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ADSORPTION OF NAPHTHALENE ONTO CARBONIC NANOMATERIAL GRAPHITIC NANOPLATELETS IN AQUEOUS SOLUTIONS

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În această lucrare se prezint[adsorbţia naftalinei pe nanostructuri de grafit (xGnP) în sisteme apoase în prezenţa unor concentraţii mici de materii organice naturale (NOM), studiindu-se influentele timpului de contact şi a concentraţiei iniţiale de sorbent.

Observaţiile experimentale din acest studiu arată că adsorbţia poate fi explicată prin diverse mecanisme de interacţie dintre poluanţii organici şi nanoparticulele pe bază de carbon, precum şi prin interacţii moleculare specifice. Izotermele de adsorbţie au fost interpretate cel mai bine cu ajutorul modelului Freundlich. S-a calculat o capacitate de adsorbţie a naftalinei pe xGnP de 1.1652 mg g^{-1}.

In this paper, we report the adsorption of naphthalene on exfoliated graphite nanoplatelets (xGnP) in aqueous systems, in the presence of small concentrations of NOM. The effect of the process variables, contact time and initial concentration of the adsorbate over the naphthalene adsorption is reported.

Experimental observations in this study indicate that the adsorption behaviour could be explained through several interaction mechanisms between organic pollutants and carbon based nanoparticles and also through, such as specific molecular level interactions and nanoscale control of surface properties.

All adsorption isotherms were fitted well using the Freundlich model and the adsorption capacity of naphthalene on xGnP was calculated to be 1.1652 mg g^{-1}.

Keywords: naphthalene, exfoliated graphite nanoplatelets, adsorption

1. Introduction

Carbonic materials like activated carbon are major adsorbents for water treatment. That is due to the wide specific graphite surface in activated carbon that allows adsorption of contaminated organic compounds such as aromatics and nitrobenzene [1]. Over the last decade, both graphene layer and oxygen functional

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groups were found to play significant roles in aromatics adsorption. Chen et al. [2] reported that adsorptive interactions between organic contaminants and graphite layers are due to the π-π electron-donor-acceptor interaction between aromatic compounds and highly polarizable graphene sheets. Adsorption sites could be varied from graphene layer to surface oxygen functional groups, switching from monolayer adsorption controlled by diffusion kinetics to two or multi-step adsorption in the isotherms by rapid adsorption kinetics [3].

Polycyclic aromatics hydrocarbons (PAHs) are chemical pollutants with two to six fused benzene rings, ubiquitous in the atmosphere, aerosols, soils and sediments and are well known toxic hazardous pollutants, causing tumors in organisms [4]. PAHs have natural and anthropogenic sources such as industrial processes, engine exhaust, terrestrials coal deposits. It is known that the reactive fate of volatile PAHs is governed by gas-phase reactions with the hydroxyl (OH) radical. Due to their low-vapour pressure and aromaticity, PAHs are mainly adsorbed on fine carbonic particles [5]. For different PAHs, adsorption seems to relate with their molecular size, the larger the molecular size, the lower the adsorbed volume capacity [6].

Adsorption treatments provide a simple approach to effectively removing organic pollutants from the aquatic environment, activated carbon being used as adsorbent for environmental purification [7]. Environmental applications of carbon nanomaterials [8, 9] have been studied for removal of organic pollutants [10] and metals [11, 12], but few studies dealt with the interfacial interactions of organic contaminants with carbon nanomaterials [13].

In recent years, exfoliated graphite nanoplatelets (xGnP) have attracted attention as inexpensive substitutes for carbon nanotubes in several nanostructured materials, because of the excellent in-plane mechanical, structural, thermal and electrical properties of graphite [14, 15]. The main challenge for a broad area of applications is to uniformly disperse it in the medium. Their hollow and layered nanosized structures make good candidates for adsorbents of environmental contaminants. Exfoliated graphite and graphite nanosheets [16] were utilized as sorbents for oils, 1,2-dichlorobenzene [17], dyes [18], methylene blue and methyl orange [19] from aqueous solutions. Sorption capacity of organic molecules towards exfoliated graphite and graphite nanosheets was found to be a function of the exfoliation process [20], particle size [21], surface area, surface modification, adsorbate/adsorbent ratio, temperature and pH [13].

Despite demonstrated good adsorption capacity for exfoliated graphite to organic contaminants, there is significant gap in elucidating the adsorption mechanisms and factors controlling the interactions between organic contaminants and the exfoliated graphite. Several adsorption mechanisms were suggested to explain the interactions between the organic molecules and carbon nanotubes (CNT). Structurally, CNTs and graphite are made up of the same building blocks

– graphene, therefore adsorption of organic molecules to the graphitic nanoplatelets may follow the same trends. π-π donor-acceptor interactions between electron rich surface of CNTs and organic molecules [22] were found to be a significant factors that influence the adsorption of polar [23] and non-polar [24] aromatic molecules. In this work, naphthalene was assigned as a representative of the PAHs compounds due to its structural characteristics among other PAHs compounds, such as molecular size and water solubility.

Natural organic matter (NOM) was shown to effectively stabilize carbon nanoparticles in aqueous suspensions [25]. Mainly composed of humic substances, NOM may greatly influence the interaction between graphitic nanoparticles and organic pollutants by modifying surface area and porosity of graphitic nanoparticles and also affecting the environmental behaviour of graphitic nanomaterials such as dispersion and transport.

In this paper, we report the adsorption of naphthalene on exfoliated graphite nanoplatelets in aqueous systems, in the presence of small concentrations of NOM for good dispersions. The effect of the process variables, contact time and initial concentration of the adsorbate over the naphthalene adsorption is reported.

2. Experimental

2.1. Materials

Exfoliated graphite nanoplatelets (xGnP) (with average diameter of 15 μm and average thickness of 15 nm) were provided by the Department of Chemical Engineering and Materials Science, Michigan State University). Fabrication, geometrical and surface characteristics can be found in [26].

Suwannee River natural organic matter (SRNOM) was purchased from the International Humic Substances Society (St. Paul, MN).

Naphthalene (> 98% purity) was purchased from Acros Organics Co.

All the other chemicals were analytical reagent grade and were purchased from Merck.

2.2. Methods

Scanning electron microscopy (SEM)

The surface morphology of as-received xGnP aggregates was studied by scanning electron microscopy (SEM) technique. A typical SEM image of the xGnP aggregates is shown on Fig.1. The samples were directly coated on the conductive surfaces and SEM images were taken by SEM microscope coupled with energy dispersive X-ray spectroscope (Philips Quanta Inspect F) at 30 kV and 2000x magnification.

Study of NOM adsorbtion on xGnP was previously done [10]. A 100 mgL^{-1} NOM aqueous solution was used for the dispersion of xGnP. The NOM solutions of this concentration of NOM and different concentrations of xGnP were sonicated for 30 min at 75 W using a Sonicator 3000 (Misonix, Inc., Farmingdale, NY), equipped with a microprobe.

Adsorption kinetics of naphthalene

For the measurement of the uptake of naphthalene onto adsorbents in time, 10 mL of naphthalene solutions in the concentration range 76.88 – 115.35 mg/L were mixed with 4.0 mg xGnP in 25 mL sorption capped flasks and stirred continuously at pH 7. The xGnPs were firstly dispersed using a MISONIX 75 W for 30 minutes. Sampling was done by fast filtration each hour for a total of 40 hours. The background solution (pH=7.0) contained 100 mg NOM. The pH of the supernatant after sorption experiments was measured, showing that the solutions pH values were were unchanged by the sorption process. Experimental uncertainties were evaluated in vials without carbon nanomaterials, the total uncertainty being less than 2% of the initial concentration. The concentration of the residual naphthalene in solution was spectrophotometrically determined and the adsorption amount q_t was calculated with equation (1):

$$q_t = (C_0 - C_t)V / m \tag{1}$$

q_t is the adsorption amount at time t, C_0 is the initial concentration of naphthalene solution, C_t is the concentration of naphthalene solution at time t, V is the volume of naphthalene solution, m is the mass of xGnP.

Adsorption isotherms

A series of naphthalene solutions with concentrations ranging from 115.3 mg/L to 76.88 mg/L was prepared by dissolving different amounts of naphthalene in distilled water. In each adsorption experiment, 4 to 5 mg of exfoliated graphitic nanoplatelets (xGnPs) was suspended in 10 mL of the naphthalene solution. Adsorption isotherms were obtained at pH 7 in capped vials; the suspensions were shaked at room temperature. Triplicate runs of all the tests different by less than 1% were achieved demonstrating the reproducibility of the obtained data. The amount of adsorbed naphthalene was calculated using a UV-VIS spectrophotometer (Jasco V-530), by subtracting the amount found in the supernatant after adsorption from the amount of naphthalene present before addition of the adsorbent. Absorbance was measured at 275 nm for the determination of the naphthalene content. Calibration experiments were done separately before each set of measurements with naphthalene solutions. Centrifugation was used before analysis to avoid potential interference between suspended scattering particles in the UV-VIS analysis. The adsorption capacities were calculated based on the differences between concentrations of solutes before and after the experiment according to equation (2):

$$q_e = (C_0 - C_e)V / m \tag{2}$$

q_e is the concentration of the adsorbed solute (mg/g); C_0 and C_e are the initial and the equilibrium concentrations of the solute in solution (mg/L); V is the volume of the solution (in mL) and m is the mass of adsorbent in g.

3. Results and discussion

Surface morphology and stability of xGnP

From a theoretical point of view, is difficult to provide structural and energetic information concerning the interaction between PAHs and carbonic surfaces because these systems are too big for efficient *ab initio* calculations. The most accurate methods for determining the geometry and binding energy of PAHs clusters are correlated quantum chemistry calculations based on large basis sets.

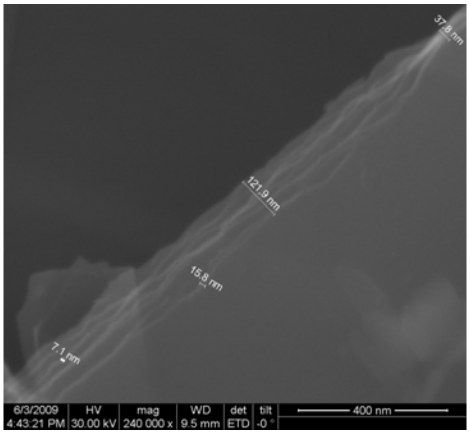

Fig. 1. SEM images of xGnPs surface (image taken at 240 000X magnification)

To understand the morphology of naphtalene adsorption on xGnPs, SEM images were taken (Fig. 1). Fig. 1 shows that xGnPs surface is approx. 10 nm in width and irregular and porous in nature.

Adsorption studies

The Freundlich and Langmuir isotherms and their linearized forms are given in Table 1.

Table 1

Isotherms and their linear forms

Isotherm	Form	Linear form	Plot	Ref
Freundlich	$q_e = K_F C_e^{1/nF}$	$\log(q_e)=\log(K_F)+1/n_F\log(C_e)$	$\log(q_e)$ vs. $\log(C_e)$	[27]
Langmuir	$q_e=(q_m K_a C_e)/(1+K_a C_e)$	$C_e/q_e = 1/q_m C_e+1/K_a q_m$	C_e/q_e vs. C_e	[24]

C_e – equilibrium solute concentration, mg/L; q_e – amount of contaminant sorbed at equilibrium mg/g; K_F – Freundlich isotherm constant (mg/g)(L/g)1/n_F; n_F – Freundlich exponent; q_m – maximum sorption capacity, mg/g; K_a – Langmuir constant related to energy of adsorption, L/mg.

The correlation coefficient r^2 values were used to obtain the best fit linear equation. The Langmuir isotherm could be linearized to at least four different types, the Langmuir constants q_m and K_a values can be calculated from the plot between C_e/q_e *vs.* C_e, $1/q_e$ *vs.* $1/C_e$, q_e *vs.* q_e/C_e and q_e/C_e *vs.* q_e for type 1, 2, 3 and 4 Langmuir isotherms, respectively. Similarly, the Freundlich isotherm constants K_F and $1/n_F$ can be calculated from the plot of log (q_e) vs. log (C_e).

Effect of the contact time and concentration

In order to establish the time needed to reach the equilibrium concentration and to find the kinetics and adsorption process mechanism, the adsorption of naphthalene on xGnP graphitic nanoplatelets was studied as a function of contact time. Results are shown in Fig. 2.

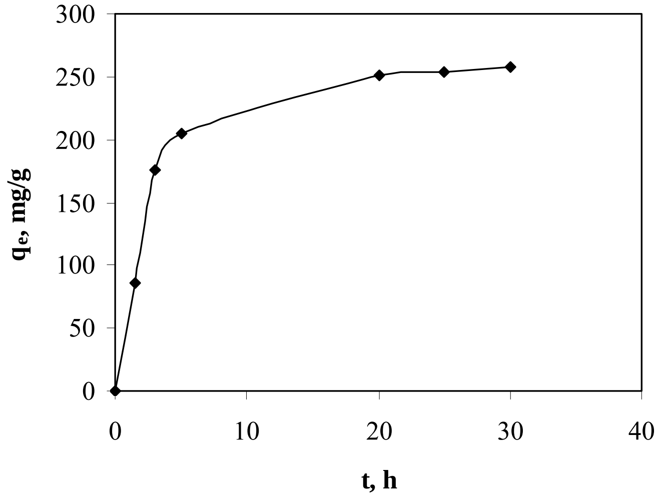

Fig. 2. Effect of contact time on naphthalene removal ($c_{naphthalene} = 10^{-3}$ M, adsorbent dosage = 0.4 g L^{-1}, T = 25°C, pH = 7)

Fig. 2 indicates that the required time for equilibrium adsorption is of about 20 hours. The equilibration time will be maintained in the future studies.

It is shown that the rate of naphthalene uptake is big at the beginning and about 50% of the adsorption is completed within the first 4 hours. For all equilibrium adsorption studies, the equilibrium period was kept at 40 hours. The effect of the concentration on the equilibration time was investigated as a function of the initial naphthalene concentration, the results presented in Fig. 3 and it was found that the equilibrium time is independent of the initial concentration.

The effect of the initial naphthalene concentration was investigated and the results are presented in Fig. 3.

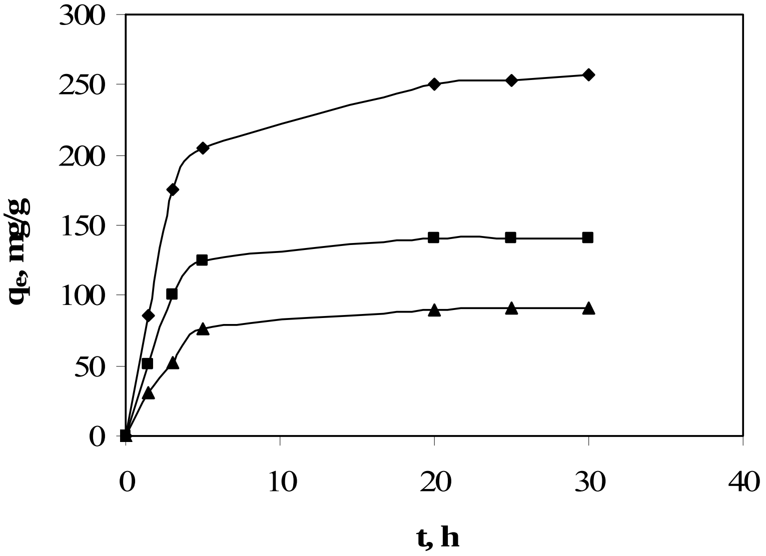

Fig. 3. Effect of the initial naphthalene concentration on the equilibration time. The concentration of naphthalene: (♦) 10^{-4} M; (■) $5x10^{-4}$ M; (▲) $3x10^{-4}$ M

It was found that the equilibration time and the time required to achieve a definite fraction of the equilibrium adsorption is independent of the initial concentration.

Kinetics of adsorption

An adsorption process is controlled by three diffusion steps: transport of the solute from bulk solution to the film surrounding the adsorbent; transport from the film to the adsorbent surface and transport from the surface to the internal sites.

Several kinetic models are used to explain the adsorption mechanism. Pseudo-first order and pseudo-second order kinetics allow the computation of the first and second order constants, k_1 and k_2, and of the linear regression correlation coefficient, r^2. The pseudo-second order equation based on equilibrium adsorption offers data about the equilibrium adsorption capacity (q_e) and about the second order constants (k) which can be determined experimentally from the slope and the intercept of plot t/q *vs.* t (Fig. 4). As it can be seen from Table 2, the calculated linear regression correlation coefficient (r^2) is 0.9988 and the experimental q_e value agrees with the calculated values obtained from the linear plots.

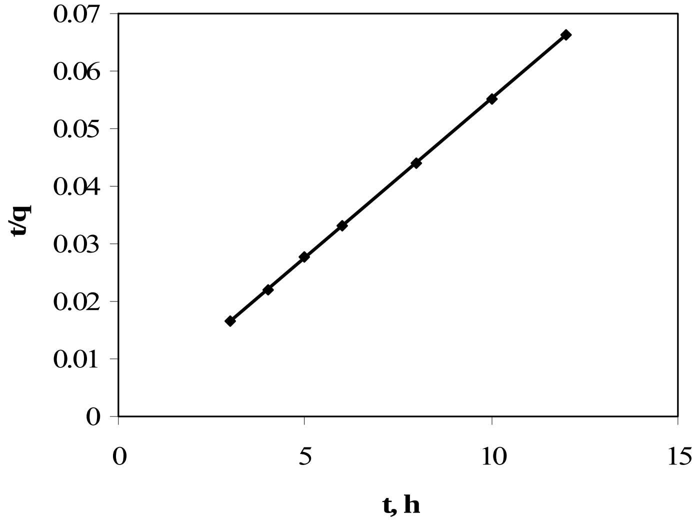

Fig. 4. Pseudo-second order kinetics plots for the removal of naphthalene, $c_{naphthalene} = 5.66x10^{-3}$ M, adsorbent dosage = 0.4 g/L, T = 25°C, pH = 7 (t/q = 0.0055 t + 5E-08)

Table 2

Pseudo-second order constants for the removal of naphthalene by exfoliated graphite nanoplatelets

Kinetics order	q_e, experimenal (mg/g)	q_e, calculated (mg/g)	K (1/mg·hour)	r^2
Pseudo-first order	250.82	235.50	-	0.8358
Pseudo-second order	250.82	252.45	0.0045	0.9988

As it can be observed from Table 2, the calculated linear regression correlation coefficient, r^2 was small, 0.8358 for the pseudo-first order equation based on the Lagergreen equation $\log(q_e\text{-}q) = \log q_e - k_i t/2.303$, where q_e, q, t and k_i are respectively, the amounts of naphthalene adsorbed at equilibrium time and at any time t (in mg/g) and k_i is the rate constant of adsorption (min^{-1}). The experimental values did not agreed with the calculated ones, obtained from the linear plots. These results indicate that the adsorption of naphthalene on xGnP follows pseudo-second order kinetics.

Adsorption isotherms

In order to evaluate the efficacy of the dispersion procedure, the equilibrium adsorption of naphthalene was studied as a function of equilibrium concentration. The adsorption isotherms of naphthalene on xGnP adsorbent dispersed in the presence of a very small concentration of NOM is presented in Fig. 5 and 6. Adsorption isotherms were studied to determine the sorption behaviour and to estimate the adsorption capacity. The adsorption process of naphthalene was tested with Langmuir and Freundlich isotherm models. Two commonly used empirical adsorption models, Freundlich and Langmuir, which correspond to heterogeneous and homogeneous adsorbent surfaces [28] were employed in this study. The comparison of Freundlich and Langmuir isotherms r^2 values showed that the value from the Freundlich isotherm (r^2=0.9895) is more appropriate for the calculation of equilibrium parameters (Table 3).

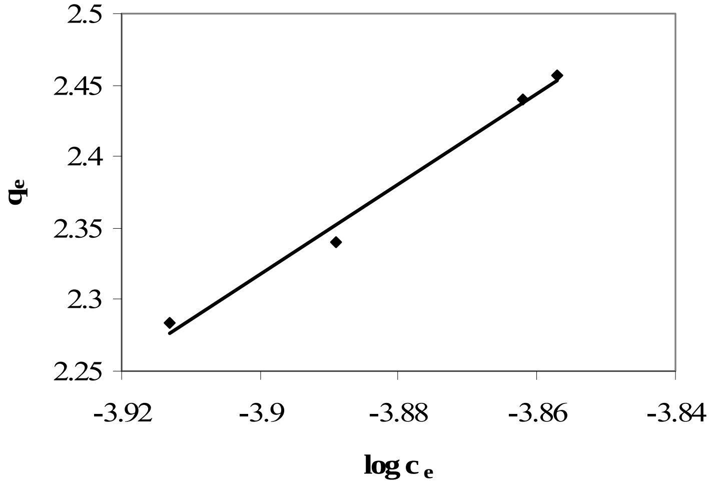

Fig. 5. Freundlich isotherm for the adsorption of naphthalene on xGnP (q_e = 3.1568 log c_e + 14.629).
(♦) experimental data; (-) calculated values

Given the monolayer adsorption volume capacity onto xGnP calculated from the BET surface area (105 $m^2/g^)$, complete monolayer coverage probably did not form from naphthalene. The density of large molecular adsorbates would decrease more than that of small ones when phase changes from solid phase to adsorbed phase, which result in the adsorbed volume capacities for large molecular adsorbate, being lower than small molecular adsorbate and its actual adsorbed volume.

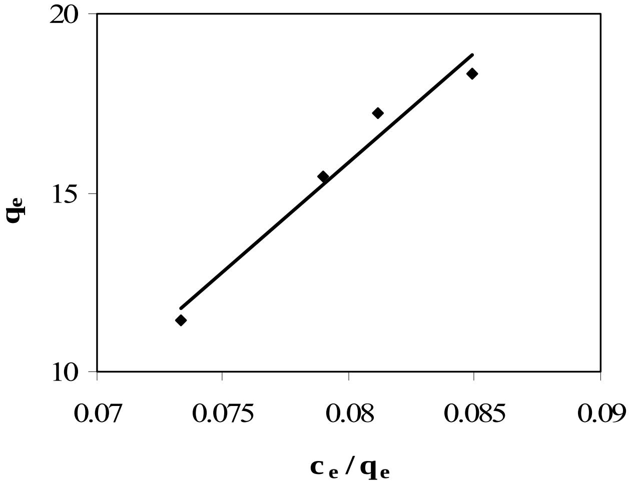

Fig. 6. Langmuir isotherm for the adsorption of naphthalene on xGnP ($q_e = 616.84\ c_e/q_e - 33.492$). (♦) experimental data; (-) calculated values

It was observed from Fig. 6, that Langmuir isotherm (type 1) shows a poor fit towards the experimental data, confirming that it is inappropriate to use these isotherm relations for the adsorption of naphthalene on xGnP.

Table 3

Isotherm parameters obtained by using linear method

Isotherm type	Parameter	Value
Freundlich	K_F, (mg/g)(L/g)^{nF} 1/n r^2	1.1652 0.316 0.9895
Langmuir	$q_{m,}$ mg g^{-1} K_a r^2	0.00162 18.43 0.8683

Overall, the fitting model results indicate that the adsorption process of PAHs on these carbonic nanomaterials would result neither in monolayer formation on a homogeneous surface, nor in simple multilayer formation. It might probably be a combination of partition and Langmuir-type adsorption domains.

Table 4

Freundlich isotherm parameters for other carbon materials used as sorbents for naphthalene, as reported by other investigators, listed together with the xGnP results from this study

Sorbent	K_F, (mg/g)(L/mg)^{nF}	n	Reference
Activated carbon	200.2	0.35	This work
xGnP as received	1.1652	0.56	This work
Nano-C60	50	0.1	[29]
Charcoal	1.7	0.32	[19]

Adsorption of naphthalene onto some carbonic nanomaterials was compared in terms of Freundlich isotherm parameters and it was found that the amount of naphthalene adsorption on xGnP is smaller in comparison with other sorbents (Table 4).

4. Conclusions

Exfoliated graphitic nanoplatelets were used for the adsorption of naphthalene. Experimental observations indicate that the adsorption behaviour could be improved through several mechanisms that enhance the interactions between organic pollutants and carbon based nanoparticles by specific molecular level interactions and nanoscale control of surface properties.

All adsorption isotherms were fitted well using the Freundlich isotherm and the adsorption capacity of naphthalene on xGnP was calculated to be 1.1652.

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