ionic strength on the adsorption of BPA by xGnP (0.1 mg of xGnP and 50 mL of 1 mg/L BPA at 298.15 K, pH=5.5

#### 4. Conclusions

In this study, commercially available exfoliated graphite nanoplatelets (xGnP) were evaluated for their sorption performance over

bisphenol A (BPA). The risks of this endocrine disruptor pollution lead to obligatory control and removal of BPA from the environment.

The influence of several parameters was studied such as: contact time, initial BPA concentration, temperature, ionic strength, and pH. Several equations of different sorption models were used in order to assess the best isotherm equation which represents the correlation of the experimental data (contact time 30 minutes, BPA concentration range between 1 and 10 mg L<sup>-1</sup>, xGnP amount 0.1 mg in 10 mL, temperature range between 293.15 K and 303.15 K, ionic strength 0.037 M NaCl).

The maximum adsorption capacities of xGnP at 293.15 K, 298.15 K, 303.15 K are 250, 850 and 550 mg/g. Based on a comparison of the R<sup>2</sup> values, the adsorption of BPA on xGnP most closely fit to Langmuir isotherm, suggesting a monolayer adsorption system on the surface.

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