

Remove of Sulphate Ion from Environmental Systems by using AlN Nanotubes

Mohammad T. Baei,^{*} Saeedeh Hashemian,[†] Parviz Torabi,[‡] and Farzaneh Hosseini[‡]

Department of Chemistry, Azadshahr Branch, Islamic Azad University, Azadshahr, Golestan, Iran
^{*}E-mail: Baei52@yahoo.com

[†]Department of Chemistry, Yazd Branch, Islamic Azad University, Yazd, Iran

[‡]Department of Chemistry, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

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The adsorption behavior of the sulphate (SO_4^{2-}) on the external surface of (5,0), (8,0), and (10,0) zigzag AlNNTs was studied by using density functional calculations. Adsorption energies in the nanotubes are about -8.59 , -8.04 , -8.60 eV with a charge transfer of 0.59, 0.48, 0.56|e| from the sulphate ion to the nanotubes, respectively. The adsorption energies indicated that sulphate ion can be absorbed strongly on the nanotubes. Therefore, these nanotubes can be used for adsorption of sulphate ion from the environmental systems. It was found that diameter of the AlNNTs has slight role in the adsorption of sulphate ion. The electronic properties of the nanotubes showed notable changes upon the adsorption process.

Key Words : Aluminum nitride nanotube, Adsorbent, Sulphate, DFT

Introduction

Sulphate (SO_4^{2-}) is a major anion in natural waters and wastewaters. The main source of sulphate in nature is the processes of chemical weathering and dissolution of sulphur containing minerals and the oxidation of sulphides and elemental sulphur. Sulphate is a nontoxic ion and sulphur is a necessary nutrient element for the synthesis of living systems such as proteins and it is released upon their degradation.¹ With degradation of the compounds, sulphate concentration will increase and will cause unbalance of the natural sulphur cycle.² Determination of sulphate is useful in assessing the redox state of the environmental systems, especially in the treatment of mining-influenced waters because sulphur is a critical element in controlling the fate and solubility of polluting elements in the aquatic environmental.³ Thus, it seems necessary to monitor and control its exposure in industrial and environments systems. In recent decade, enormous efforts have been experimentally devoted for development of rapid, simple, and sensitive methods for sulphate adsorption.⁴⁻⁶ For example, Mulinari *et al.*⁴ have investigated adsorption of sulphate ions by modification of sugarcane bagasse cellulose and showed a good adsorption capacity. Removal of sulphate ions from aqueous solution using modified rice straw was studied by Cao *et al.*⁵ Their results exhibit a good sulphate adsorption performance. Also, the properties of sulphate adsorption have been theoretically studied by different groups.⁷ In addition, there have been many investigations about the adsorption of sulphate on metal surfaces.⁸ While, there are few studies about the adsorption of sulphate on nanotubes and semiconducting surfaces and further study of the sulphate adsorption on nanotubes remains interesting.

Aluminum nitride nanotubes (AlNNTs) are inorganic analogs carbon nanotubes (CNTs). They are isoelectronic with

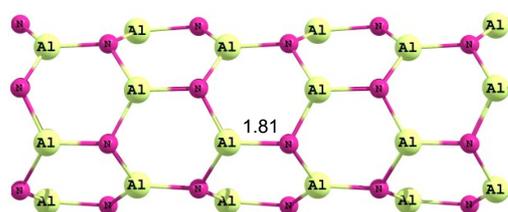
CNTs, and have been successfully synthesized by different research groups.⁹⁻¹¹ These nanotubes have good physical properties for a broad variety of applications such as use in adsorption of small compounds.¹² Unlike carbon nanotubes (CNTs), AlNNTs exhibit electronic properties and semiconductor behavior independent of its lengths, tubular diameter and chirality. Tuning the electronic structures of the semiconducting AlNNTs for specific application is important in building specific electronic and mechanical devices. Improving the sensing performance of the pristine nanotubes and nano sheets by manipulating their structure is too expensive; and thus, finding high sensitive pristine nanotubes is a highly scientific interest. However, to our knowledge, a quantum mechanical study of the interaction of the sulphate with AlNNTs surface has not been reported. Therefore, it is important to understand the advantages and disadvantages of the sulphate adsorption on the nanotubes. All the above mentioned problems have motivated us to verify heteropolar aluminum nitride nanotubes (AlNNTs) as an adsorbent, investigating their interactions with sulphate ion using DFT calculations.

Computational Methods

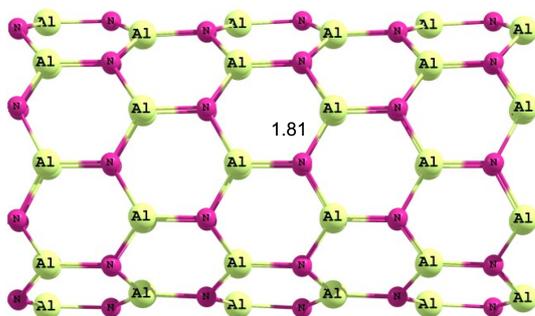
A (5,0), (8,0), and (10,0) zigzag AlNNT in which the ends of the nanotubes are saturated by hydrogen atoms was selected. The hydrogenated (5,0), (8,0), and (10,0) AlNNTs consist of 70 ($\text{Al}_{30}\text{N}_{30}\text{H}_{10}$), 112 ($\text{B}_{48}\text{N}_{48}\text{H}_{16}$), and 140 ($\text{B}_{60}\text{N}_{60}\text{H}_{20}$) atoms. The full geometry optimizations, energy calculations, natural bond orbital (NBO), and density of states (DOS) analysis have been performed on the AlNNTs and different SO_4^{2-} /AlNNT complexes at B3LYP level of theory with 6-31G* basis set as implemented in GAMESS suite of program.¹³ The B3LYP is a popular functional which has been commonly used for nanostructures.^{14,15} The use of

localized basis sets reliably reduces the amount of computational work required when using them with large vacuum regions in the unit cell. However, finiteness of the localized basis sets leads to basis set superposition errors (BSSE) as described by Tournus *et al.* in a study of benzene on CNTs.¹⁶ To overcome this problem, BSSE has been estimated for the $\text{SO}_4^{2-}/\text{AlNNT}$ complexes by B3LYP in the gas phase. This method was used to calculate the adsorption energy (E_{ad}) of sulphate on the AlNNTs wall as follows:

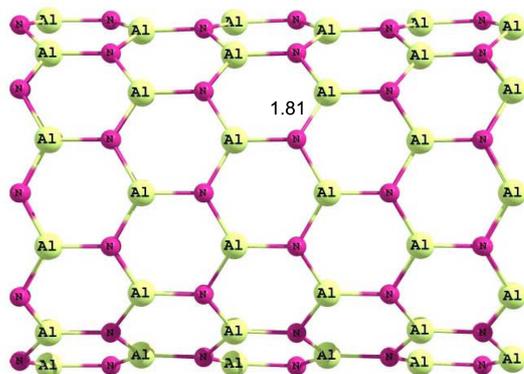
$$E_{ad} = [E_{\text{SO}_4^{2-}/\text{AlNNT}}] - [E_{\text{AlNNT}} + E_{\text{SO}_4^{2-}}] + E_{\text{BSSE}} \quad (1)$$



(5,0)



(8,0)



(10,0)

Where $E_{\text{SO}_4^{2-}/\text{AlNNT}}$ is the total energy of the adsorbed sulphate on the AlNNT surface. E_{AlNNT} and $E_{\text{SO}_4^{2-}}$ are the total energies of the pristine AlNNT and a sulphate ion, respectively. E_{BSSE} is the basis set superposition errors (BSSE) corrected for all E_{ad} values. Negative value of E_{ad} is referred to exothermicity of the adsorption. Solvation effects (water) have been investigated on the sulphate/AlNNT complexes by using polarized continuum model (PCM). Finally from the optimized complexes, the quantum molecular descriptors^{17,18} including hardness (η) and electrophilicity index (ω)¹⁹ was calculated as follows:

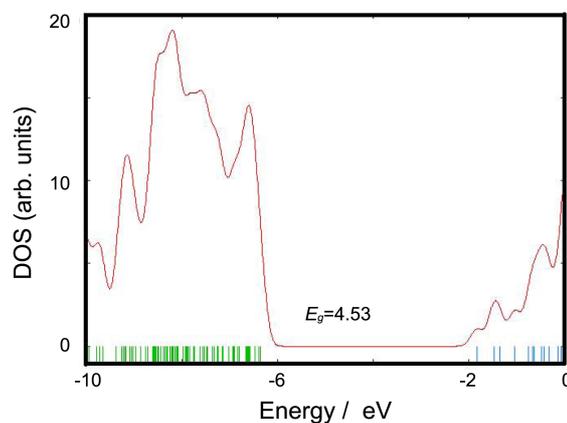
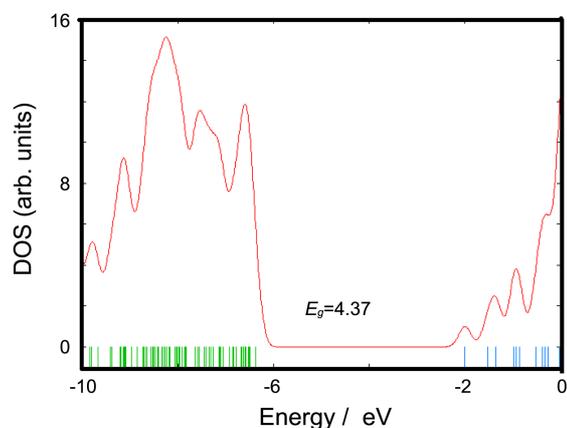
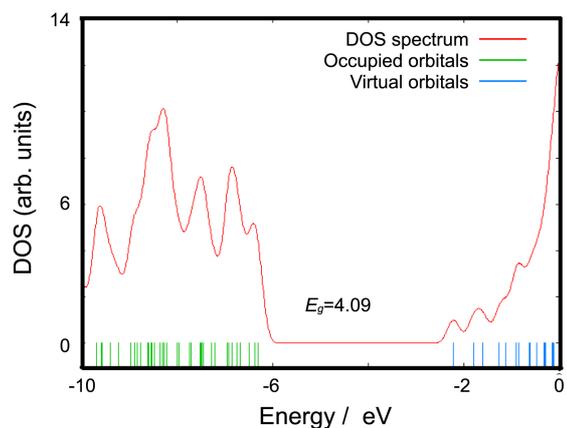


Figure 1. Partial structures of optimized the (5,0), (8,0), and (10,0) zigzag AlNNTs and their density of states (DOS). Bonds are in Å.

$$\eta = -(E_{HOMO} - E_{LUMO})/2 \quad (2)$$

$$\omega = \mu^2/2\eta \quad (3)$$

where HOMO and LUMO are the highest occupied molecular orbital and the lowest un-occupied molecular orbital (LUMO) of the structures, respectively.

Results and Discussion

The partial structures of optimized the (5,0), (8,0), and

(10,0) zigzag AlNNTs are shown in Figure 1. Bond Length of the Al-N in the structures is 1.81 Å. The Mulliken population charge analysis of the tubes shows a net charge transfer of 0.82 |e| from Al to N atoms, indicating strong ionicity nature of Al-N bonds. Calculated DOSs of the (5,0), (8,0), and (10,0) AlNNTs are plotted in Figure 1. They are indicating that AlNNTs are semiconductor that AlNNTs are a semiconductor with the HOMO/LUMO gap of about 4.09, 4.37, 4.53 eV for the tubes, respectively. After structural optimization of the nanotubes, the Al atoms relax inwardly

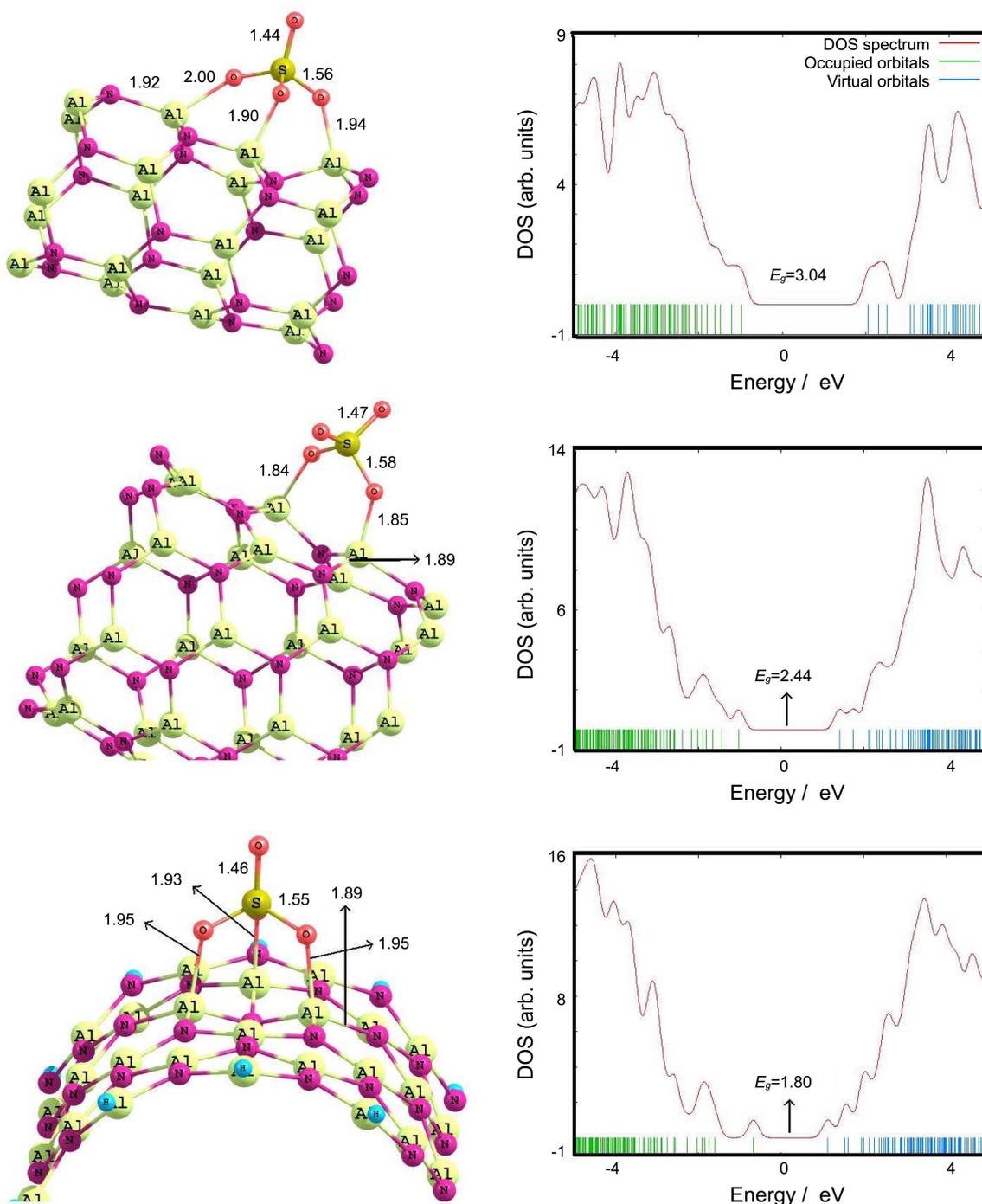


Figure 2. Models for sulphate adsorption on the (5,0), (8,0), and (10,0) zigzag AlNNTs and their density of states (DOS). Bonds are in Å.

while N atoms relax outwardly of the AlNNTs surfaces. More detailed information including electronic properties, hardness (η), and electrophilicity (ω), and dipole moment (D_M) of the zigzag AlNNTs are listed in Table 1.

In order to determine the most stable structures for the adsorption of sulphate ion on the (5,0), (8,0), and (10,0) zigzag AlNNTs, four possible sites (*i.e.*, the center site, above the hexagon, the Al and N sites above the aluminum and nitrogen atoms, and the Z site above the zigzag and axial Al–N bond) for each of the nanotubes were considered. At first, the structures were allowed to relax by all atomic geometrical parameters in the optimization at the DFT level of B3LYP exchange-functional and 6-31G* standard basis set. After careful structural optimizations without any constraints, it was found that sulphate adsorption on center, nitrogen, and Z sites of the nanotubes are energetically unstable and were collapsed to the aluminum sites, which are energetically favorable and are shown in Figure 2.

For evaluation of interaction of sulphate with the zigzag AlNNTs, the adsorption energies (E_{ad}) are studied. The E_{ad} value of the $\text{SO}_4^{2-}/(5,0)$ AlNNT complex is -8.59 eV and a net NBO charge of $0.59|e|$ is transferred from the sulphate to the (5,0) AlNNT. Very high negative E_{ad} shows that in this complex, the sulphate undergoes a strong chemisorption adsorption on the (5,0) zigzag AlNNT due to the partial negative charge on the O atoms of sulphate which makes it reactive toward the Lewis acid sites of Al atoms. Based on the NBO results and geometry analysis after the adsorption process of sulphate, the new bonds of Al–O are formed with bond length of about 1.90–2.00 Å (see Fig. 2). Also, the length of Al–N bond in adsorbed rings is increased from 1.81 in the pristine (5,0) AlNNT to 1.92 Å in the complex, indicating a local structural deformation on the nanotube. NBO analysis shows that during the strong adsorption of sulphate on the tube surface, the hybridization of the Al atoms is changed from sp^2 to nearly sp^3 . On the other hand, it is necessary to comment the structural changes of sulphate ion. When the sulphate is adsorbed on the tube, the length of S–O bonds is changed from 1.52 Å in the isolated sulphate to

1.44 and 1.56 Å.

Subsequently, adsorption of sulphate ion on the surfaces of (8,0) and (10,0) zigzag AlNNTs was investigated. The calculated E_{ad} for the (8,0) and (10,0) zigzag AlNNTs indicates that sulphate ion is strongly chemisorbed on the Al sites with E_{ad} of -8.04 and -8.60 eV, respectively. When the AlNNT diameter increases, the E_{ad} of sulphate is slightly changed. For example, sulphate binds on the (5,0) AlNNT with -8.59 eV, whereas it binds on the (10,0) AlNNT with -8.60 eV. An interesting conclusion that can be drawn from these investigations is that the diameter of the nanotubes has slight role in determining the E_{ad} of the sulphate ion. The corresponding interaction distances between the Al atoms of (8,0) and (10,0) zigzag AlNNTs and the O atoms of sulphate ion are about 1.85 and 1.95 Å (see Fig. 2). In these complexes a significant NBO charge of 0.48 and $0.56|e|$ is transferred from the ion to the nanotubes. Also, the adsorption of sulphate ion on the surface of (8,0) and (10,0) zigzag AlNNTs shows an apparent local structural deformation on both the sulphate ion and the nanotubes. The above results indicate that the sulphate ion has strongly chemisorbed on the AlNNTs and the tubes can be a promising candidate for the adsorption of the ions from the environmental systems.

In the next step, the influence of the sulphate adsorption on the electronic properties of the nanotubes is investigated. Calculated DOS plots for the complexes in Figure 2 show a considerable change, indicating that the electronic properties of the AlNNTs are very sensitive to the sulphate adsorption. As shown in Table 1, the largest change in electronic properties is predicted in $\text{SO}_4^{2-}/(10,0)$ AlNNT complex, so that the difference in energy between the HOMO and the LUMO, energy gap (E_g) of the nanotube is obviously decreased from 4.53 to 1.80 eV (about 60.26% change) in adsorbed form, which would result in an electrical conductivity change of the defected nanotubes according to the following equation²⁰:

$$\sigma \propto \exp\left(\frac{-E_g}{2kT}\right) \quad (4)$$

Table 1. Calculated adsorption energy (E_{ad}), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), HOMO–LUMO energy gap (E_g), Fermi level energy (E_{FL}), hardness (η), and electrophilicity (ω) of systems in eV and dipole moment (D_M) in Debye in gas phase

Property	(5,0) AlNNT	(8,0) AlNNT	(10,0) AlNNT	$\text{SO}_4^{2-}/(5,0)$ AlNNT	$\text{SO}_4^{2-}/(8,0)$ AlNNT	$\text{SO}_4^{2-}/(10,0)$ AlNNT
E_{ad}	–	–	–	-8.59	-8.04	-8.60
E_{HOMO}	-6.31	-6.37	-6.36	-0.98	-1.02	-0.66
E_{LUMO}	-2.22	-2.00	-1.83	2.06	1.42	1.14
E_g	4.09	4.37	4.53	3.04	2.44	1.80
^a ΔE_g (%)	–	–	–	25.67	44.16	60.26
^b $Q_T e $	–	–	–	0.59	0.48	0.56
E_{FL}	-4.26	-4.18	-4.10	0.54	0.20	0.24
D_M	12.34	15.90	18.61	83.42	91.79	29.70
$\eta = -(E_{HOMO} - E_{LUMO})/2$	2.04	2.18	2.26	1.52	1.22	0.90
$\omega = \mu^2/2\eta$	4.45	4.01	3.70	0.10	0.02	0.03

^aThe change of HOMO–LUMO gap of AlNNTs after sulphate adsorption. ^b Q_T is defined as the NBO charges transferred from the sulphate to the nanotube

Where σ is the electric conductivity of the complexes and k is the Boltzmann's constant. According to the above equation, smaller energy gap (E_g) at an especial temperature leads to the larger electric conductivity. However, in the complexes, the E_g show a considerable change. The significantly change in E_g values, shows the high sensitivity of the electronic properties of AlNNTs towards the adsorption of sulphate. Table 1 indicates that the Fermi level energy (E_{FL}) of the complexes is increased. This increasing of E_{FL} with sulphate adsorption leads to a decrement in the work function. The decrement in the work function values shows that the field emission properties of the complexes are improved upon the sulphate adsorption.

In order to consider the influence of sulphate adsorption on electronic properties of the AlNNTs, the hardness (η) and electrophilicity (ω) of the complexes are analyzed. The results of Table 1 show that the sulphate adsorption on the AlNNTs leads to lower hardness values than pristine AlNNTs. Consequently, the stability of the complexes is lowered and their reactivity increased. The electrophilicity index is a measure of the electrophilic power of a molecule. When two molecules react with each other, one molecule behaves as a nucleophile, whereas the other one acts as an electrophile. A higher electrophilicity index shows higher electrophilicity of a molecule. In sulphate-adsorbed AlNNTs the electrophilicity of the complexes are very lower than that of the pristine forms. Therefore, adsorption of sulphate can increase the reactivity of the nanotubes.

Finally, solvation effects (water) have been investigated in adsorption of sulphate on the AlNNTs. Solvation energies (E_{solv}) for the pristine and adsorbed sulphate on the (5,0), (8,0), and (10,0) zigzag AlNNTs have been calculated by optimizing the structures in gaseous and aqueous phases. The difference between these optimization energies is defined as E_{solv} . The E_{solv} for the pristine (5,0), (8,0), and (10,0) zigzag AlNNT models is -135.68, -147.26, and -154.23 kcal/mol and for the SO_4^{2-} /AlNNT complex models is -136.30, -148.23, and -154.98 kcal/mol, respectively. The results indicating that the solubility of the AlNNT remains almost unchanged in presence of sulphate ion. This trend is in agreement with change of the electric dipole moment (D_M) of the complexes. For example, dipole moment of the (5,0) complex is slightly increased from 83.42 Debye in gas phase to 86.66 Debye in solvent phase. Therefore, the solubility of the complex remains almost unchanged that maybe is originated from the slight change of dipole moment. Briefly, study of the electronic properties of the nanotubes show also that the sulphate ion has strongly chemisorbed on the AlNNTs and the nanotubes can be used for adsorption of the ion in the environmental systems.

Conclusions

The adsorptions of sulphate ion on zigzag configurations

of (5,0), (8,0), and (10,0) AlNNTs was studied using density functional calculations in terms of geometric, energetic, and electronic properties. On the basis of our calculations, it seems that pristine AlNNTs can significantly detect sulphate ion and the pure AlNNTs can be a potential efficient adsorbent for adsorption of the ions from the environmental systems. Diameter of the AlNNTs has no significant role in determining the E_{ad} of the sulphate. The electronic properties of the pure AlNNTs are significantly changed upon the adsorption process, especially in the zigzag of (10,0) AlNNT. Also, the field electron emission is improved upon the adsorption of sulphate. Solvation studies indicated that the solubility of the AlNNTs remain almost unchanged in presence of sulphate ion.

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