Kinetic Adsorption of Humic Acids Mixture Obtained from Microalgae on Exfoliated Graphite Nanoplatelets

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The dehydration of polysaccharides fraction in the presence of acid catalysts, is a chemical process in which results as secondary product humic matter. In our work, the humic acid mixture was for the first time based on our knowledge extracted from defatted microalgae biomass rich in polysaccharides by standard alkali treatment, followed by precipitation at acidic pH. The dried humic acid mixture has been characterized using infrared spectroscopic measurements (FT-IR). Exfoliated graphite nanoplatelets (xGnP) were used as new adsorbents for this type of humic acids mixture, their adsorption being investigated. The effect of several parameters such as: contact time, concentration of humic acid mixture, concentration of xGnP, temperature and pH of the solutions were studied. The process of adsorption took place with good results, in the following conditions: at a concentration of humic acid mixture of 18.6 mg L^{-1}, an xGnP amount of 0.01 mg in 25 mL of solution, at a temperature of 25 °Ñ and at acidic pH values, in aqueous solution.

Keywords: defatted algal biomass, polysaccharides, humic acids mixture, exfoliated graphite nanoplatelets, adsorption

In recent years, biomass is known to gain high potential as renewable feedstock for chemical production. Humic substances (HS) can be divided into three components: fulvic acids (FAs), humic acids (HAs) and humins. One of the most important parts of humic substances is the HAs mixture. Humic and fulvic acids represent alkali-soluble fractions, meanwhile humins represents the insoluble residue due to the own molecular structure. The mechanisms of the formation of HS can be slightly different and depending on geographical, climatic, physical and biological circumstances, these compounds can be made up in several ways [1]. HAs represent the most important components of the HS that help the transfer of micronutrients from soil to plants, promote the water retention, increase seeds germination and improve soil fertility [2], having excellent sorption properties for reducing available contaminants from the soil, too [3].

Carbon nanomaterials (CNMs) have become candidates for numerous applications in nanocomposites, microelectric devices, sensors, energy storage, microelectronics, biomedicines, and mechanical resonators [4]. Among these, exfoliated graphite nanoplateletes (xGnP) have recently attracted attention due to their great potential for retention of environmental contaminants [5]. However to maximize the advantage of exfoliated graphite nanoplateletes (e.g., as effective adsorbents in water), they should not form aggregates and must be well dispersed, so that dispersed and stabilized CNMs in solution can greatly increase the interaction of CNMs with, for example, contaminants in solutions. In our previous study [6] it was shown that the presence of humic acids improves the dispersability and the stability of several carbon nanomaterials. Based on these aspects it can be supposed that their sorption capacity might increase in environmental samples and these nanomaterials can be further used as new sorbents for environmental contaminants.

Therefore, in this study the synthesis of a new adsorbent with high affinity for several pollutants from the environment is proposed. The new sorbent it is based on functionalized exfoliated graphite nanoplatelets with high dispersability due to the interactions of HAs mixture with the hydrophobic xGnP surfaces. To the best of our knowledge it is the first time when these carbon based nanostructures are used as sorbents for humic acids mixture in order to estimate the effect of these organic acids over their sorption capacity.

Experimental part
Materials and methods
Reagents and materials

All reagents were analytical-grade and were used as received. Deionised distilled water was used in all experiments. All experiments in this work were carried out at a temperature of 25 ± 1°Ñ and at atmospheric pressure. Commercial exfoliated graphite nanoplatelets (xGnP) were purchased as powder from XG Sciences, Inc, Michigan, US. The thick graphite platelets with the following structure characteristics: length <10 nm, average diameter around 15 μm and surface area of 100 m^2/g, were provided from XG Sciences, Inc. East Lansing, MI 48823 [7].

Microalgae cultivation and algal oil extraction

The microalgae *Nannochloris sp.* 424-1, original strain cod CCAP/10 (Culture Collection of Algae and Protozoa, Scottish Marine Institute, Scotland), were grown on mixotrophic conditions with glycerin as additional source of organic carbon, to improve biomass production, and with voluntary stress conditions by reducing inorganic nitrogen from medium, in order to increase lipids and carbohydrates
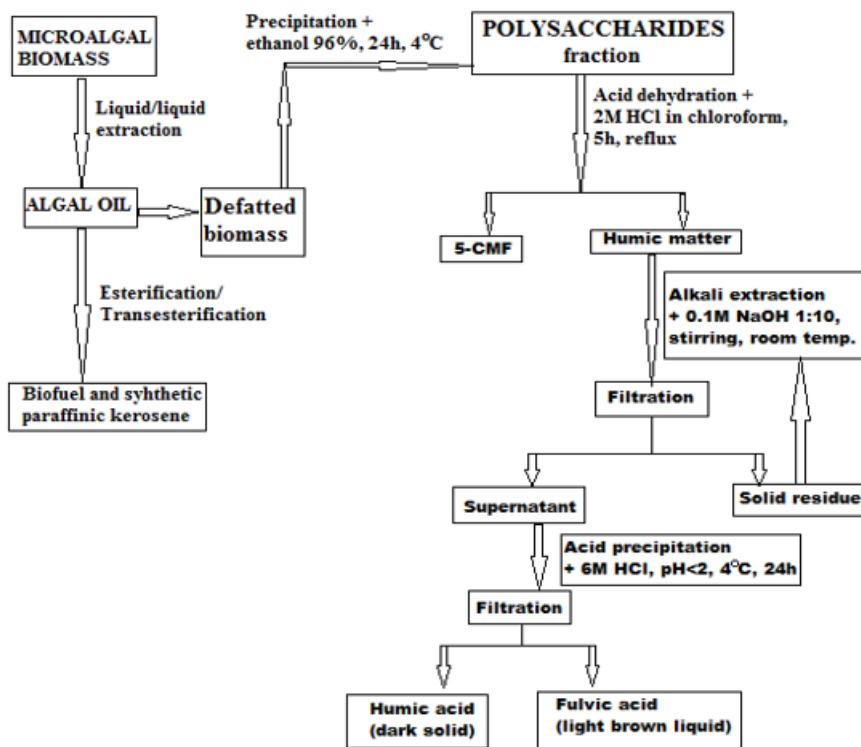
Fig.1 The extraction of humic acids mixture from algae biomass from residual humic matter of polysaccharides conversion

productivity. The defatted biomass was mixed with water by stirring for 15 min. Soluble polysaccharides were then precipitated with ethanol 96%, keeping the suspension at refrigerator overnight. The precipitate was separated by centrifugation at 4000 rpm, at 4 °C and dry at 105 °C.

Extraction of humic acids mixture

The extraction of humic acids mixture is presented in figure 1. The final concentration of 62 mg L^{-1} Has, according to the total organic carbon (TOC) measurements, was obtained. This stock solution was stored at 2-8 °C for further experiments.

Characterization of humic acids mixture

The spectrum of humic acids mixture was recordet using a 1650 Spectrum GXFTIR spectrometer (Perkin Elmer, Germany) using KBr discs, in a spectral range of 4000–500 cm^{-1}.

Results and discussions
FT-IR characterization

The IR spectrum of the humic acids mixture shown in figure 2 presents a diversity of bands typical for humic materials. Major absorption bands are in the regions of 3680 -3243 cm^{-1} (H-bonded OH groups), 2899-2825 cm^{-1} (aliphatic C-H stretching), 1742-1706 cm^{-1} (C O stretching of COOH), 1622 cm^{-1} (aromatic C-C, COO-, H-bonded C-O), 1261-1209 cm^{-1} (C-O stretching and OH deformation of COOH) and 1020 cm^{-1}(C-O stretching of poly-saccharides). The spectrum shows predominance of -OH, -COOH and -COO- groups which are the most characteristic functional groups of humic acids [8].

Another analysis that supports adsorption process is SEM analysis. As it can be seen in figure 3, the changes in morphological aspects indicate a high interaction of HAs mixture with xGnP surface, by increased distance between nanosheets. Therefore, the improved dispersion facilitates the disponibility for adsorption of further contaminants.

Sorption experiments

The HAs concentrations in the solutions were calculated based on TOC measurements of stock solution. All samples
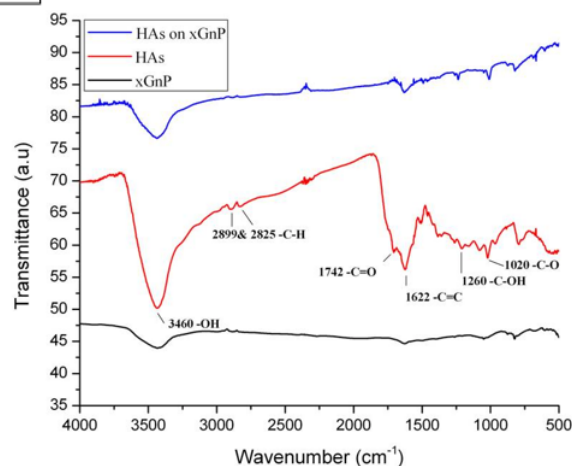

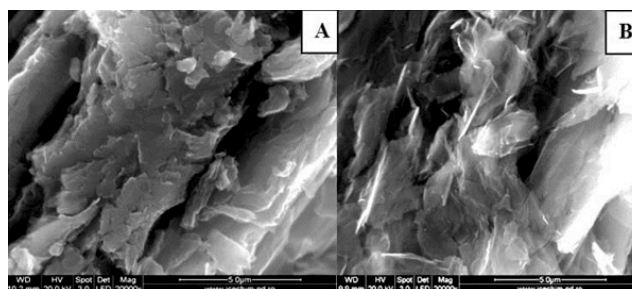Fig. 2. FT-IR spectra of xGnp, HAs mixture and HAs mixture adsorbed on xGnP

Fig. 3 SEM images of xGnP (A) and HAs mixture adsorbed on xGnP (B)

were run in duplicate. The calibration graph (fig. 4) was prepared by plotting the absorbance at 254 nm versus concentration of HAs mixture and the regression equation was calculated. The equation was used to calculate at certain times the variation of HAs concentration in sample solutions.

Solutions with different amounts of xGnP (0.0108mg, 0.108 mg and 1.08 mg), with same concentration of 18.6 mg/L HAs, in 25 mL volume of solution, at 20 , 25 and 30 °C temperature, sonicated at 37 Hz, were tested for five days, in order to determine the optimum conditions to be used in further measurements. The results obtained give indication
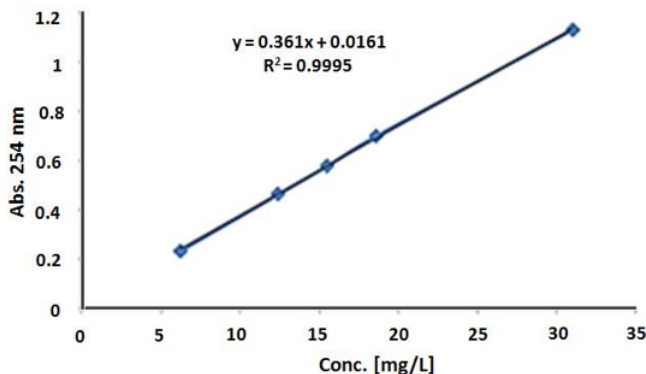
Fig. 4. Calibration curve for HAs mixture extracted from residual humic matter of polysaccharides conversion

about the correlation between quantity of nanomaterial and suitable concentration of HAs and the contact time for attaining sorption equilibrium. The selected conditions for further adsorption experiments were: HAs concentration of 18.6 mg L^{-1}, 0.01 mg x GnP in 25 mL, temperature of 20 °C, contact time 5 days.

Effect of pH on sorption

The calculated concentrations variation of HAs after sorption on xGnP at different *p*H values (fig. 5) between 2 and 7, in a temperature range from 293 to 303 K show that the initial concentration of HAs decreased at *p*H values below 2, caused by the re-precipitation of HAs and depending on the temperature of the solution, but still the sorption capacity of the xGnP presents the highest values obtained in these experiments in the *p*H range between 2.10 and 2.5. It was found that the process of adsorption takes place in favourable conditions at 293K, and a *p*H value of 2.

Adsorption kinetics

Studying the kinetics of the adsorption process provides useful information on its order and rate constants. The equations of several kinetic models are presented in table 1.
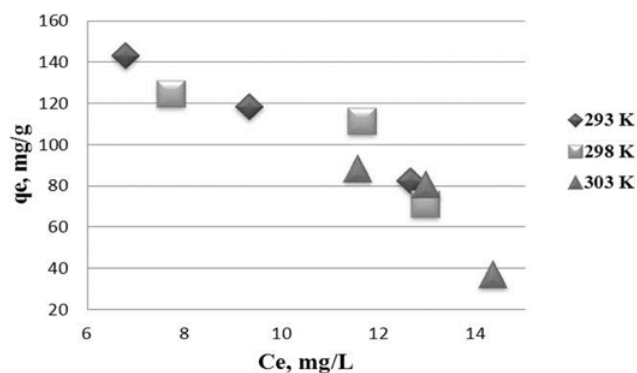

Fig. 5. Effect of *p*H over the isotherms of sorption of HAs mixture to xGnP, at three *p*H values between 2.10 – 6, V= 25 mL, 0.01 mg xGnP, at three temperatures, 293, 298 and 303 K

Table 1
THE EQUATIONS FOR SEVERAL KINETIC MODELS

Kinetics Model	Functional Form
Pseudo-first order model (Lagergreen)	$\dfrac{dq}{dt} = k_1 (q_e - q_t)$
Intra-particle diffusion model	$q = k_i t^{1/2} + C$
Pseudo-second order model	$\dfrac{dq}{dt} = k_2 (q_e - q_t)^2$

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*

The pseudo-first order kinetic model by Lagergreen is used as follows:

$$\frac{dq}{dt} = k(q_t - q_e)$$

For t values larger than zero, the equation is integrated as follows:

$$\ln(q_t - q_e) = \ln(q_e) - k_1/t,$$

where, q_e is the amount of solute adsorbed at equilibrium, q_t is the amount of solute adsorbed at any given time *t* and k_1 is the rate constant of the pseudo-first order adsorption (min^{-1}). The slope of the plot is determined from the graphical representation of $\ln(q_t - q_e)$ versus t, the rate constant of pseudo-first order adsorption and the capacity of sorption q_e being calculated. From the calculations the capacity of sorption q_e has a value of 131.8 mg/g and k_1 a value of 0.00138 min^{-1}. $R^2 = 0.990$ (fig. 6a).

The intra-particle diffusion model is expressed as follows:

$$q = k_i t^{1/2} + C$$

where C is the intercept and k_i is the intra-particle diffusion rate constant (mg/g $min^{1/2}$). The k_i constant involved in the intra-particle diffusion model can be evaluated from the slope of the graphical dependence for q_t versus $t^{1/2}$ (fig. 6b)

The k_i and C values are 0.0013 mg $g^{-1}min^{-1}$ and 142.1, respectively, $R^2 = 0.9860$.

The pseudo-second order equation based on the adsorption equilibrium capacity can be expressed as follows:

$$\frac{dq}{dt} = k(q_t - q)^2$$

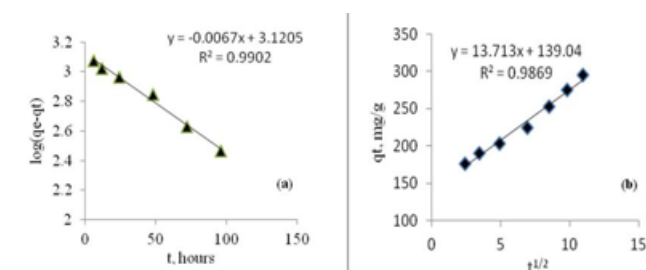Fig. 6. Adsorption kinetics of HAs mixture on xGnP, pseudo-first order (a), intra-particle diffusion (b) and pseudo-second order (c) models

The integrated linear form of the above equation is represented as:

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

A plot of the t/q_t versus t yields a linear relationship from which q_e and k_2 can be determined from the slope and the intercept. The k_2 and q_e values are 0.0033 g mg^{-1} min^{-1} and 100.0 mg g^{-1}, respectively, and the $R^2 = 0.994$ (fig. 6c). Comparing the figures of the kinetic models, it appears that pseudo-second order model has the best agreement with the experimental results.

The adsorption isotherms of the humic acids mixture on xGnP

The adsorption isotherms are important for describing how solutes interact with the nano carbon-based adsorbents, which indicates when the adsorption process reaches its equilibrium, the most significant of which is indicated in table 2.

Table 2

THE FUNCTIONAL EQUATIONS OF DIFFERENT SORPTION MODELS

Isotherm	Functional Form
Freundlich	$q_e = K_F C_e^{1/n}$
Langmuir	$q_e = q_{max} \dfrac{K_L C_e}{1 + K_L C_e}$
Temkin	$q_e = \dfrac{RT}{b} \ln(aC_e)$
Halsey	$q_e = (\dfrac{K_H}{C_e})^{1/n_H}$
Harkins-Jura	$1/q_e^2 = (A/B) - (1/A)\log C_e$

Nomenclature: C_e – equilibrium concentration, mg/L; C_s – adsorbate concentration at a given temperature, mg/L; E_0 – solid characteristic energy towards a reference compound; q_e – amount adsorbed, mg/g; q_{max} saturated monolayer sorption capacity, mg/g
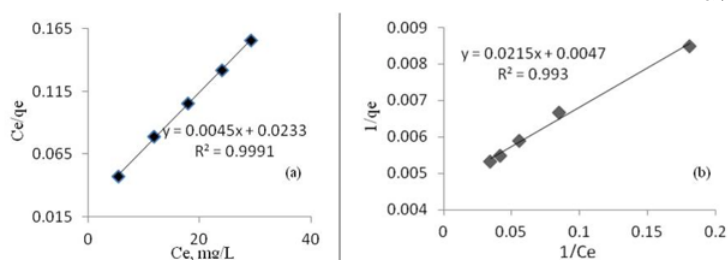
Our study was developed by using the following isotherm models: Freundlich and Langmuir 1 and 2 and a model's suitability determined on the basis of each correlation coefficient value.

Langmuir isotherm
The Langmuir isotherm can be linearized on the basis of different equations two of these types were used in our study. The Langmuir model is expressed as follows:

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e}$$

where q_{max} (mg/g) and K_L (L/mg) are Langmuir constants related to the adsorption capacity and energy of adsorption [9, 10]. K_L is the adsorption equilibrium constant in L/mg related to the apparent energy of adsorption, and q_e is the amount adsorbed on the unit mass of the adsorbent (mg/g) when the equilibrium concentration is C_e (mg/L). The separation factor R_L describes the type of isotherm and is defined as follows:

$$R_L = 1/(1 + KC_0)$$

The R_L values indicate if the sorption process is more ($R_L < 1$) or less favorable (($R_L > 1$).
During this process, the R_L parameter for the Langmuir 1 isotherm has a 0.32 value, which favors the adsorption process indicating a favorable adsorption process on xGnP (fig. 7a) $K_L = 0.00069$ L/mg, $q_m = 1250$ mg/g and $R^2 = 0.9990$. Langmuir 2 isotherm has a R_L value of 0.64, which favors the adsorption process indicating a favorable adsorption process on xGnP (fig. 7b) $K_L = 0.0019$ L/mg, $q_m = 1250$ mg/g and $R^2 = 0.993$.

Freundlich isotherm
The Freundlich isotherm provides little physical insight into the adsorption mechanism. This isotherm represents the first studied adsorption model, and it can be expressed as follows:

$$q_e = K_F C_e^{1/n}$$

where K_F and 1/n are the Freundlich constants that indicate the adsorption capacity and the adsorption intensity, respectively. The magnitude of 1/n is related to the favorability of the adsorption and the heterogeneous surface of xGnP.
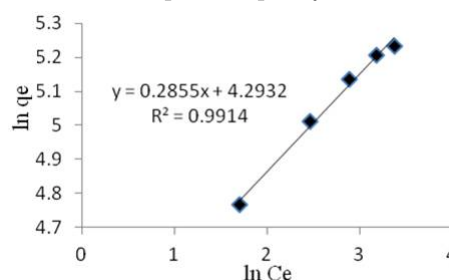If 1/n presents sub-unity values, the adsorption is favorable and the adsorption capacity increases [11,12].

Fig. 7. Langmuir 1 and Langmuir 2 isotherms of sorption for HAs mixture on the xGnP surface

Fig. 8. Freundlich adsorption isotherm of sorption for HAs mixture on the xGnP surface

Isotherm	Linear form	Parameters			
Freundlich	$\ln q_e = \ln K_F + 1/n \ln C_e$	K_F(mg/g)=72.96	1/n=0.285	$R^2 = 0.991$	
Langmuir 1	$C_e/q_e = 1/Kq_m + 1/Kq_m C_e$	K_L=0.00069	q_m=1250	R^2=0.9990	R_L= 0.32
Langmuir 2	$1/q_e = 1/q_m + 1/Kq_m C_e$	K_L= 0.0019	q_m=1250	R^2=0.993	R_L= 0.64

Table 3

LANGMUIR 1 AND 2 AND FREUNDLICH ISOTHERM PARAMETERS DATA FOR THE SORPTION OF HAS MIXTURE ON XGNP

During the absorption of HAs mixture to xGnP, the value of $1/n$ is 0.285, suggesting a favorable adsorption process (n = 3.508, K_F = 72.96 mg/g, and R^2=0.991). These values indicate a favorable adsorption, the value of $1/n$ indication the heterogeneity of the surface, too.

Thermodynamic studies

Experimental data obtained at 293, 298 and 303 K are used to calculate the Gibbs free energy change ($\Delta G°$), the enthalpy change ($\Delta H°$) and the entropy change ($\Delta S°$). The Gibbs free energy change of the sorption reaction is calculated as follows:

$$\Delta G° = -RT\ln K_e; \Delta G° = \Delta H° - T\Delta S°$$

where K_e is the equilibrium constant that can be obtained from the Langmuir isotherm, R is universal gas constant 8.314 Jmol^{-1}K^{-1} and T is the absolute temperature (K). The negative value of $\Delta G°$ confirms the feasibility of the process based on a natural adsorption of HAs mixture on the xGnP surface (fig. 9).
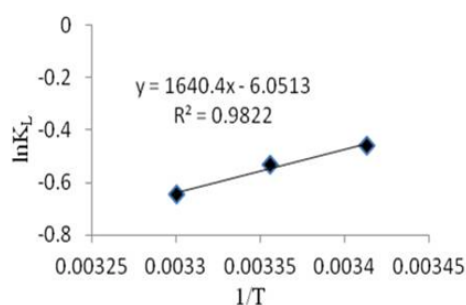
Fig. 9. A plot of $\ln K_L$ variation by $1/T$ for HAs mixture adsorption on xGnP

The $\Delta H°$ and $\Delta S°$ are obtained from the slope and the intercept of the dependence between Gibbs free energy change $\Delta G° = -TR\ln K_L$ and temperature T. The calculated values of $\Delta H°$ and $\Delta S°$ are 136.34 kJ mol^{-1} and -50.30 J mol^{-1}K^{-1} for the temperature range between 293 and 303 K (fig. 10). The negative value of $\Delta H°$ indicates an endothermic process and the positive one of $\Delta S°$ indicates a homogeneous distribution of HAs mixture at the solid/solution interface.
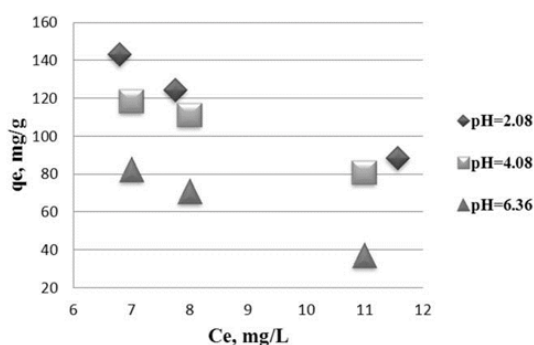
Fig. 10. Adsorption kinetics of HAs mixture on xGnP at pH = 2.08 (♦), pH = 4.08 (■) and pH = 6.36 (▲)

In another paper was studied the vancomycin sorbtion on piritine and ixidized exfoliated graphite nanoplatelets [13].

Conclusions

The purpose of this work was to study the sorption of humic acids mixture obtained from defatted algal biomass on exfoliated graphite nanoplatelets. The process of adsorption takes place with good results, in the following conditions: at HAs mixture concentration of 18.6 mg L^{-1}, an xGnP amount of 0.01 mg in 25 mL of solution, at a temperature of 25°C and at acidic pH values, in aqueous solution. This study could be a model to explain the better affinity of xGnP for organic contaminants in aquatic environmental samples in which natural organic matter is ubiquitous and it can influence the overall sorption as a main factor of the surface area modifications of nanomaterials.

References

1. OGLESBY RT, CHRISTMAN RF, DRIVER CH., Adv Appl Microbiol., 9, 1967, p. 171-184.
2. PETTIT RE., Published paper http://www.humates.com/pdf/ORGANICMATTERPettit.pdf.
3. DERCOVA K, SEJAKOVA Z, SKOKANOVA M, BARANCIKOVA G, MAKOVNIKOVA J., Chemosphere, 66, 2007, p. 783–790.
4. AL-HAMADANI YAJ, CHU KH, SON AHJEONG, HEO J, HER N, JANG M, PARK CM, YOON Y., Sep Purif Technol., 156, 2015, p. 861–874.
5. STAFIEJ A, PYRZYNSKA K., Microchem J., 89, 1, 2008, p. 29-30.
6. ION AC, ALPATOVA A, ION I, CULETU A., Mat Sci Eng B-Solid, 176, 7, 2011, p. 588-595.
7. KALAITZIDOU K, FUKUSHIMA H, DRZAL LT., Composites: Part A, 38, 2007, p. 1675–1682.
8. WANG Y, LIU X, HUANG Y, HAYAT T, ALSAEDI A, LI J., J Radioanal Nucl Che., 2016, p. 1-9.
9. FAKHRI A, ADAMI S., Arabian J of Chemistry, 2013, in press.
10. NEAGU M., POPOVICI D.R., VIJAN L.E, CALIN C., Rev Chim.(Bucharest), **68**, no. 3, 2017, p. 496
11. VASANTH KUMAR K, SIVANESAN S., J Hazard Mater, B126, 2005, p. 198-201.
12. NEAGU M., POPOVICI D.R., DUSESCU C.M., CALIN C., Rev Chim.(Bucharest), **68**, 1, 2017, p. 139
13. RADU, E. STOICA, R., DONCEA, S.M., VASILIEVICI, G., OPRESCU, E.E., BOLOCAN, I., AL OGAIDI, A.J.M., ION, I, ION, A.C., Rev. Chim. (Bucharest), **67**, no. 3, 2016, p. 401