

Adsorption of F⁻, Cl⁻, Li⁺ and Na⁺ on the Exterior Surface of Mg₁₂O₁₂ Nanocage in the Gas Phase and Water Media: A DFT Study

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DFT calculations were used to investigate adsorption of F⁻, Cl⁻, Li⁺ and Na⁺ ions on the exterior surface of Mg₁₂O₁₂ nanocage in the gas phase and water media. The most favorite position for adsorption of the studied anions and cations are atop of Mg and O atoms of Mg₁₂O₁₂, respectively. The strongest interaction is obtained when fluoride is located atop of Mg atom with the adsorption energy of -2.92 eV. In water media, adsorption energy of ions is reduced due to hydration of ions and nanocage. Adsorption of the studied ions on the Mg₁₂O₁₂ nanocage is compared with adsorption of these ions on AlNNT surface. It is shown that Mg₁₂O₁₂ is more convenient adsorbent for fluoride ion than AlNNT.

Keywords: Adsorption of F⁻, Cl⁻, Li⁺ and Na⁺, Mg₁₂O₁₂ nanocage

INTRODUCTION

Almost, all the liquid water existed in nature such as river, sea, ocean, lake and also biological liquid include dissolved ions (fluoride, chloride, and sodium). Convenient amount of fluoride prevents dental cavities but at high concentration (more than 4 mg per liter) can increase the risk of dental and skeletal fluorosis [1,2]. Sodium ion regulates pH, blood pressure, blood volume and osmotic equilibrium. The tolerable upper intake levels (UL) of this ion is 2.3 gram per day [3] and plussage of it can lead to hypertension [4]. In addition, in terms of industry, chloride ion existed in water is one of the most important agents in metal corrosion. Therefore, recognition and separation of these ions is in order.

Among different adsorbent materials, nanostructures are very attractive for their sensitive electronic properties, large surface to volume ratio, wide band gap and high resistance.

A few studies were carried out on adsorption of Na⁺, Li⁺, F⁻ and Cl⁻ with nanostructures. Baei *et al.* have investigated the adsorption of fluoride and chloride ions on the surface of BC₂N nanotube [5]. Adsorption of Na⁺, Li⁺, F⁻ and Cl⁻ ions on AlN nanotube were considered by Samadzadeh *et al.* [6]. Based on the reported studies, fluoride ion is adsorbed more tightly on BC₂N and AlN nanotubes than other ions.

X₁₂Y₁₂ nanocages have been theoretically predicted as the most stable structures among different types of X_nY_n fullerene-like cages [7-9]. In recent years, Mg₁₂O₁₂ nanocage has been studied as a gas sensor and adsorbent material. One of the first attempts made on Mg₁₂O₁₂ nanocage as an adsorbent cage has been documented by Nicholas and coworker [10]. They have considered adsorption of acetylene on the surface of Mg₁₂O₁₂ using DFT calculations and solid state NMR. Peyghan and Noei have investigated the electronic response of Mg₁₂O₁₂ nanocage in the absence and presence of NO [11]. Shakerzadeh and coworkers studied the interaction of Mg₁₂O₁₂ with alkali metals and its effect on electrical, structural and nonlinear optical properties of this nanocage

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[12]. The present work will scrutinize the adsorption of Li^+ , Na^+ , F^- and Cl^- ions onto exterior surface of pristine $\text{Mg}_{12}\text{O}_{12}$ nanocage. It is expected that $\text{Mg}_{12}\text{O}_{12}$ acts as a more efficient adsorbent for these ions compared with previous reported ones due to more ionic character of Mg-O bond.

Due to the ionic character of $\text{Mg}_{12}\text{O}_{12}$ nanocage [13], it is expected that this nanostructure becomes a good adsorbent for these ions with respect to the adsorbents proposed previously.

COMPUTATIONAL DETAILS

The geometries of $\text{Mg}_{12}\text{O}_{12}$ nanocage and corresponding ion-complexes were optimized at the B3LYP/6-31+G(d) level [14]. It is noticeable that B3LYP method is conventionally used for considering the nanostructures [15-17]. All optimized structures were characterized as potential energy minima at B3LYP/6-31+G(d) level by verifying that all vibrational frequencies are real. Solvent effects were investigated using the polarizable continuum model (PCM) in water media. The adsorption energy of ions on the considered nanocage (E_{ads}) is calculated as:

$$E_{\text{ads}} = E_{\text{Mg}_{12}\text{O}_{12}-X} - E_{\text{Mg}_{12}\text{O}_{12}} - E_X \quad (1)$$

where $E_{\text{Mg}_{12}\text{O}_{12}-X}$ is total energy of ion- $\text{Mg}_{12}\text{O}_{12}$ nanocage complex, $E_{\text{Mg}_{12}\text{O}_{12}}$ and E_X are isolated energies of $\text{Mg}_{12}\text{O}_{12}$ nanocage and ion, respectively. In the gas phase, Boys and Bernardi method was used to correct adsorption energies for basis set superposition error (BSSE) [18]. Adsorption energy is defined as summation of interaction energy (E_{int}) and deformation energy (E_{def}) contributions, occurring throughout the adsorption process:

$$E_{\text{ads}} = E_{\text{int}} + E_{\text{def}} \quad (2)$$

$$E_{\text{int}} = E_{\text{Mg}_{12}\text{O}_{12}-X} - E_{\text{Mg}_{12}\text{O}_{12}} - E_X \quad (3)$$

$$E_{\text{def}} = E_{\text{Mg}_{12}\text{O}_{12}} - E_{\text{Mg}_{12}\text{O}_{12} \text{ isolated}} \quad (4)$$

where $E_{\text{Mg}_{12}\text{O}_{12}}$ is energy of $\text{Mg}_{12}\text{O}_{12}$ nanocage in the geometry of complex.

The charge transfer between ions and $\text{Mg}_{12}\text{O}_{12}$ nanocage was calculated using natural bond orbital (NBO) analysis [19]. To gain a deep understanding of the adsorption, energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of $\text{Mg}_{12}\text{O}_{12}$ nanocage and complexes were obtained at the same level of optimization. All calculations were carried out by the GAMESS quantum chemistry package [20].

Quantum molecular descriptors including energy gap (E_g), chemical potential (μ), electronegativity (χ), hardness (η) and electrophilicity index (ω) were computed in this study. The energy gap (E_g) is the difference of HOMO and LUMO energies, formulated as follows:

$$E_g = \varepsilon_L + \varepsilon_H \quad (5)$$

where ε_H and ε_L are referred to HOMO and LUMO energies respectively. Based on Parr *et al.* [21] and Junk's approximation [22], in N-electron system at a fixed external potential ($v(r)$) and constant temperature, quantum molecular descriptor can be calculated as:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(r),T} \cong \frac{(\varepsilon_L + \varepsilon_H)}{2} \quad (6)$$

$$\chi = -\mu \quad (7)$$

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r),T} \cong \frac{(\varepsilon_L + \varepsilon_H)}{2} \quad (8)$$

Parr *et al.* proposed to calculate the measure of electrophilicity as [23]:

$$\omega = \frac{\mu^2}{2\eta} \quad (9)$$

Finally, for title nanocage and its complexes, density of states (DOS) analysis were performed employing the Gauss Sum program [24].

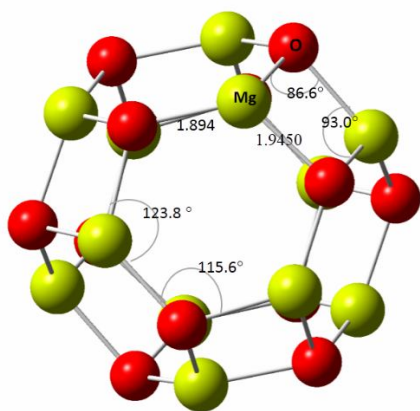
RESULTS AND DISCUSSION

The most stable configuration of $\text{Mg}_{12}\text{O}_{12}$ nanocage was taken from the literature and optimized at B3LYP/6-

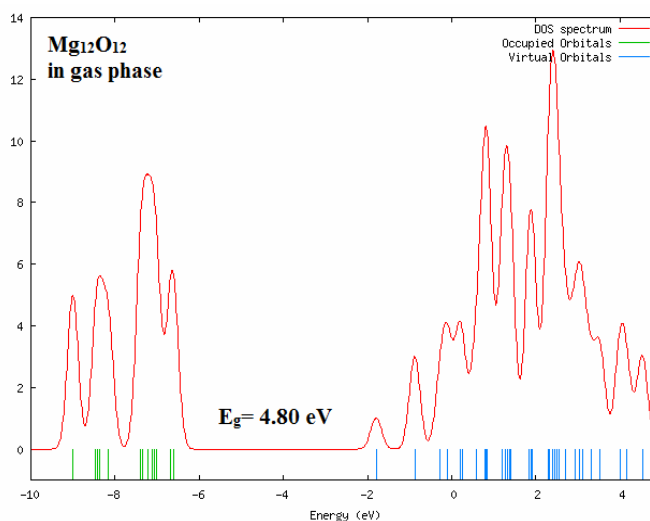
31+G(d) level of the theory [8,11]. Figure 1 shows the structure as well as MEP surface and DOS plot of pristine Mg₁₂O₁₂. This nanocage is consisted of eight hexagonal and six tetragonal rings. There are two types of Mg-O bonds in this nanocage: one type with a bond length of 1.894 Å located between two hexagonal rings and the other one with a bond length of 1.9450 Å placed between hexagonal and

tetragonal rings. Mg-O-Mg and O-Mg-O angles were obtained 115.6° and 123.7° in hexagonal rings, respectively. The size of these angles has been reduced to 86.6° and 93.0° in tetragonal rings. The NBO analysis, as well as MEP, indicates strong ionic nature of Mg-O bond in Mg₁₂O₁₂ nanocage whereas the calculated natural charges of Mg and O atoms are +1.62 and -1.62 |e| respectively. According to

A



C



B

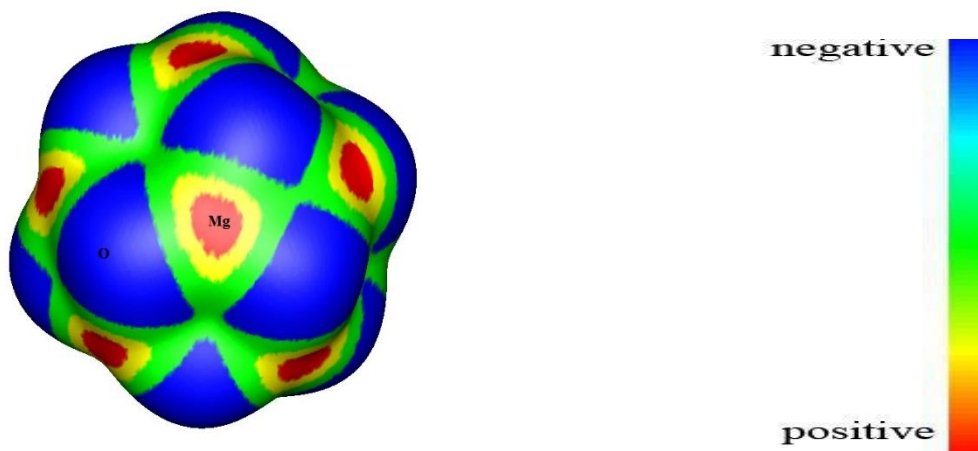


Fig. 1. (A) Structure, (B) MEP and (C) DOS analysis of Mg₁₂O₁₂ nanocage in the gas phase. The surfaces are defined by the 0.001 electrons/b³ contour of the electronic density. Color ranges, in a.u.

the MEP figure, the electron density (blue color in Fig. 1) is located on the O atoms of nanocage. The computed energy gap (E_g) using Density of states (DOS) analysis is 4.80 eV, indicating that $Mg_{12}O_{12}$ nanocage is a semiconductor material.

Structure and electrical properties of pristine $Mg_{12}O_{12}$ in water media are changed partially. There are increases in Mg-O, Mg-O-Mg and O-Mg-O bond lengths and angles in water media. The ionic nature of Mg-O bond increases as well as calculated natural charge of Mg and O atoms. The difference between HOMO and LUMO energies is raised to 4.94 eV. Figure 2 shows the structure of $Mg_{12}O_{12}$ in water media accompanied with corresponding DOS analysis.

Adsorption of Li^+ , Na^+ , F^- and Cl^- Ions on $Mg_{12}O_{12}$ in the Gas Phase

In the first step of the present study, an attempt has been made to study the adsorption of Li^+ , Na^+ , F^- and Cl^- ions on exterior surface of $Mg_{12}O_{12}$ nanocage in the gas phase. All the probable locations of adsorption including atop of Mg or O atom, above two types of the Mg-O bond, center of the hexagonal and tetragonal rings, were considered for each ion. All the calculated adsorption energies were corrected using counterpoise method for BSSE. The contribution of basis set superposition error in adsorption energies was

found between 1.4-5.7%. Therefore, 6-31+G(d) is considered as a suitable basis set for investigating adsorption of ions on $Mg_{12}O_{12}$.

Fluoride ion is adsorbed on three different positions of $Mg_{12}O_{12}$ surface including atop of Mg atom, center of hexagonal and tetragonal rings. The strongest interaction is obtained when fluoride is located atop of Mg atom with the adsorption energy of -2.92 eV. Adsorption of F^- on Mg atom reduces the energy difference of HOMO and LUMO, E_g , to 3.67 eV. The NBO analysis shows that 0.13 |e| charge is transferred from F^- to $Mg_{12}O_{12}$ nanocage. The different positions of adsorption on the surface of $Mg_{12}O_{12}$ nanocage, as well as their DOS analyses, are shown in Fig. 3. It has been depicted in Fig. 3 that new HOMO level is formed between the original HOMO and LUMO of pristine $Mg_{12}O_{12}$. The obtained electronic properties of the studied complexes have been summarized in Table 1. Based on the results reported in Table 1, adsorption of fluoride ion on Mg atom is much probable than other locations.

Chloride ion is adsorbed on the Mg atom and above the center of hexagonal ring. Adsorption of Cl^- on the Mg atom is stronger than that on atop of the center of hexagonal ring (Table 1). Geometrical deformation of $Mg_{12}O_{12}$ nanocage due to adsorption of F^- is more than Cl^- . On the other hand, alteration of electronic properties of $Mg_{12}O_{12}$ due to

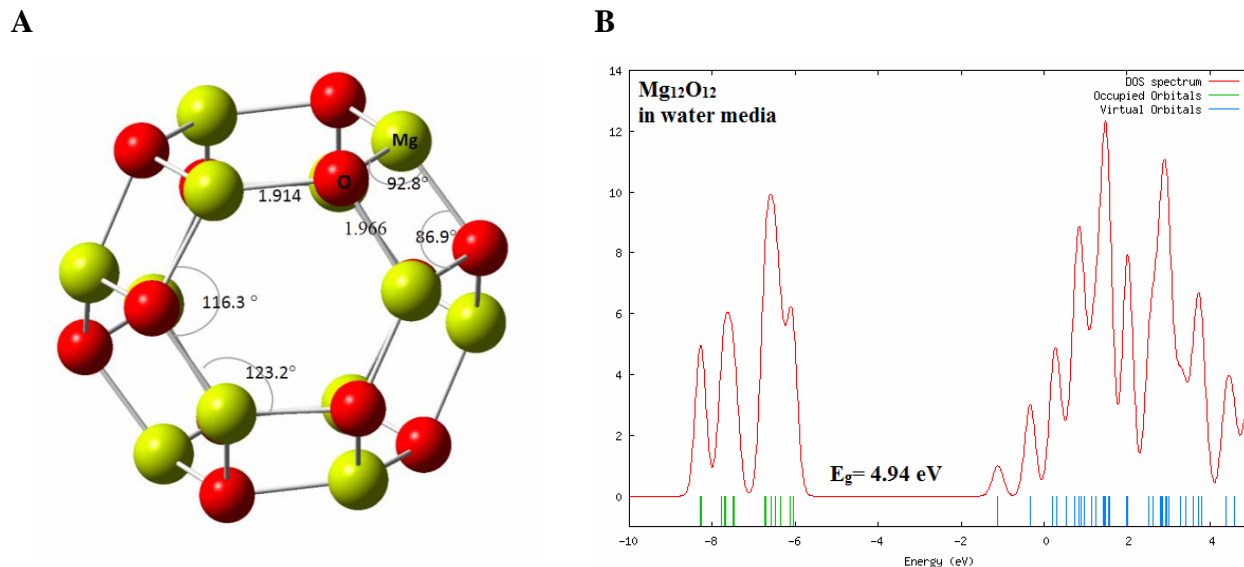
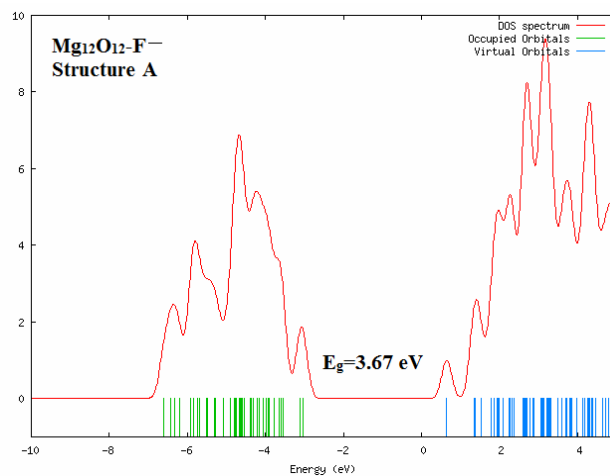
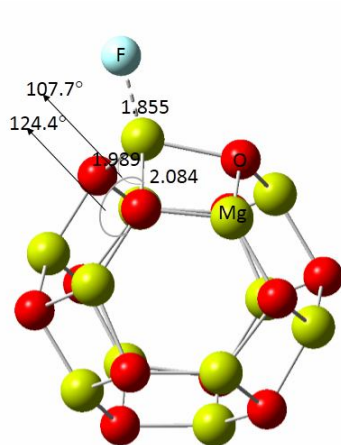
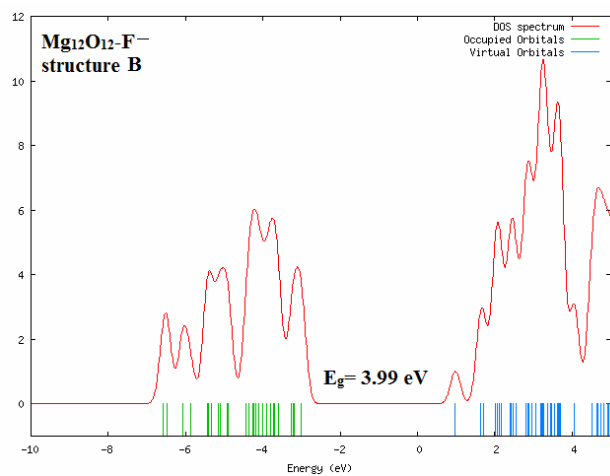
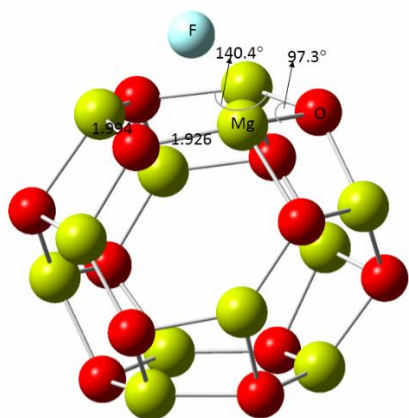


Fig. 2. (A) Structure and (B) DOS analysis of $Mg_{12}O_{12}$ nanocage in the water media.

A



B



C

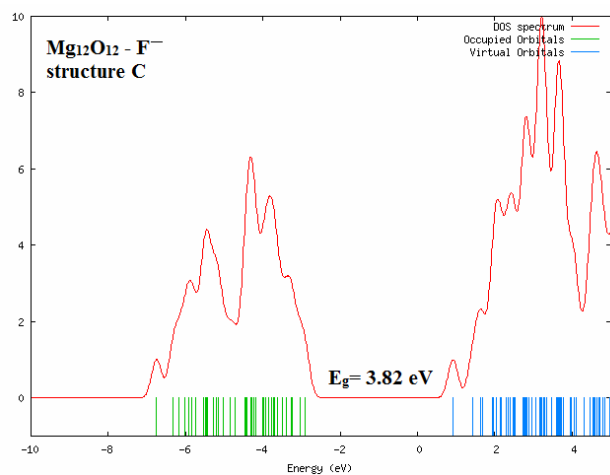
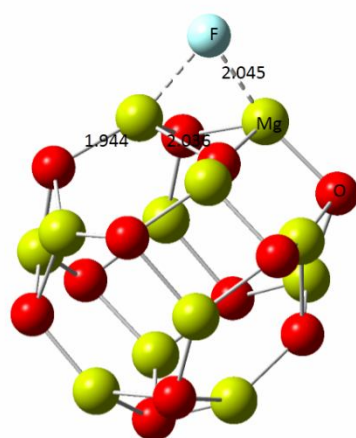


Fig. 3. Structure and DOS analysis of adsorption of F⁻ (A) on Mg atom, (B) atop of center of the hexagonal ring and (C) atop of center of the tetragonal ring of Mg₁₂O₁₂ nanocage in the gas phase.

adsorption of Cl^- is more than F^- . Different configurations as well as DOS analyses for adsorption of Cl^- on $\text{Mg}_{12}\text{O}_{12}$, are depicted in Fig. 4. In these complexes, high energy level as the newly formed HOMO reclining between the original HOMO and LUMO of pristine $\text{Mg}_{12}\text{O}_{12}$.

It is obvious from MEP of $\text{Mg}_{12}\text{O}_{12}$ that this nanocage is also a good adsorbent for Li^+ and Na^+ cations. Adsorption and deformation energies for adsorption of Li^+ and Na^+ on

the surface of nanocage are reported in Table 1. The most favorite site of adsorption for cations belongs to oxygen atom. Adsorption of Li^+ and Na^+ on oxygen atom reduces energy difference between HOMO and LUMO to 3.57 and 3.31 eV, respectively. Different configurations for adsorption of Li^+ and Na^+ on $\text{Mg}_{12}\text{O}_{12}$ as well as their DOS analyses are shown in Figs. 5 and 6. It is shown that, in these complexes, LUMO orbital with the upper energy is

Table 1. Adsorption Energy, Basis Set Superposition Error (BSSE), Deformation Energy, Energies of HOMO and LUMO and their Difference, the Change of Energy Gap of Nanocage after Adsorption ($\Delta E_g(\%)$) and Charge Transfer between Ion and Nanocage for $\text{Mg}_{12}\text{O}_{12}$ Nanocage and Ion- $\text{Mg}_{12}\text{O}_{12}$ Complexes in the Gas Phase

Complex	E_{ads} (eV) ^a	BSSE (eV)	E_{def} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	$\Delta E_g(\%)$	ΔQ (e) ^b
$\text{Mg}_{12}\text{O}_{12}$	-		-	-6.60	-1.80	4.80	-	-
$\text{Mg}_{12}\text{O}_{12}\text{-F}^-$								
A	-2.92	0.09	0.66	-3.02	0.65	3.67	-23.56	0.13
B	-2.36	0.11	1.80	-3.01	0.98	3.99	-17.02	0.18
C	-2.37	0.11	2.30	-2.90	0.92	3.82	-20.4	0.17
$\text{Mg}_{12}\text{O}_{12}\text{-Cl}^-$								
A	-1.72	0.03	0.53	-3.01	0.56	3.57	-25.71	0.22
B	-1.08	0.05	0.98	-3.15	0.80	3.95	-17.75	0.24
$\text{Mg}_{12}\text{O}_{12}\text{-Li}^+$								
A	-2.54	0.06	0.42	-8.94	-5.37	3.57	-25.71	-0.04
B	-2.66	0.03	1.63	-9.64	-4.87	4.77	-0.80	-0.25
C	-2.17	0.05	1.28	-9.21	-5.00	4.21	-12.45	-0.1
$\text{Mg}_{12}\text{O}_{12}\text{-Na}^+$								
A	-1.64	0.07	0.32	-8.82	-5.51	3.31	-31.04	-0.01
B	-1.59	0.06	1.03	-9.32	-4.94	4.38	-8.84	-0.06
C	-1.32	0.08	0.80	-9.02	-5.19	3.83	-20.28	-0.02

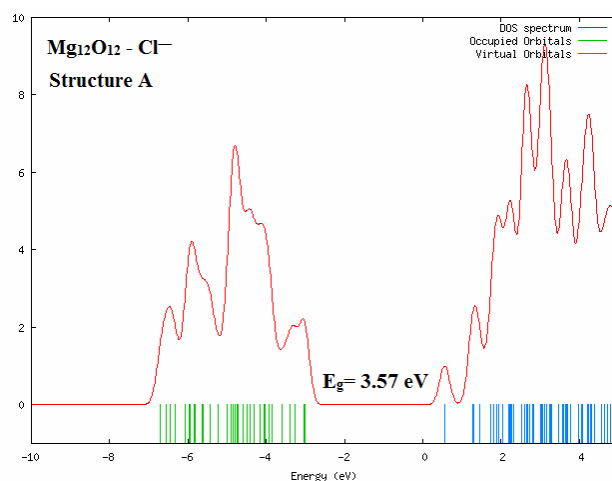
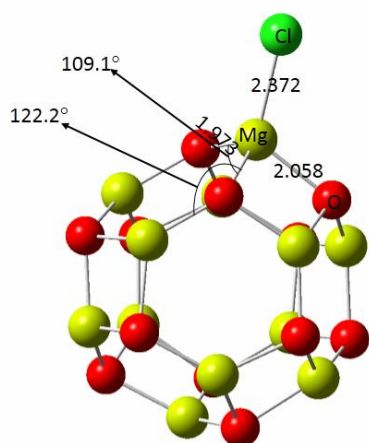
^aAll of Adsorption energies have been corrected by counterpoise method. ^bThe negative values mean charge transfer from nanocage to cations.

formed, so the energy gap between HOMO and LUMO is reduced.

Table 2 shows quantum molecular descriptors and thermodynamic properties calculated for Mg₁₂O₁₂ and Mg₁₂O₁₂-ion complexes in their most stable configurations. Adsorption of anions on Mg₁₂O₁₂ nanocage reduces electronegativity and electrophilicity. This means that tendency of nanocage to adsorb anions is reduced after adsorbing the first anion. On the other hand, the

electronegativity and electrophilicity are increased dramatically with adsorption of cations on nanocage. After adsorption of the first cation or anion, tendency of nanocage toward adsorbing more cation or anion is reduced noticeably. The negative amounts of enthalpy changes confirm that adsorption process of Li⁺, Na⁺, F⁻ and Cl⁻ ions on Mg₁₂O₁₂ nanocage is exothermic process. Adsorption of smaller ions (Li⁺ and F⁻) releases more heat than bigger ions. The negative amounts of Gibbs free energy indicate

A



B

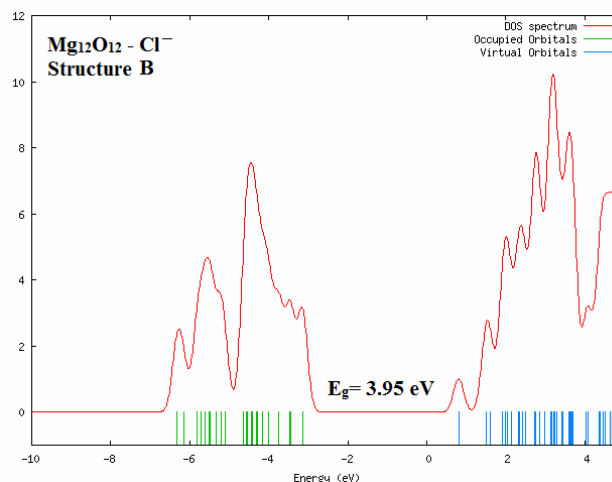
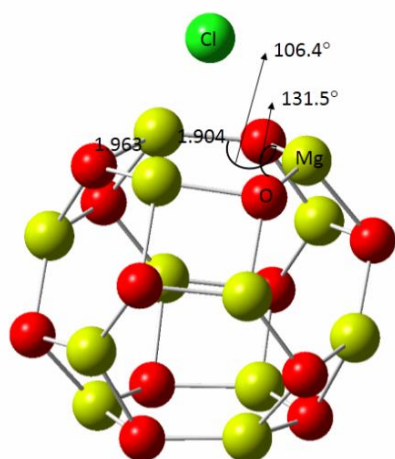
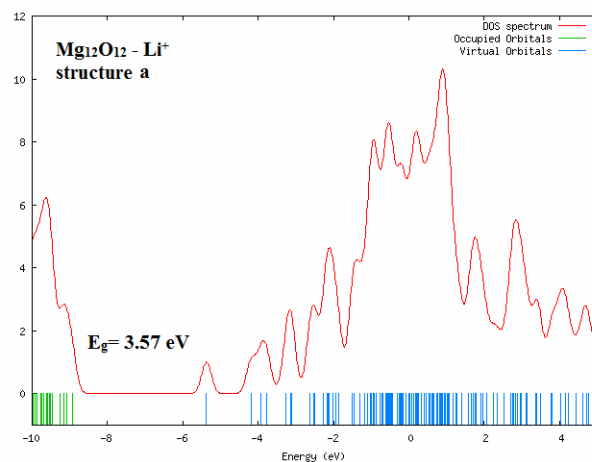
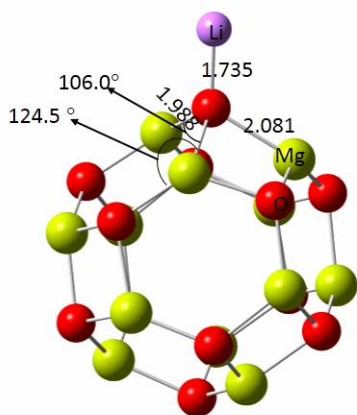
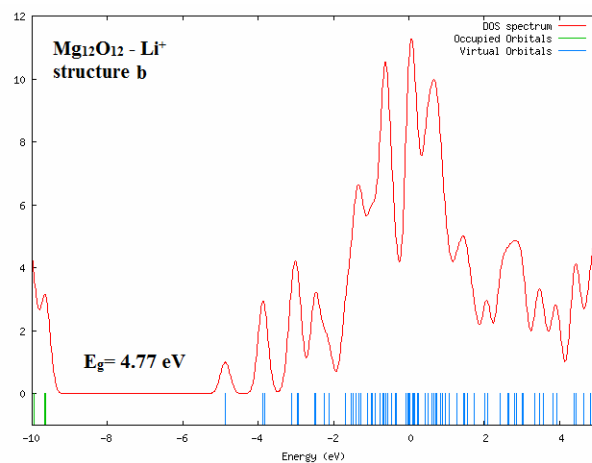
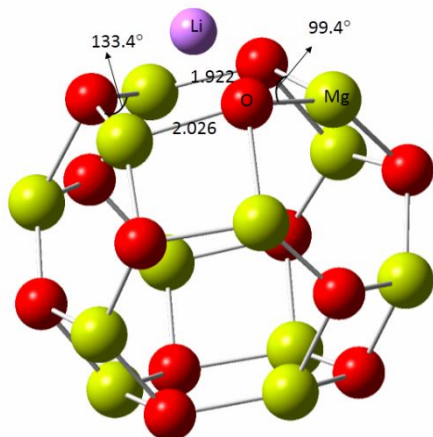


Fig. 4. Structure and DOS analysis of adsorption of Cl⁻ (A) on Mg atom and (B) atop of center of the hexagonal ring of the surface of Mg₁₂O₁₂ nanocage in the gas phase.

A



B



C

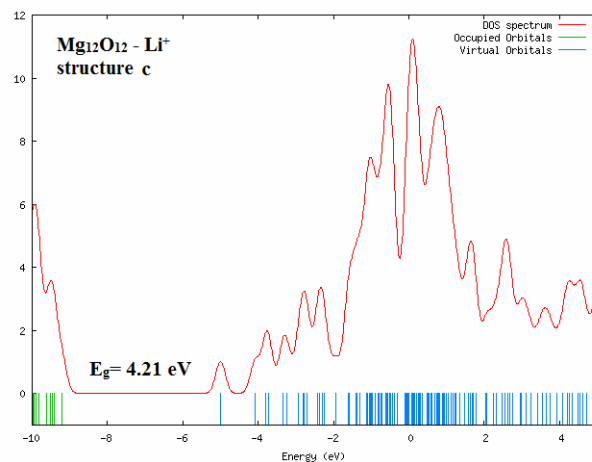
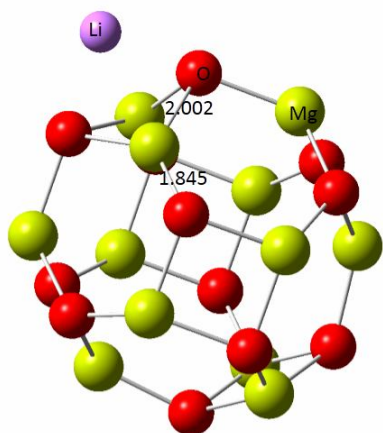
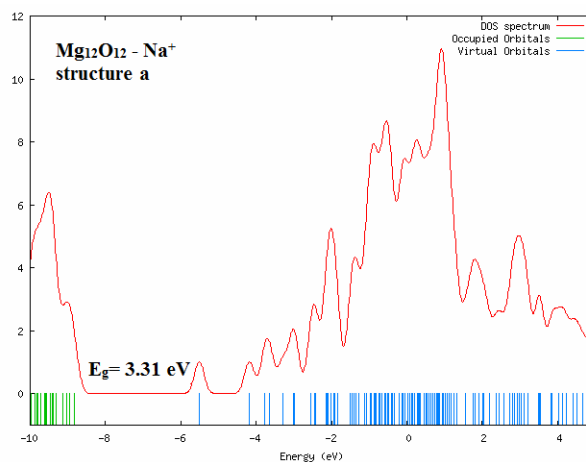
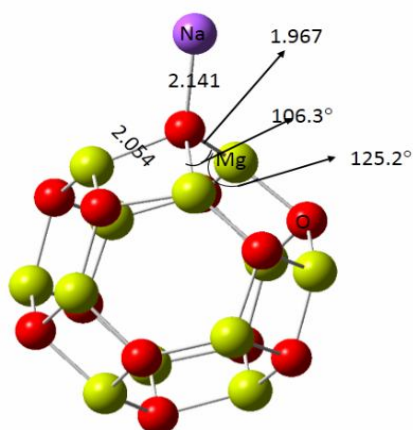
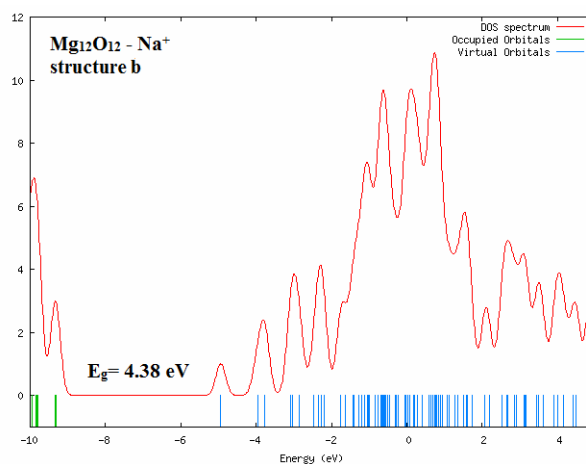
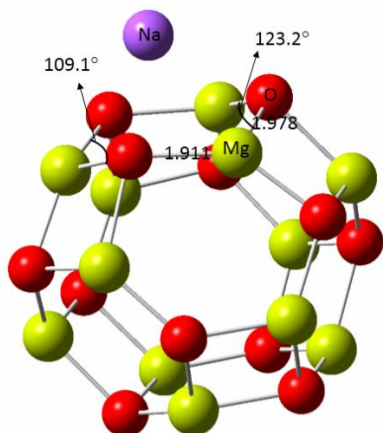


Fig. 5. Structure and DOS analysis of adsorption of Li^+ (A) on O atom, (B) atop of center of the hexagonal ring and (C) atop of center of the tetragonal ring of $\text{Mg}_{12}\text{O}_{12}$ nanocage in the gas phase.

A



B



C

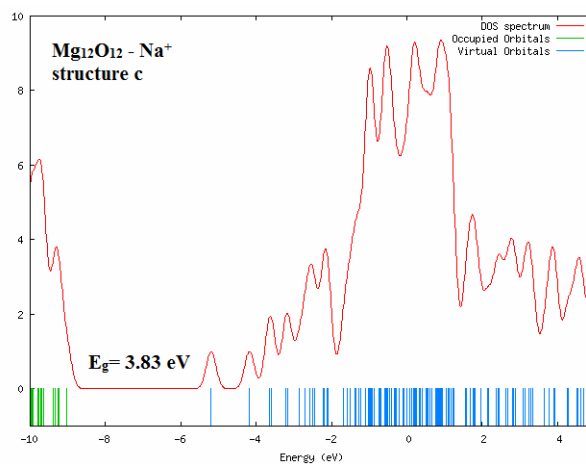
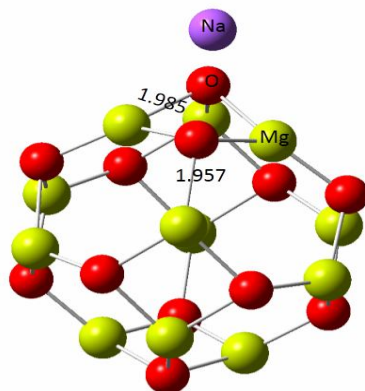


Fig. 6. Structure and DOS analysis of adsorption of Na⁺ (A) on O atom, (B) atop of center of the hexagonal ring and (C) atop of center of the tetragonal ring of Mg₁₂O₁₂ nanocage in the gas phase.

that the adsorption of these ions on nanocage is a spontaneous process at room temperature.

Adsorption of Li⁺, Na⁺, F⁻ and Cl⁻ Ions on Mg₁₂O₁₂ in Water Media

Ions usually exist in the solution phase and are rarely

found in the gas phase. Therefore, investigation of solvent effects on the adsorption of ions is in order.

In water media, hydration of Mg₁₂O₁₂ and ions lead to the reduction of interactions between them. The calculated electronic properties of the studied complexes at the water media have been tabulated in Tables 3 and 4. In addition,

Table 2. Quantum Molecular Descriptors and Thermodynamic Properties Calculated for Mg₁₂O₁₂ and Mg₁₂O₁₂-ion Complexes in the most Stable Configuration in the Gas Phase

Configuration	μ (eV)	χ (eV)	η (eV)	ω (eV)	ΔH (kcal mol ⁻¹)	ΔS (cal mol ⁻¹ K ⁻¹)	ΔG (kcal mol ⁻¹)
Mg ₁₂ O ₁₂	-4.20	4.20	2.40	3.67	-	-	-
Mg ₁₂ O ₁₂ -F ⁻ (A)	-1.19	1.19	1.84	0.38	-69.11	-19.79	-63.22
Mg ₁₂ O ₁₂ -Cl ⁻ (A)	-1.23	1.23	1.78	0.42	-40.20	-18.53	-34.68
Mg ₁₂ O ₁₂ -Li ⁺ (A)	-7.17	7.17	1.66	15.5	-58.59	-19.08	-52.91
Mg ₁₂ O ₁₂ -Na ⁺ (A)	-7.15	7.15	1.78	14.35	-38.89	-18.60	-33.34

Table 3. Adsorption Energy, Deformation Energy, Energies of HOMO and LUMO and their Difference, the Change of Energy Gap of Nanocage after Adsorption (ΔE_g (%)) and Charge Transfer between Ion and Nanocage for Mg₁₂O₁₂ Nanocage and Ion-Mg₁₂O₁₂ Complexes in their Favorite Configuration in the Water Media

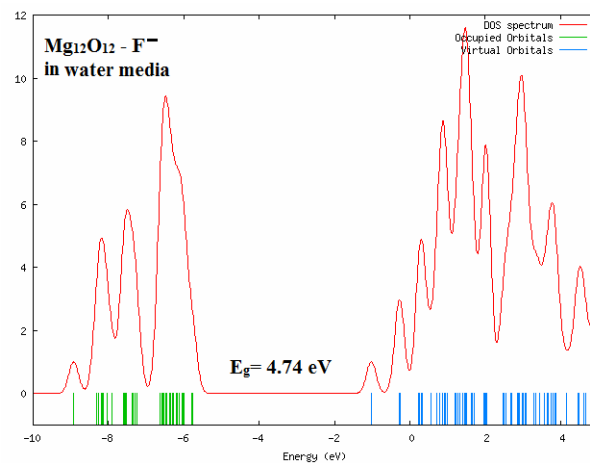
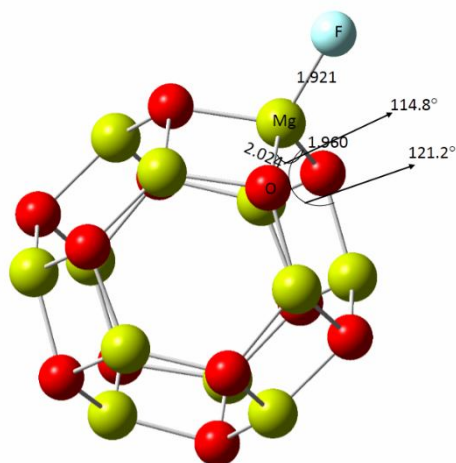
Complex	E_{ads} (eV) ^a	E_{def} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	ΔE_g (%)	ΔQ (e) ^b
Mg ₁₂ O ₁₂	-	-	-6.05	-1.11	4.94	-	-
Mg ₁₂ O ₁₂ -F ⁻							
A	-1.04	0.02	-5.77	-1.02	4.74	-3.92	0.11
Mg ₁₂ O ₁₂ -Cl ⁻							
A	-0.38	0.00	-5.84	-1.03	4.81	-2.57	0.16
Mg ₁₂ O ₁₂ -Li ⁺							
A	-0.76	0	-6.08	-1.14	4.93	-0.09	-0.02
Mg ₁₂ O ₁₂ -Na ⁺							
A	-0.55	0	-6.07	-1.16	4.91	-0.47	-0.04

^aAll of Adsorption energies are without BSSE correction in water media. ^bThe negative values mean charge transfer from nanocage to cation.

Table 4. Quantum Molecular Descriptors Calculated for Mg₁₂O₁₂ and Mg₁₂O₁₂-Ion Complexes in the most Stable Configuration in the Water Media

Configuration	μ (eV)	χ (eV)	η (eV)	ω (eV)
Mg ₁₂ O ₁₂	-3.59	3.59	2.47	2.60
Mg ₁₂ O ₁₂ -F ⁻ (A)	-3.40	3.40	2.37	2.43
Mg ₁₂ O ₁₂ -Cl ⁻ (A)	-3.43	3.43	2.40	2.45
Mg ₁₂ O ₁₂ -Li ⁺ (A)	-3.61	3.61	2.47	2.64
Mg ₁₂ O ₁₂ -Na ⁺ (A)	-3.61	3.61	2.46	2.66

A



B

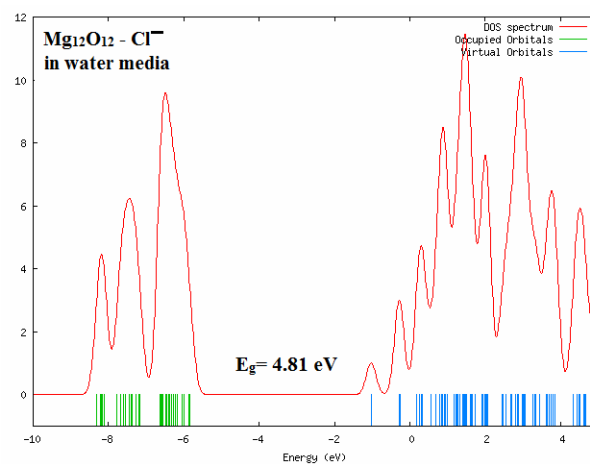
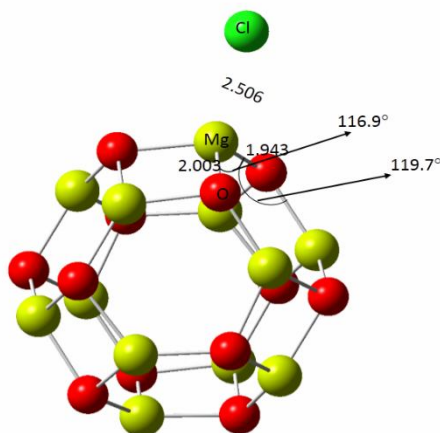


Fig. 7. Structure and DOS analysis of adsorption of (A) F⁻, (B) Cl⁻, (C) Li⁺ and (D) Na⁺ on the surface of Mg₁₂O₁₂ nanocage in the water media.

the studied complexes and corresponding DOS analyses are depicted in Fig. 7. It is obvious that formation of HOMO with the lower energy leads to the reduction of energy gap between HOMO and LUMO.

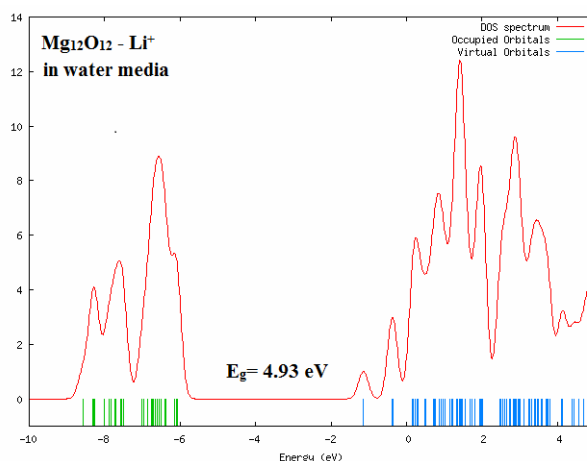
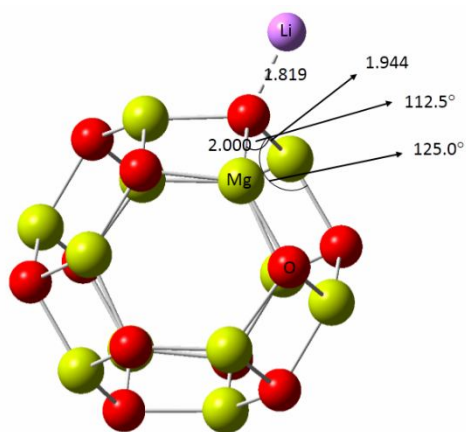
Adsorption of fluoride ion on the $\text{Mg}_{12}\text{O}_{12}$ nanocage gives $E_{\text{ads}} = -1.04$ eV. During this process 0.11 |e| charge is transferred from ion to the nanocage and energy difference between HOMO and LUMO is reduced to 4.74 eV. Adsorption energy of Li^+ ion is calculated -0.76 eV. Adsorption of Li^+ on nanocage slightly changes the energy difference of HOMO and LUMO. The weakest adsorption is related to chloride ion with adsorption energy of -0.38 eV. During the adsorption of chloride on the surface of the

nanocage, 0.16 |e| charge is transferred from ion to $\text{Mg}_{12}\text{O}_{12}$ and E_{g} is reduced to 4.81 eV. Also, adsorption of Na^+ on the surface of $\text{Mg}_{12}\text{O}_{12}$ gives $E_{\text{ads}} = -0.55$ eV with the reduction of E_{g} to 4.91 eV.

Comparison of $\text{Mg}_{12}\text{O}_{12}$ Nanocage with AlN Nanotube as Adsorbent of F^- , Cl^- , Li^+ and Na^+ Ions

Samadzadeh and coworker investigated the adsorption of F^- , Cl^- , Li^+ and Na^+ ions on AlN nanotube (denoted AlNNT) at B3LYP/6-31g(d) level [6]. To better comparison, all the calculations performed on $\text{Mg}_{12}\text{O}_{12}$ with and without adsorbed ions were repeated at the same level. In Table 5, adsorption of ions on $\text{Mg}_{12}\text{O}_{12}$ and AlNNT is compared. Accordingly, adsorption of cations on the

C



D

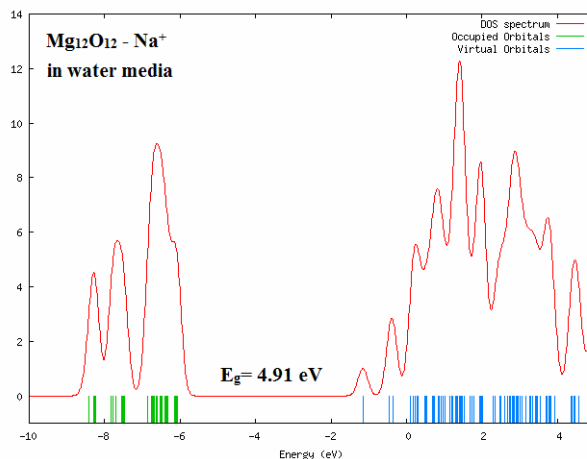
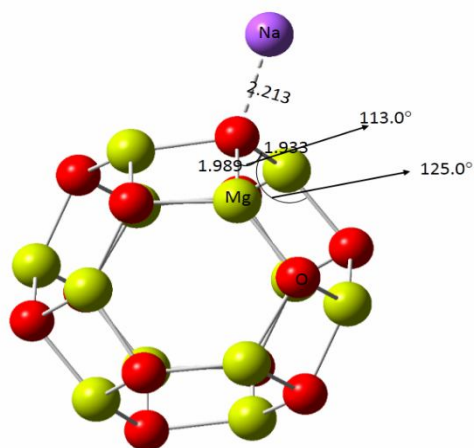


Fig. 7. Continued.

AlNNT surface is very weak, therefore Mg₁₂O₁₂ is a better adsorbent for cations while adsorption of anions on AlNNT is stronger than Mg₁₂O₁₂.

The fluoride ion is strongly adsorbed on Mg₁₂O₁₂ and AlNNT surfaces. A significant increase in adsorption energy can cause to prolong recovery time of adsorbent. Based on the conventional transition state theory, the recovery time can be defined as [25]:

$$\tau \propto \nu_0^{-1} \exp\left(\frac{E_{ads}}{kT}\right) \quad (10)$$

where k is the Boltzmann's constant, T is the temperature and ν_0 is the attempt frequency. According to Eq. (10), enhancement of adsorption energy leads to the increase in recovery time. In consequence, due to strong adsorption accompanied by the short recovery time, Mg₁₂O₁₂ is suitable adsorbent for F⁻ than AlNNT.

CONCLUSIONS

In the present work, adsorption of F⁻, Cl⁻, Li⁺ and Na⁺ on the surface of Mg₁₂O₁₂ nanocage was investigated at the

Table 5. The Comparison Adsorption Energy, the Energy Difference between HOMO and LUMO, the Change of Energy Gap of Nanocage after Adsorption ($\Delta E_g(\%)$) and Quantum Molecular Descriptors of Adsorption of F⁻, Cl⁻, Li⁺ and Na⁺ on Mg₁₂O₁₂ with Corresponding Results Calculated for Adsorption these Ions on AlNNT (all the Calculations were Performed at B3LYP/6-31G(d))

Complex	E _{ads} (eV)	E _g (eV)	ΔE_g (%)	χ (eV)	η (eV)	ω (eV)
Mg ₁₂ O ₁₂		5.02		3.47	2.51	2.4
AlNNT		4.20		4.10	2.10	4.00
Adsorption F ⁻						
Mg ₁₂ O ₁₂	-3.31	4.81	-4.16	3.25	2.4	2.20
AlNNT	-4.46	3.91	-6.9	3.74	1.95	3.58
Adsorption Cl ⁻						
Mg ₁₂ O ₁₂	-0.68	4.89	-2.57	3.30	2.44	2.22
AlNNT	-1.12	3.97	-5.4	3.79	1.98	3.62
Adsorption Li ⁺						
Mg ₁₂ O ₁₂	-0.81	4.99	-0.43	3.5	2.50	2.46
AlNNT	-0.17	4.20	0.0	4.19	2.10	4.18
Adsorption Na ⁺						
Mg ₁₂ O ₁₂	-0.57	4.95	-1.36	3.52	2.47	2.50
AlNNT	-0.12	4.18	0.4	4.18	2.09	4.18

B3LYP/6-31+G(d) level. The most favorite adsorption site is above Mg atom for anions and above oxygen atom for cations. Adsorption of F⁻, Cl⁻, Li⁺ and Na⁺ on the surface of Mg₁₂O₁₂ in the most favorite site give E_{ads}= -2.92, -1.72, -2.54 and -1.64 eV, respectively. Considering quantum molecular descriptors, tendency of nanocage toward adsorption more ions is strongly reduced after adsorbing the first ion.

In water media, adsorption energy of ions is reduced due to hydration of ions and nanocage. Adsorption of ions on the Mg₁₂O₁₂ nanocage was compared with on AlNNT surface. Adsorption of cations on the Mg₁₂O₁₂ nanocage is stronger than that on AlNNT. Also, comparing adsorption energy and recovery time of adsorption fluoride on the Mg₁₂O₁₂ nanocage with those on the AlNNT shows that Mg₁₂O₁₂ is more convenient adsorbent for fluoride ion than AlNNT.

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