

Ammonium Adsorption on Exfoliated Graphite Nanoplatelets

DANIELA BOGDAN, GEORGE AURELIAN RIZEA, ION ION, ALINA CATRINEL ION*

University Politehnica of Bucharest, Department of Analytical Chemistry and Environmental Engineering, 1-7 Polizu Str., 011061, Bucharest, Romania

Ammonium ions are often encountered in fresh surface and underground water bodies, their maximum allowed concentrations being limited by international and national legislation. Among various techniques for removal of ammonium ions from aqueous solutions, nanotechnologies offer major application for water treatment, adsorption being among them. Nano-adsorbents offer significant solutions, based on their high specific surface area and associated sorption sites, the carbon-based ones being intensively studied in the last year and applied as environmental and food sorbents. Hence, in this study, exfoliated graphite nanoplatelets (xGnP) were used for the removal of ammonium ions by adsorption techniques. The influence of several parameters such as pH, temperature and contact time was studied and kinetic and isotherm models were validated to understand the mechanism of adsorption of ammonium by xGnP.

Keywords: exfoliated graphite nanoplatelets, adsorption, ammonium

Water represents a vital resource for humans. Human health is indissolubly connected on water quality and price. Increasing water quality standards have imposed new challenges on water capture, treatment and distribution systems. Growing pressure on water supplies places mineral waters in an invaluable position on the basis of their chemical composition, purity and reduced contamination from both chemical and microbiological contaminants. There are many pollutants in groundwater and surface water but less in mineral water, the most important pollutants including inorganic anions and cations in addition to organic compounds. To remove these compounds, various carbon materials and ion-exchangers [1-3] and, more recently, carbon nanotubes [4] were investigated in adsorption studies. In comparison, graphite-based nanomaterials have been shown to have important adsorption capacities for water pollutants. The legislative limitations imposed on treatment technologies and the infrastructure associated with mineral water bottling offer the field of nanotechnology some amazing opportunities to develop a new generation of tools for use in water supply systems. The very efficient modular and multifunctional components based on different types of nanomaterials confer nanotechnologies with high-performance, affordable mineral waters and sophisticated treatment solutions that are less reliant on huge infrastructures. Nanotechnology-enabled mineral water treatment has the potential to provide treatment capabilities that have never been used before, and these capabilities could allow for the economic utilization of the involved materials and consequentially lead to less chemical contamination, better microbiological decontamination and better preservation of the natural purity of these waters.

Nanomaterials are defined as material structures that are based on particles smaller than 100 nm, and they possess novel physical and chemical properties related to their high specific surface area such as fast dissolution, high reactivity and strong sorption. Among these applications, adsorption, membrane processes, photocatalysis, disinfection and microbial control, sensing and monitoring have been achieved over the last few years [18].

Adsorption is a very common process for removing organic and inorganic contaminants during water treatment. Conventional adsorbents are often limited to activated carbon, which can effectively reduce organic contaminants such as benzene, chlorobenzenes, trichloroethylene, carbon tetrachloride, methylene chloride and vinyl chloride, pesticides such as atrazine, disinfection by-products such as chlorine, chloramines, heavy metals such as lead and cadmium and radioactive species such as radon and uranium. All treatment methods based on activated carbon have limitations and must be used in combination to effectively treat water. Activated carbon will not remove microbial contaminants (bacteria and viruses), excess fluoride, ammonium, nitrate, nitrite and other compounds. In comparison, nano-adsorbents offer significant improvement with their high specific surface area, associated sorption sites, short intra-particle diffusion distance and tunable pore size and surface chemistry. Graphene has recently been shown to have biological properties [5,6] that are superior to those of activated carbon because of its superior biocompatibility [7]. The biological applications of graphene include antimicrobial properties in conjunction with NIR irradiation [8, 9]. Among the nano-adsorbents used in ammonium removal from water, there are numerous carbon-based adsorbents, metal-based nano-adsorbents and polymeric nano-adsorbents. All of them can be integrated into adsorbents (fixed or fluidized) as pellets, beads or porous granules. The most prominent among these are the carbon-based nano-adsorbents, which exhibit higher efficiencies than activated carbon for inorganic or organic chemicals [10]. Carbon nanotubes (CNT), pristine and functionalized display a higher efficiency than activated carbon in the adsorption of molecules with oxygen containing functional groups, because of their accessible pores and sorption sites. Even in the aqueous phase, (CNT) aggregates contain interstitial spaces with high adsorption energy sites for several molecules [11,12]. Their possible interactions include hydrophobic effects, π - π interactions, hydrogen bonding, covalent bonding and electrostatic interactions [13]. The π electrons from the CNT surface allow π - π interactions with polar aromatic compounds [14,15], the functional groups -COOH, -OH and -NH₂ form hydrogen

* email: ac_ion@yahoo.com; Phone: (+40)723295334

bonds with the donor graphitic carbon from the CNT surface [16], and electrostatic interactions facilitate the adsorption of positively charged organic molecules [17].

The adsorption characteristics of ammonium on exfoliated graphite nanoplatelets (xGnP) were investigated in this study. The adsorption isotherms and kinetics of the adsorption processes were measured, and the equilibrium data were fitted to Langmuir, Freundlich, Temkin, Harkin-Jura and Halsey equations to determine the correlations between the isotherm models and the experimental data. Thermodynamic and kinetic parameters were calculated to determine the adsorption mechanisms and several influences such as the pH, temperature, and initial NH_4^+ concentration were also studied.

The results obtained were compared with those from traditional adsorption methods for polluted water remediation are based on solid adsorbents such as activated carbon [19,20] and porous zeolites [21–23]. Graphene and some of its functionalized forms were recently shown to adsorb organic and inorganic species [24,25]. High ammonium adsorption was observed on oxidized graphene because of acid-base interactions with the oxygen-containing functional groups located at the edges of the graphene layers [26]. The reduced graphene was prepared by reducing the oxidized compound to present different adsorption capacities for ammonium based on the oxidized forms [27]. An increased porosity after reduction did not enhance ammonium adsorption, emphasizing the importance of chemical adsorption [28]. Based on the high surface area and the hydrogen bonding interactions, [29], we found that NH_4^+ adsorption on xGnP is strong, and it can be applied in removing it from aqueous solutions.

Experimental part

Chemical reagents and instrumentation

Ion chromatograph: 850 Professional IC (ion chromatography) AnCat-MCS using a Metrohm intelligent Partial Loop (MiPT) technique with a conductivity detector; cation separator column-Metrosep C4-150/4.0; cation guard column-MetrosepRP 2 Guard/3.5; Detector: 850 Professional conductivity detector (0-15,000 $\mu\text{S}/\text{cm}$); Professional drift < 0.2 nS cm/h; Professional sample processor; and Metrohm patented Dosino technology, Metrohm, Herisau, Switzerland.

Reagents

Commercial exfoliated graphite nanoplatelets (xGnP) with an average diameter of 15 μm and average length <0.01 μm were purchased as powder from XG Sciences, Inc., Michigan US. Geometrical and surface characterization was provided by the producer.

Reagent water: ultrapure water (UPW) from Millipore Direct Q3 with UV lamp: resistivity > 18.2 M Ω cm (25 $^\circ\text{C}$); flow = 0.5 L/min; total organic carbon TOC < 5 ppb; particles not larger than 0.22 μm .

Ammonium chloride salt (NH_4Cl) (molecular weight of 53.16 g/mol, was supplied by Merck, Germany.

Eluent solution: 1.7 mM HNO_3 and 0.7 mM dipicolinic acid

Stock standard anion solutions: 1,000 mg L^{-1} stocks were purchased as certified solutions or prepared from ACS reagent grade, potassium or sodium salts from Merck.

Analytic standardized IC methods SREN ISO 10304-1:2,009 were used for the anion determinations and SREN ISO 14911 was used for the cation determinations in water.

All bottles were soaked in Milli-Q water, placed in an ultrasonic bath and rinsed three times with Milli-Q water before use. An aliquot (20 mL) of the samples was transferred into propylene vials and degassed for 30 minutes before analysis. The instrument was calibrated weekly against an external standard solution and a regression fit value of 0.995 was required for each element. The preparation and analysis of samples, standards and blanks were performed in triplicate. The method detection limit (MDL) for the anions was calculated by taking three times the standard deviation of a blank sample signal that was analyzed 10 times [30]. Several cations (Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+}) including NH_4^+ were analyzed by IC.

Results and discussions

Characterization of xGnP

Surface morphology of xGnP before and after the adsorption of ammonium ions is presented in figure 1. It shows the presence of a porous structure of the carbon surface, before the adsorption of ammonium, this porous aspect being due to the dispersion agent.

Figure 1 shows the image of xGnP before and after ammonium adsorption. In figure 1bit can be observed that

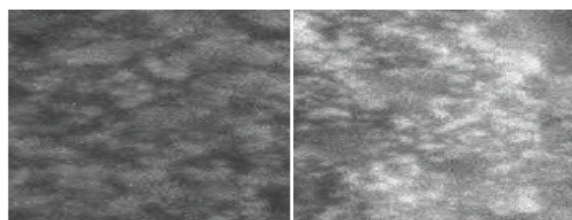


Fig. 1. Scanning electron microscopy before and after the adsorption of ammonium ion

the pores are masked by a white mass, this aspect confirming the ammonium ion adsorption on the surface.

Contact time effect

To determine the time required for NH_4^+ adsorption onto xGnP, 50 mL of 20 mg/L NH_4Cl solution was shaken with 1 mg xGnP. The equilibrium studies were performed with contact times ranging from 10 to 90 min. The removal efficiency did not increase after 30 min of stirring. Based on these results, the contact time for further studies was 30 min with permanent stirring.

Temperature effects on adsorption

The temperature effect on adsorption was studied between 25 and 45 $^\circ\text{C}$ by using 50 mL of 20 mg/L NH_4Cl solution with 1 mg xGnP. The results showed that the adsorption capacity of the xGnP decreased by increasing temperature, indicating an exothermic process.

Kinetics Model	Functional Form
Pseudo-first order model (Lagergreen)	$\frac{dq}{dt} = k_1 (q_e - q_t)$
Intra-particle diffusion model	$q = k_2 t^{1/2} + C$
Pseudo-second order model	$\frac{dq}{dt} = k_3 (q_e - q_t)^2$

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

Table 1
THE EQUATIONS FOR
SEVERAL KINETIC
MODELS

The effect of the initial ammonium concentration

The effect of the initial ammonium concentration was studied at different ammonium ion concentrations in a range from 20 to 100 mg/L at 25°C with 1 mg xGnP for 30 min. The adsorption capacity of the ammonium ions increased by increasing concentration in solutions up to 70 mg/L, and then it remained constant.

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.

The most often used model is the pseudo-first order kinetic model by Lagergren 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

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.

The values of k_1 and q_e are $4.29 \times 10^{-3} \text{ min}^{-1}$ and 414.95 mg g^{-1} , respectively, $R^2 = 0.9826$ (fig.2a).

The intra-particle diffusion model is expressed as follows:

$$q = k_2 t^{1/2} + C$$

where:

C is the intercept

k_2 is the intraparticle diffusion rate constant ($\text{mg} / \text{g} \text{ min}^{1/2}$).

The k_2 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. 2b).

The k_2 and C values are $32.93 \text{ mg g}^{-1} \text{ min}^{-1/2}$ and 280.03 , respectively, $R^2 = 0.9986$.

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

$$\frac{dq}{dt} = k_3(q_e - q)^2$$

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

$$t/q_t = 1 / (k_3 q_e^2) + t / q_e$$

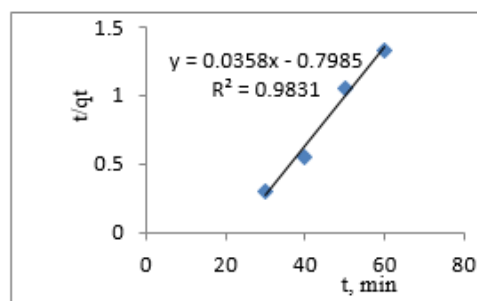
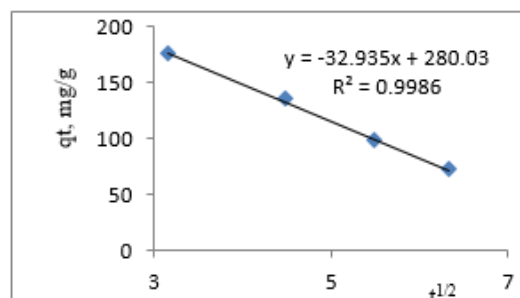
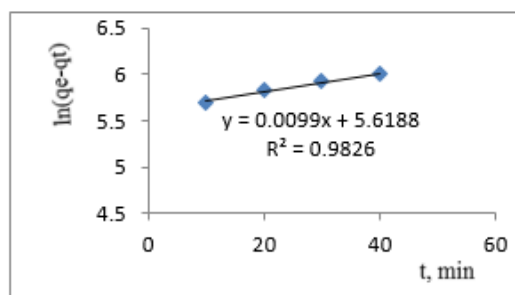


Fig. 2. Pseudo-first order (a), intra-particle diffusion (b) and pseudo-second order (c) kinetic model plots of ammonium adsorption onto xGnP

A plot of the t/q_t versus t yields a linear relationship from which q_e and k_3 can be determined from the slope and the intercept. The k_3 and q_e values are $0.00102 \text{ g mg}^{-1} \text{ min}^{-1}$ and 279.32 mg g^{-1} , respectively, and the $R^2 = 0.9831$ (fig. 2c).

From these results, 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 ammonium ion

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

Our study was developed by using the following isotherm models: Freundlich, Langmuir, Temkin, Halsey

Isotherm	Functional Form
Freundlich	$q_e = K_F C_e^{1/n}$
Langmuir	$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e}$
Halsey	$q_e = \left(\frac{K_H}{C_e}\right)^{1/n_H}$
Harkins-Jura	$1/q_e^2 = (A/B) - (1/A) \log C_e$

Table 2
THE FUNCTIONAL EQUATIONS OF DIFFERENT ADSORPTION MODELS

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.

and Harkins-Jura, and model's suitability was determined on the basis of each correlation coefficient value.

Langmuir isotherm

The Langmuir isotherm can be linearized on the basis of four different equations and 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 [31]. 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 0.90 value, indicating a favorable adsorption process on xGnP. (fig. 3a) $K_L = 0.0025$ L/mg, $q_m = 1660$ mg/g and $R^2 = 0.9652$. Langmuir 2 isotherm has the same value of $R_L = 0.90$, which moderately favors the adsorption process on xGnP (fig. 3 b) $K_L = 0.0021$ L/mg, $q_m = 1666$ mg/g and $R^2 = 0.9986$.

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 n presents sub-unity values, the adsorption is favorable and the adsorption capacity increases [32]. During the absorption of NH_4^+ ions to xGnP, the value of $1/n$ is 1.6037, suggesting a favorable adsorption process (fig. 4), $K_F = 1.062$ mg/g and $R^2 = 0.9897$. These values indicate a favorable adsorption, the value of $1/n$ indicating the heterogeneity of the surface, too.

Harkins-Jura and Halsey isotherms

Both models are useful for multilayer adsorption on adsorbents with heterogeneous pore distribution. Both are very useful for expressing the multilayered nature of the xGnP.

The Harkins-Jura adsorption isotherm is given as follows:

$$1/q_e^2 = (A/B) - (1/A) \log C_e$$

where A and B are connected to multilayer adsorption, which take place on surfaces with heterogeneous pore distribution.

The experimental adsorption capacity and the predicted adsorption capacity based on the Harkin-Jura adsorption isotherm indicate a multilayer adsorption on xGnP. $A = 24.390$, $B = 1.68$, $R^2 = 0.9800$. From the obtained values, the existence of a heterogeneous pore distribution can be estimated.

The Halsey adsorption isotherm [34] is given as follows:

$$q_e = \left(\frac{K_H}{C_e} \right)^{1/n_H}$$

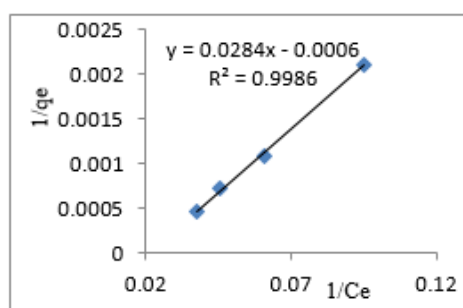
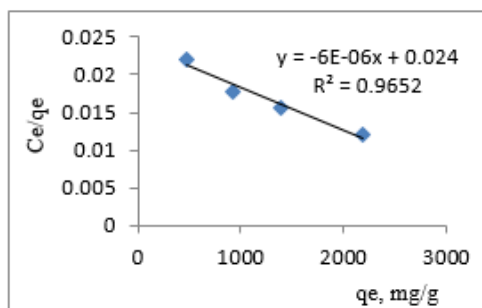


Fig. 3. Langmuir isotherms of sorption for ammonium ions on the xGnP surface

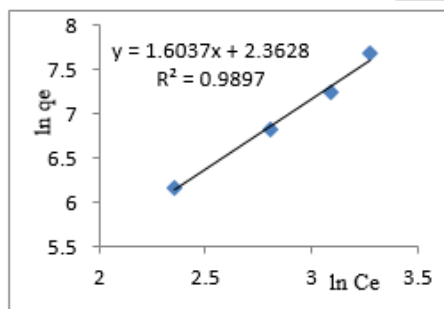


Fig. 4. Freundlich adsorption isotherm of sorption for ammonium ions on the xGnP surface

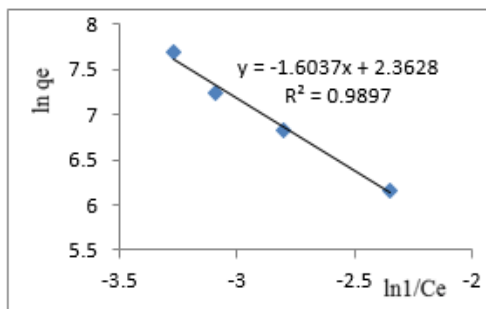
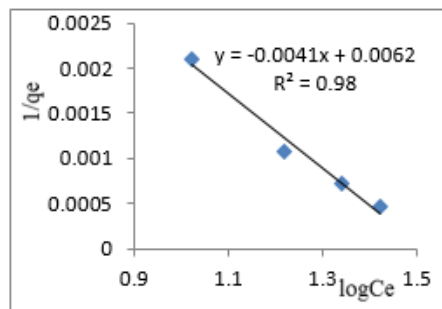


Fig. 5. Harkin-Jura and Halsey adsorption isotherms for ammonium ions on the xGnP surface

Table 3

LANGMUIR 1 AND 2, FREUNDLICH, HARKINS-JURA AND HALSEY ISOTHERM PARAMETERS DATA FOR THE SORPTION OF AMMONIUM ON xGNP

Isotherm	Linear form	Parameters			
Freundlich	$\ln q_e = \ln K_F + 1/n \ln C_e$	$K_F(\text{mg/g})=1.062$	$1/n=1.6037$	$R^2 = 0.9897$	
Langmuir 1 Langmuir 2	$C_e/q_e = 1/K_L q_m + 1/K_L q_m C_e$ $1/q_e = 1/q_m + 1/K_L q_m C_e$	$K_L=0.0025$ $K_L=0.0021$	$Q_m=1666\text{mg/L}$ $Q_m=1666\text{mg/L}$	$R^2=0.9652$ $R^2=0.9986$	$R_L=0.90$ $R_L=0.90$
Halsey	$\ln q_e = (1/n) \ln K - (1/n) \ln C_e$	$n=0.6235$	$k=4.4234$	$R^2=0.9897$	
Harkins-Jura	$1/q_e^2 = (A/B) - (1/A) \log C_e^*$	$A=24.39$	$B=1.68$	$R^2=0.9800$	

where K_H and n_H are the Halsey constants, connected to the adsorption capacity and the adsorption intensity of the process. $K_H = 4.4234$ and $n_H = 0.6235$, $R^2=0.9897$ indicate a multilayer adsorption, especially based on the good fitting of Halsey equation.

The predicted adsorption capacities and the corresponding isotherm parameters together with the regression coefficients are presented in table 3.

Thermodynamic studies

Experimental data obtained at 25 °C are used to calculate the Gibbs free energy change (ΔG°), the enthalpy change (ΔH°) and the entropy change (ΔS°). The Gibbs free energy change of the sorption reaction is calculated as follows:

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

where K_e is the equilibrium constant that can be obtained from the Langmuir isotherm, R is universal gas constant 8.314 J mol⁻¹K⁻¹ and T is the absolute temperature (K). The negative value of ΔG° confirms the feasibility of the process based on a natural adsorption of NH₄⁺ ions on the xGNP surface.

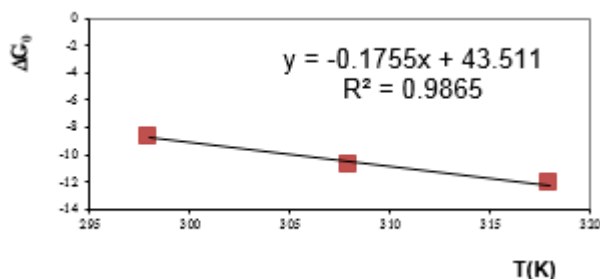


Fig. 6. A plot of Gibbs free energy change by temperature for NH₄⁺ adsorption on xGNP

The ΔH° and ΔS° are obtained from the slope and the intercept of the dependence between Gibbs free energy change ΔG° and temperature T. The calculated values of ΔH° and ΔS° are 49.82 kJ mol⁻¹ and 83.14 J mol⁻¹K⁻¹ for the temperature range between 298 and 328 K (fig. 6). The positive values of both ΔH° and ΔS° indicate an endothermic process of adsorption and an agglomeration of ammonium molecules at the solid/solution interface.

Conclusions

Adsorption isotherm experiments were developed for the adsorption of ammonium ions from aqueous solutions by using exfoliated graphite nanoplatelets as nano-adsorbents. The adsorption characteristics were examined at different contact times, initial concentrations of the ammonium ions, pH values and temperatures. Langmuir, Freundlich, Harkin-Jura and Halsey models were used to describe the adsorption processes. The kinetic studies included a pseudo-first order kinetic model of a Lagergren

curve, a pseudo-second order model and an intra-particle diffusion model to elucidate the adsorption mechanisms and the adsorption control rates. The dependence of ammonium adsorption on temperature was also studied, and the thermodynamic parameters ΔH° , ΔG° and ΔS° were calculated, yielding results that described an endothermic process. The mechanisms of adsorption include chemical and physical interactions, the adsorption of ammonium on xGNP being primarily a chemisorption process. On the basis of its chemical and structural stability, the xGNP could become a very good adsorbent with applications for water remediation. Beyond these applications, assembling xGNP into macroscopic hybrid architectures with controllable pore dimensions can significantly improve their capabilities as sorbents for inorganic, organic and microbiological contaminants.

Acknowledgement: This research was partially performed in the frame of ERA-NET SIIN, funded by the European Commission within the 7th Framework Programme and supported by the Romanian Executive Agency of Higher Education and RDI funding (UEFISCDI).

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Manuscript received: 5.10.2015