**A computational study on iron oxide magnetite nanoparticles as adsorbents of anionic pollutants**

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**Abstract**

Water scarcity and pollution are two of the most important concerns affecting communities today. Thanks to modern technologies, nanofiltrated water may now be generated on a massive scale. The present study investigates anion adsorption on iron oxide nanoparticles as well as their removal from drinking water and effluents. Three sizes of amorphous Fe3O4 nanoparticles (Fe3O4, Fe6O8, and Fe9O12) and SO42-, NO3- and Cl- anions were examined for this purpose. The geometries, bonding, and electronic structure properties of anion/nanoparticle complexes were explored using the Becke-3-Lee–Yang–Parr (B3LYP) exchange-correlation functional in combination with the 6-31G and 6-311+G\*/LANL2DZ basis sets. The conductor-like polarizable continuum model (CPCM) was used to account for water solvent effects. The atoms-in-molecules (AIM) analysis was employed to thoroughly investigate the nature of anions-nanoparticles interactions. The presence of donor-acceptor interactions between the anions and the nanoparticles was verified by the AIM analysis. Furthermore, the strength of donor-acceptor bonds and anion-nanoparticle interaction energies coincide quite well. The results showed that small-size iron oxide nanoparticles are better anion adsorbents than large ones, and iron oxide nanoparticles adsorb SO42- anion more efficiently. We hope that the findings of this work will aid in the manufacture and development of nanofilters, analytical devices, drugs, and other similar products by allowing them to choose highly effective Fe3O4 nanoadsorbents based on their electronic structure properties.

**Keywords:** adsorption, anion, DFT, Fe3O4, nanoparticle.

**مطالعه محاسباتی نانوذرات مگنتیت اکسید آهن به عنوان جاذب آلاینده های آنیونی**

**فرزانه زنجانچی\***

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**چکیده:**

کمبود و آلودگی آب دو مورد از مهم­ترین نگرانی­های جوامع امروزی است. در حال حاضر به کمک فناوری‌های مدرن، آب نانوفیلتر شده در مقیاس وسیع تولید می‌شود. مطالعه حاضر به بررسی جذب آنیون بر روی نانوذرات اکسید آهن و همچنین حذف آن­ها از آب آشامیدنی و پساب می‌پردازد. سه نانوذره با اندازه­های مختلف و ساختار آمورفFe3O4) ، Fe6O8 و (Fe9O12 و آنیون­های SO42-،NO3- و Cl- برای این منظور مورد بررسی قرار گرفتند. خواص ساختار هندسی، پیوندی و الکترونی کمپلکس‌های آنیون\نانوذره با استفاده از تابعیت همبستگی تبادلی Becke-3-Lee-Yang-Parr (B3LYP) در ترکیب با مجموعه پایه­های 6-31G و6-311+G\*/LANL2DZ مورد بررسی قرار گرفت. مدل پیوسته قطبش­پذیر رسانا مانند (CPCM) برای توضیح اثرات حلال آب استفاده شد. تجزیه و تحلیل اتم در مولکول (AIM) برای بررسی کامل ماهیت برهمکنش­های آنیون- نانوذرات استفاده شد. وجود برهمکنش­های دهنده-گیرنده بین آنیون­ها و نانوذرات با تجزیه و تحلیل AIM تأیید شد. علاوه بر این، قدرت پیوندهای دهنده-گیرنده و انرژی­های برهمکنش آنیون- نانوذره کاملاً با هم مطابقت دارند. نتایج نشان می­دهد که نانوذرات اکسید آهن با اندازه کوچک جاذب آنیونی بهتری نسبت به ذرات بزرگ هستند و نانوذرات اکسید آهن، آنیون SO42- را موثرتر جذب می‌کنند. ما امیدواریم که یافته‌های این کار به ساخت و توسعه نانوفیلترها، دستگاه‌های تحلیلی، داروها و سایر محصولات مشابه کمک کند و به آن‌ها اجازه می‌دهد نانوجاذب‌های بسیار موثرFe3O4 را بر اساس ویژگی‌های ساختار الکترونی شان انتخاب کنند.

**کلیدواژه­ها:** جذب سطحی، آنیون، DFT، Fe3O4، نانوذره

**1. Introduction**

As the world’s population has continued to grow in recent decades, supplying clean and safe water to meet human needs has remained a challenge. Hence, cost-effective water and wastewater treatment technologies are required to meet global requirements and high water grading norms. Nanotechnology has recently been used as the greatest choice for expanding access to water resources by minimizing pollution and providing numerous techniques for obtaining unconventional resources [1]. In general, nanoparticles are more efficient than powder particles at removing pollutants; nevertheless, they are difficult to separate and recycle from treated water. As a result, from an economic standpoint, the usage of nanoparticles on an industrial scale is unsuitable, and this problem may be remedied by using magnetic characteristics. When a magnetic field is applied to magnetic nanoparticles, they quickly gather together and, this serves as a simple and cost-effective separation procedure for removing them from aqueous solutions. When the magnetic field is removed, the nanoparticles rapidly lose their magnetic characteristics and may be readily dispersed in the case of super paramagnetic materials [1-3]. Hence, magnetic nanoparticles offer two major benefits over nonmagnetic particles. The first is their simple separation, and the second is rapid and easy recycling, both of which are made possible by the application of an external magnetic field that increases their function. Iron oxide nanoparticles have become increasingly popular due to their unique properties such as very small size, high surface-to-volume ratio, surface modifiability, outstanding magnetic properties, excellent biocompatibility, quick kinetics, strong adsorption capacity, and high reactivity [1-10]. Among the iron oxide nanoparticles, Fe3O4 is a smart material with extremely strong magnetic characteristics [9-13]. Because of its large surface-to-volume ratio, it has greater surface areas for the chemical reaction of surface adsorption. In addition to the applications given above, iron oxide nanoparticles have shown tremendous promise in medical applications in recent years due to their non-toxicity in biological systems as well as their magnetic and semiconductor capabilities. These nanoparticles have also been designed as antibacterial, antifungal, and anti-cancer compounds [14-16].

The primary mineral anions (i.e., chloride, sulfate, and nitrate) are naturally occurring chemicals that can be found in extremely low amounts in groundwater. However, human-produced industrial, domestic, and agricultural effluents may include high levels of these anions, which can have acute or chronic impacts on the receiving soil or aquatic environment. Demineralization, reverse osmosis, coagulation, precipitation, electrodialysis, and other techniques have been frequently used to remove these anions in wastewater. However, the investment and maintenance costs for such procedures are prohibitively expensive; hence, water filtering using nanoscale filters can greatly lower the cost of water treatment as a significant advancement in water recycling [17-19]. This study aims to propose an alternative approach for removing anions from wastewater, as well as to investigate the feasibility of Fe3O4 nanoparticles as an adsorbent for the removal of chloride, sulfate, and nitrate anions.

To date, the behavior of Fe3O4 nanoparticles and nanocomposites as nanoadsorbents has been studied experimentally and theoretically [3-6, 20-24], but to the best of the authors’ knowledge, no theoretical study of the adsorption of chloride, sulfate, and nitrate anions on Fe3O4 nanoparticles has been reported. Herein, using the density functional theory (DFT), we investigate the adsorption characteristics of chloride, sulfate, and nitrate anions on Fe3O4 nanoparticles. Atom-in-molecule (AIM) analysis [25] isused to assess the nature of interactions of the anions with the Fe3O4 nanoparticles. We hope that the findings of this work will aid in the manufacture and development of nanofilters, analytical devices, drugs, and other similar products by allowing them to choose highly effective Fe3O4 nanoadsorbents based on their electronic structure properties.

**2. Main body of paper**

In this study, the geometries of (Fe3O4)n nanoparticles (n =1-3), SO42-, NO3- and Cl- anions were first drawn in *GaussView* [26] and then optimized by the *Gaussian 09* program [25] using the Becke-3-Lee–Yang–Parr (B3LYP) [28] hybrid functional and the 6-31G and 6-311+G\*+LANL2DZ (LANL2DZ for the Fe atom and the 6-311+G\*\* basis set for others). The LAN2DZ replaces the innermost 18 electrons in Fe (1s2s2p3s3p) by an effective core potential (ECP) and treats the remaining electrons (3d4s) explicitly with a double zeta (DZ) basis. To account for the water solvent effect, the conductor-like polarizable continuum model (CPCM) was used. All DFT calculations were performed using a spin-polarized scheme, by employing an unconstrained singlet spin state for the Fe atoms due to its greater stability compared to other spin states.

The LANL2DZ basis set consists of a source identifier, LANL for “Los Alamos National Laboratory”, 2 for the number of outer shells retained, and DZ for the number of zeta sets (double-zeta) for each of the two outermost shells. The LANL2DZ is a type of ECP (effective core potential) basis set, in which the basis functions are only used for the outermost one or two shells, with the remaining inner core electrons substituted by an “effective core” or “pseudopotential”. The use of an ECP basis set reduces the cost of calculations in three ways: (I) by decrease the quantity of basis functions, (II) by minimizing basis-set superposition error, and (III) by solving a nonrelativistic wave equation for valence orbitals in the presence of a relativistic ECP rather than a relativistic all-electron wave equation to include the relativistic effects [29-31].

In addition, the “6-31G” basis set is a standard split-valence double-zeta basis set, while the “6-311+G\*” basis set includes additional basis functions for valence orbitals, as well as polarization and diffuse functions on heavy atoms. To accurately explain chemical bonding, polarization functions (higher angular momentum than the valence orbitals) are employed. Diffuse functions are helpful for describing anion interactions and/or long-range interactions. As a result, the basis functions used in 6-311+G\* are larger than the 6-31G, and therefore should 6-311+G\* produce better and more trustworthy results when compared to smaller basis sets. However, the smaller basis set (6-31G) allows all computations for large nanoparticles to be performed [32, 33].

The conductor-like polarizable continuum model (CPCM) considers the solvent to be a continuous environment with a uniform dielectric constant inside which the soluble stays as a spherical cavity. Bipolarity in the environment can be caused by molecular polarity, and the electric field created by solvent polarity can interact with soluble molecule polarity, resulting in system stability [34].

The frontier molecular orbitals (FMOs) including the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were used to find the most reactive sites of nanoparticles against anions after full optimization and vibrational frequency calculations. According to the frontier molecular orbital theory (also known as the Fukui theory of reactivity and selection), the sites with the largest HOMO electron density, are the most sensitive sites for an electrophilic attack, whereas the largest LUMO electron density determines active sites against a nucleophilic attack. Electrophilic and nucleophilic frontier electron density,  and , at the atomic position 'r' can be calculated as follows,

 (1)

 (2)

where i is the number of atomic orbitals [35-37]. The greater the amount of , the more reactive that place in nanoparticles is to anions attack. The anion/(Fe3O4)n complexes were then designed and optimized using the information obtained in this section.

According to Koopmans' theorem, the HOMO and LUMO energies are equal to the negative ionization potential (IP) and electron affinity (EA), respectively [38]. The IP and EA values (or the HOMO and LUMO energies) are used to calculate global reactivity parameters, which are as follows [39-42]:

Electronegativity (*χ*) =  (3)

Chemical potential (*μ*) = -*χ* = (4)

Chemical hardness (*η*) =  (5)

Chemical softness (*σ*) =1/*η* (6)

The HOMO and LUMO energies, EHOMO and ELUMO, reflect the molecule’s sensitivity to electrophilic and nucleophilic attacks, respectively. The smaller the HOMO-LUMO energy gap, the greater a molecule’s chemical reactivity. Of fact, chemical potential, *μ*, and hardness, *η*, are often used to predict chemical behavior. *μ* is represented by the negative electronegativity, *χ*, and measures the tendency of the molecule to gain or lose electrons. A large negative *μ* value denotes a high electron acceptor capacity, whereas a small negative *μ* denotes electron donor tendency. The hardness, *η*, is defined as the rate of change of with *μ* respect to the electron density, *ρ*. A hard system is one in which a minor change in *ρ* results in a large change in *μ* [42, 43].

However, in the present study, there are two sets of singly-occupied HOMO and LUMO (α- HOMO, α-LUMO, β-HOMO and β-LUMO) for Fe3O4 nanoparticles corresponding to their unrestricted open-shell configurations.

Moreover, the Koopmans’ theorem has only been applied to the α-HOMO, α-LUMO energy levels in these systems, and it is related to the HSAB principle. The HSAB concept is formalized by seeing an acid–base chemical reaction, A + :B→A:B, as a two-step process: (I) charge transfer from :B to A, and (II) A-B bond formation [40, 41]. Δ*N* computes the charge transferred from B to A in the A:B formation as follows:

 (7)

In which *μ* and *η* represent the electron chemical potential and hardness of the A and B species, respectively. In this study, the interaction of an anion with Fe3O4 nanoparticles is considered to have a B and A role, respectively.

Electronic densities and intermolecular interactions of A/(Fe3O4)n complexes were investigated based on the quantum theory of atoms in molecules (AIM) and using *AIM2000* program [44]. The AIM allows the characterization of the interactions through the topological parameters at the bond critical points, BCPs, (i.e., the electron density, *ρ*BCP, the Laplacian of the electron density,∇2*ρ*BCP, kinetic energy density, *G*BCP, potential energy density, *V*BCP, and total energy density, *H*BCP, at the bond critical points) and their classification into the two classes of “shared” and “closed-shell” interactions. In an AIM graph that shows the overall electronic state and the bonding interactions, the bond paths are the shortest gradient paths that pass through the two nuclei and the bonding critical points [45, 46]. On the basis of the values obtained for the mentioned topological parameters, the types of bonds can be classified as Figure 1.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Shared Interactions  *ρ*BCPhigh |  | Covalent bonding | |  | *V*BCP<<0  *G*BCP<<  *H*BCP<<0  ∇2*ρ*BCP<0 |
| Polar-covalent bonding | |  | *V*BCP<<0  *G*BCP<<  *H*BCP<<0  ∇2*ρ*BCP can be of either sign |
|  | | | | | |
| Closed-Shell Interactions  *ρ*BCPLow  > 0 |  | | Dative bonding |  | *V*BCP< 0  *G*BCP ≈  *H*BCP<<0 |
| Metallic Bonding |  | *V*BCP < 0  *G*BCP ≈  *H*BCP <0  ≈ 0 |
| Ionic Bonding |  | *V*BCP<0  *G*BCP ≈  *H*BCP > 0  ≈ 0 |
| Hydrogen bonding and van der Waals Bonding |  | *V*BCP<0  *G*BCP ≈  *H*BCP > 0 but can also be negative  ≈ 0 |

Figure 1.The classification of interactions based on the QTAIM parameters.

These topological parameters are correlated as follows:

 (8)

 (9)

The Laplacian of electron density is negative for “shared” interactions such as covalent and polarized bonds because there is a decrease in potential energy density, *V*BCP, associated with a concentration of electron density inside the atom-atom area. The Laplacian of electron density is positive for “closed-shell” interactions such as van der Waals contacts, hydrogen bonds, ionic bonds, and so on because of the dominance of kinetic energy, *G*BCP, and the depletion of electron density within the atom-atom area. As a result, the Laplacian sign reveals the type of contact. Because the electron density at BCP, *ρ*BCP, is generally a good predictor of the interaction strength [39, 44-48], there is an exponential relationship between the bonding distance, daa (and the interaction energy) and the *ρ*BCP. Numerous studies have indicated relationships between interaction energy and *ρ*BCP [42,43].

**3. Results and Discussion**

To investigate the adsorption and removal of SO42-, NO3-, and Cl- anions from wastewater by magnetite nanoparticles, three iron oxide nanoparticles including Fe3O4, Fe6O8, and Fe9O12, were chosen and their geometries were optimized using the *Gaussian 09* [27] and the B3LYP density functional. To study the influence of basis set and solvent effect, calculations were performed respectively using two types of basis sets (6-31G basis set and 6-311+G\* mixed basis set for all atoms except Fe atoms and LANL2DZ for Fe atoms) in the gas phase and using 6-31G basis set and CPCM in the water phase. The Fe6O8 and Fe9O12 were generated by properly orienting two and three Fe3O4 nanoparticles, respectively, and then minimizing energy for the resulting structures. Vibrational frequency calculations were conducted on the optimized structures at the same levels of theory to assure structural stability and to determine thermodynamic quantities (at *T*=298.15 K and *P*= 1 atm). The vibrational frequency calculations show that all of the structures under consideration have real vibrational frequencies (number of imaginary frequencies is zero). Figure 2 depicts the optimized structure and numbering schemes of the Fe3O4, Fe6O8, and Fe9O12 nanoparticles, as well as the SO42-, NO3-, and Cl- anions.

|  |  |  |
| --- | --- | --- |
|  |  |  |
| (a) | (b) | (c) |
|  |  |  |
| (d) | (e) | (f) |

Figure 2. The optimized geometries of (a) Fe3O4; (b) Fe6O8; (c) Fe9O12 nanoparticles at the UB3LYP/6-311+G\*+LANL2DZ level of theory and (d) SO42-; (e) NO3-; (f) Cl- anions at B3LYP/6-311+G\* level of theory.

After full geometry optimization and assurance of structural stability, the Fukui Theory of Reactivity and Selection [36] was used to determine the most reactive sites of nanoparticles against anions. Table 1 shows the values of the electrophilic frontier electron density, , for the different atoms of Fe3O4, Fe6O8, and Fe9O12 nanoparticles, and Table 2 shows the values of the nucleophilic frontier electron density, , for the different atoms of the anions. From Table 1, it is evident that the Fukui functions of Fe atoms with labels 6, 5, and 5 have the maximum values in the Fe3O4, Fe6O8, and Fe9O12, respectively. As a result, these atoms are more prone to adsorb anions. Moreover, Table 2 shows that the  Fukui functions of S atom in SO42- and N atom in NO3- anion are both zero, and their oxygen atoms have the identical  value. As a result, the adsorption orientation must be from the oxygen atoms. To simulate the adsorption process, the anions are first approached in the appropriate direction to the atoms of nanoparticles with the highest  (Fe6, Fe5 and Fe5 atoms, respectively in the Fe3O4, Fe6O8 and Fe9O12 nanoparticles) so that the initial distance of these atoms with the atoms of anions with the highestis about 2Å; then the resulting system is fully optimized at the aforementioned levels of theory.

Vibrational frequency calculations are also performed on optimized structures to assure the stability of the resulting system and to determine the associated thermodynamic quantities (at *T*=298.15 K and *P*= 1 atm). Figure 3 depicts the optimized systems at the UB3LYP/(6-311+G\*+LANL2DZ) level of theory. The optimization of A/Fe9O12 systems ("A/" denotes the anions adsorbed on the nanoparticles) was not carried out at the UB3LYP/(6-311+G\*+LANL2DZ) level of theory. As a result, their optimized structures at the UB3LYP/6-31G level of theory are shown in Figure 3.

Table 1. Electrophilic frontier electron density of atomic positions, , of the optimized nanoparticles at the UB3LYP/6-31G level of theory.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Fe3O4 |  | Fe6O8 |  | Fe9O12 |  |
| O1  O2  O3  Fe4  Fe5  Fe6  O7 | 0.042  0.042  0.042  0.211  0.230  0.235  0.072 | O1  O2  O3  Fe4  Fe5  Fe6  O7  O8  O9  O10  Fe11  Fe12  Fe13  O14 | 0.010  0.014  0.004  0.106  0.294  0.132  0.020  0.004  0.032  0.007  0.082  0.033  0.126  0.013 | O1  O2  O3  Fe4  Fe5  Fe6  O7  O8  O9  O10  Fe11  Fe12  Fe13  O14  O15  O16  O17  Fe18  Fe19  Fe20  O21 | 0.013  0.001  0.013  0.023  0.297  0.045  0.014  0.004  0.001  0.029  0.002  0.174  0.042  0.001  0.001  0.013  0.002  0.057  0.190  0.052  0.041 |

Table 2. Nucleophilic frontier electron density of atomic positions, , of the optimized anions at the B3LYP/6-31G level of theory.

|  |  |  |  |
| --- | --- | --- | --- |
| SO42- |  | NO3- |  |
| S1  O2  O3  O4  O5 | 0.000  0.175  0.175  0.175  0.175 | N1  O2  O3  O4 | 0.000  0.251  0.251  0.251 |

|  |  |  |
| --- | --- | --- |
|  |  |  |
| (a) | (b) | (c) |
|  |  |  |
| (d) | (e) | (f) |
|  |  |  |
| (g) | (h) | (i) |

Figure 3. The fully optimized geometries of (a) SO42-/Fe3O4; (b) NO3-/Fe3O4; (c) Cl-/Fe3O4; (d) SO42-/Fe6O8; (e) NO3-/Fe6O8; (f) Cl-/Fe6O8 complexes at the UB3LYP/(6-311+G\*+LANL2DZ) level of theory and (g) SO42-/Fe9O12; (h) NO3-/Fe9O12; (i) Cl-/Fe9O12 complexes at the UB3LYP/6-31G level of theory.

The binding distances between the anions and nanoparticles (the Fe atom with the greatest  value) were measured before and after the adsorption (denoted by dba and daa symbols, respectively) and are presented in Table 3.

Table 3. The initial guess and the final value of bond lengths (in Å) respectively, before and after adsorption, dba and daa, between the atoms with the maximum values of  and  obtained atUB3LYP and CPCM+UB3LYP functionals and different basis sets.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | SO42-/Fe3O4 | NO3-/Fe3O4 | Cl-/Fe3O4 | SO42-/Fe6O8 | NO3-/Fe6O8 | Cl-/Fe6O8 | SO42-/Fe9O12 | NO3-/Fe9O12 | Cl-/Fe9O12 |
| dba |  | 2.00945 | 2.00536 | 2.00945 | 2.04311 | 2.04311 | 2.00680 | 2.05569 | 2.05569 | 2.00021 |
| daa | 6-31G | 2.29946 | 1.90459 | 1.66374, 1.77661 | 2.29334 | 1.93728 | 1.76609 | 2.23061 | 1.89015 | 1.82556 |
| daa | 6-311+G\*  +LANL2DZ | \_ | \_\_ | \_\_ | 2.24229 | 1.93838 | 1.91976 | 2.18193 | 1.94500 | 1.85583 |
| daa | 6-31G  (water phase) | 2.50271 | 2.02534 | 1.87250 | 2.40173 | 1.9613 | 1.92155 | 2.37193 | 1.89603 | 2.00932 |

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | SO42-/Fe3O4 | NO3-/Fe3O4 | Cl-/Fe3O4 | SO42-/Fe6O8 | NO3-/Fe6O8 | Cl-/Fe6O8 | SO42-/Fe9O12 | NO3-/Fe9O12 | Cl-/Fe9O12 |
| 6-31G | -141.6 | -109.9 | -69.4 | -127.5 | -44.2 | 29.0 | -21.2 | 40.5 | 61.7 |
| 6-311+G\*  +LANL2DZ | -178.5 | -83.9 | -60.3 | -157.7 | -50.2 | -32.4 | \_\_ | \_\_ | \_\_ |
| 6-31G  (water phase) | -47.8 | -45.6 | -24.2 | -15.96 | 4.4 | 2.2 | -3.4 | 18.9 | 57.2 |

In all situations, the distance between the atoms that are likely to attract each other was considered to be around 2 Å (dba ≈ 2 Å). The results show that the dba decreases after the absorption of SO42- and NO3- anions on the nanoparticles (daa< 2 Å), while increases after the absorption of Cl- anion (daa> 2 Å; since the Cl- ionic radius is 1.8 Å). Due to the more accurate calculation of interactions with the mixed basis set, the absolute values of the difference daa-dba in the calculation with the 6-311+G\*+LANL2DZ mixed basis set are less than those in the 6-31G basis set. For SO42- and NO3- anions, daa(6-31G) < daa(6-311+G\*+LANL2DZ) while for Cl- anion, a reverse tendency is found [daa(6-31G) > daa(6-311+G\*+LANL2DZ)]. In most instances, the value of daa increases with the size of the nanoparticle. The values of daa for each complex in the water phase are greater than those in the gas phase [daa(CPCM-UB3LYP) > daa(UB3LYP)], but the changes are the same in both approaches.

To more properly investigate the adsorption process, the interaction energy (Δ*E*int) between the anions and the nanoparticles is computed using the following equation,

 n = 1,2 or 3 (10)

where , *E*(A) and  are the energy of the fully optimized anion/nanoparticle complex, free anion and nanoparticle in the gas or water phase, respectively. The energies of interaction between the anions and nanoparticles are listed in Table 4.

The interaction energies of the A/Fe3O4 and A/Fe6O8 complexes are negative (except for the Cl-/Fe6O8 complex), showing that anions and nanoparticles are attracted favourably to each other. The absolute values of interaction energy are determined to be greater for A/Fe3O4 complexes than for A/Fe6O8, and the calculated interaction energies for A/Fe9O12 complexes are positive. These results demonstrate that as the nanoparticles get larger, their interaction with the anions weakens, and in most situations, the interaction energy estimated using the 6-311+G\*+LANL2DZ mixed basis set is more negative than the interaction energy predicted with the 6-31G basis set. The absolute values of the interaction energies computed using the 6-31G basis in the water phase are less than those obtained in the gas phase. However, the interaction energy varies with nanoparticle size and the type of anion absorbed in both phases. The order of interaction energies of the anions with the nanoparticles is as follows:

│∆*E*int[SO42-/(Fe3O4)n]│>│∆*E*int[NO3-/(Fe3O4)n]│> │∆*E*int[Cl-/(Fe3O4)n]│ n=1,2 or 3 (11)

Table 4. The interaction energies between anion and nanoparticle, ∆Eint, (kcal/mol) in the fully optimized complexes, A-/(Fe3O4)n, obtained atUB3LYP and CPCM+UB3LYP functionals and different basis sets.

The thermodynamic quantities of adsorption process, including enthalpy change, Δ*H*ad, entropy change, Δ*S*ad, and Gibbs free energy change, Δ*G*ad, are derived for the binary complexes discussed above, and their values are presented in Table 5.

Because of the limitations of our hardware facilities, attempts to calculate vibrational frequencies of A/Fe9O12 complexes failed at the UB3LYP/(6-311+G\*+LANL2DZ) level of theory; however, based on the results obtained at the UB3LYP/6-31G level of theory, it can be predicted that the adsorption process of anions on Fe9O12 nanoparticles at the UB3LYP/(6-311+G\*+LANL2DZ) would be an exothermic process with decreasing entropy and non-spontaneous. The results reveal that as the nanoparticles grow in size, the absolute values of Δ*G*ad decrease and the Δ*G*ad of A/Fe9O12 complex becomes positive, implying that the adsorption process is not possible at ambient temperature. According to the results in Table 5, the absorption of SO42- seems to be more desirable than that of NO3-, and that of NO3- is favorable than that of Cl- anion absorption. These findings are consistent with those found for bond lengths and interaction energy (Tables 3 and 4). The variation of the examined values is the same in both the gas and water phases.

Table 5. Thermodynamic quantities, ∆*H*ad (kcal/mol), ∆*S*ad (cal/mol K) and ∆*G*ad (kcal/mol) for the fully optimized complexes of anions with nanoparticles, A/(Fe3O4)n, obtained atUB3LYP and CPCM+UB3LYP functionals and different basis sets.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | SO42-/Fe3O4 | | | NO3-/Fe3O4 | | | Cl-/Fe3O4 | | |
|  | ∆*H*ad | ∆*S*ad | ∆*G*ad | ∆*H*ad | ∆*S*ad | ∆*G*ad | ∆*H*ad | ∆*S*ad | ∆*G*ad |
| 6-31G | -140.74 | -40.60 | -128.65 | -109.30 | -33.14 | -99.42 | -69.34 | -26.36 | -62.09 |
| 6-311+G\*  +LANL2DZ | -177.03 | -41.07 | -164.76 | -203.78 | -28.90 | -74.66 | -60.24 | -22.19 | -53.63 |
| 6-31G  (water phase) | -46.25 | -30.89 | -37.04 | -44.17 | -41.48 | -31.80 | -23.28 | -20.91 | -17.05 |
|  | SO42-/Fe6O8 | | | NO3-/Fe6O8 | | | Cl-/Fe6O8 | | |
| 6-31G | -126.78 | -36.33 | -115.96 | -42.49 | -33.27 | -32.57 | 29.11 | -29.77 | 37.98 |
| 6-311+G\*  +LANL2DZ | -156.47 | -48.79 | -141.92 | -48.69 | -34.16 | -38.51 | -31.87 | -28.11 | -23.49 |
| 6-31G  (water phase) | -13.60 | -31.46 | -4.23 | 6.248 | -38.19 | 17.64 | 2.96 | -24.06 | 10.13 |
|  | SO42-/Fe9O12 | | | NO3-/Fe9O12 | | | Cl-/Fe9O12 | | |
| 6-31G | -21.80 | -48.90 | -36.38 | 41.48 | -42.40 | 54.12 | 37.26 | -29.42 | 46.03 |
| 6-31G  (water phase) | -1.89 | -46.21 | 11.89 | 19.14 | -44.21 | 32.32 | 57.63 | -31.76 | 67.10 |

Table 6 shows the calculated values of the molecular properties of the nanoparticles. Because of the similar changes in bonding lengths, daa, interaction energies, Δ*E*int, and thermodynamic quantities (*H*ad, *S*ad, and *G*ad) in the anion adsorption process on nanoparticles in two gas and water phases, the water phase is neglected in this section.

The calculated values of *E*HOMO, *E*LUMO, *μ* and *η* for SO42-, NO3-, and Cl- anions at both levels of theory (given in Table 7) are used to derive ∆*N*. (Table 6). ∆*N* measures the transfer of electrons from anion to the surface of nanoparticles if ∆*N*> 0 and vice versa, if ∆*N*<0. The results reveal that the values of the HOMO-LUMO gap, ∆, and electronegativity, *χ*, increase with the size of the nanoparticles. The calculated ∆ value at the UB3LYP/(6-311+G\*+LAN2LDZ) level is larger than that of UB3LYP/6-31G. Moreover, the trend seen for the variation of ∆ with nanoparticles size is consistent with the reported absorption energies and thermodynamic data (Tables 4 and 5). The ∆ value of each nanoparticle increases when anion adsorption occurs on it, implying that its reactivity diminishes. The negative values of *μ* for nanoparticles and positive *μ* for anions show that they are electron acceptors and electron donors, respectively. SO42- anion is more involved in electron transport to nanoparticles of any size than NO3-, and NO3-is more involved in electron transport to nanoparticles of any size than Cl- anion, according to ∆*N* values. The resulting ∆*N* values are proportional to the difference in electronegativity between nanoparticles and SO42-, NO3-, and Cl- anions.

Table 6. The global reactivity parameters, HOMO and LUMO energies (EHOMO and ELUMO), HOMO-LUMO gap (∆), chemical potential (*μ*), and chemical hardness (η) (all in eV) of (Fe3O4)n nanoparticles and A/(Fe3O4)n complexes, and electron transfer values from anion to nanoparticle (Δ*N*) within A/(Fe3O4)n complexes obtained at different levels of theory.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | UB3LYP/6-31G | | | | | | | | | | | |
|  | Fe3O4 | SO42-/Fe3O4 | NO3-/Fe3O4 | Cl-  /Fe3O4 | Fe6O8 | SO42-/Fe6O8 | NO3-/Fe6O8 | Cl-  /Fe6O8 | Fe9O12 | SO42-/Fe9O12 | NO3-/Fe9O12 | Cl-  /Fe9O12 |
| *E*HOMO | -5.561 | 2.159 | -1.584 | -1.406 | -5.993 | 0.367 | -3.277 | -2.763 | -6.182 | 0.837 | -3.290 | -2.727 |
| *E*LUMO | -3.714 | 4.211 | 0.758 | 0.660 | -4.345 | 2.462 | -0.461 | -0.430 | -3.884 | 1.726 | -1.014 | -1.233 |
| ∆ | 1.847 | 2.052 | 2.342 | 2.067 | 1.648 | 2.095 | 3.665 | 2.263 | 2.298 | 0.889 | 2.275 | 1.494 |
| *μ* | -4.638 | -3.185 | -0.413 | -0.373 | -5.169 | -1.415 | -1.869 | -1.631 | -5.033 | -1.282 | -2.152 | -1.980 |
| *η* | 0.924 | 1.026 | 1.171 | 1.033 | 0.824 | 1.048 | 1.408 | 1.167 | 1.149 | 0.444 | 1.138 | 0.747 |
| ∆*N* |  | 1.486 | 0.947 | 0.715 |  | 1.590 | 1.049 | 0.750 |  | 1.455 | 0.943 | 0.718 |
|  | UB3LYP/6-311+G\*+LANL2DZ | | | | | | | | | | | |
|  | Fe3O4 | SO42-/Fe3O4 | NO3-/Fe3O4 | Cl-  /Fe3O4 | Fe6O8 | SO42-/Fe6O8 | NO3-/Fe6O8 | Cl-  /Fe6O8 | Fe9O12 | SO42-/Fe9O12 | NO3-/Fe9O12 | Cl-  /Fe9O12 |
| *E*HOMO | -5.960 | 1.850 | -2.425 | -1.548 | -6.474 | 0.300 | -2.538 | -2.700 | -6.718 | \_\_ | \_\_ | \_\_ |
| *E*LUMO | -4.021 | 3.726 | 0.671 | 0.600 | -4.209 | 2.791 | -0.725 | -0.398 | -4.389 | \_\_ | \_\_ | \_\_ |
| ∆ | 1.939 | 1.876 | 3.096 | 2.148 | 2.266 | 2.490 | 1.812 | 2.302 | 2.329 | \_\_ | \_\_ | \_\_ |
| *μ* | -4.990 | -2.788 | -0.877 | -0.474 | -5.341 | -1.545 | -1.632 | -1.549 | -5.553 | \_\_ | \_\_ | \_\_ |
| *η* | 0.970 | 0.938 | 1.548 | 1.074 | 1.133 | 1.246 | 0.907 | 1.151 | 1.165 | \_\_ | \_\_ | \_\_ |
| ∆*N* |  | 1.645 | 0.873 | 0.868 |  | 1.618 | 0.881 | 0.876 |  | 1.634 | 0.901 | 0.893 |

Table 7. The global reactivity parameters, HOMO and LUMO energies (EHOMO and ELUMO), HOMO-LUMO gap (∆), chemical potential (*μ*) and chemical hardness (*η*) of the anions (all in eV) obtained at different levels of theory.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | B3LYP/6-31G | | | B3LYP/6-311+G\* | | |
|  | SO42- | NO3- | Cl- | SO42- | NO3- | Cl- |
| *E*HOMO | 4.354 | 0.478 | 0.405 | 3.607 | -1.202 | -0.745 |
| *E*LUMO | 10.684 | 4.913 | 17.736 | 8.327 | 4.419 | 6.203 |
| *μ* (= -*χ*) | 7.519 | 2.218 | 9.071 | 5.967 | 1.609 | 2.729 |
| *η* | 3.165 | 2.696 | 8.666 | 2.360 | 2.811 | 3.474 |

AIM calculations are carried out using the wave functions computed for the A/(Fe3O4)n complexes with the UB3LYP/6-31G optimized structures. Figure 4 shows the AIM molecular graphs for these complexes. The changes in the bond paths in these graphs indicate how the three anions interact with (Fe3O4)n nanoparticles. Table 8 also includes average values of chosen topological characteristics at the BCPs corresponding to the A/(Fe3O4)n complexes bond paths (the bond paths between atoms of anions and nanoparticles).

Table 8. Topological Parameters (in au), interactions and bonds type at the bond critical points of the A/ complexes.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | SO42-/Fe3O4 | NO3-/Fe3O4 | Cl-/Fe3O4 | SO42-/Fe6O8 | NO3-/Fe6O8 | Cl-/Fe6O8 | SO42-/Fe9O12 | NO3-/Fe9O12 | Cl-/Fe9O12 |
| *ρ*BCP | 0.1222  0.0780 | 0.0793  0.0489 | 0.0767 | 0.1413 | 0.0855 | 0.0640 | 0.1364  0.1912  0.0172 | 0.0933  0.0085 | 0.0647 |
|  | 0.7934  0.4313 | 0.4247  0.1860 | 0.1949 | 0.8240 | 0.5583 | 0.1929 | 0.8548  1.0589  0.0644 | 0.5890  0.0311 | 0.1700 |
| *G*BCP | 0.1934  0.1118 | 0.1121  0.0546 | 0.0715 | 0.2254 | 0.1363 | 0.0629 | 0.2281  0.3174  0.0151 | 0.1469  0.0074 | 0.0592 |
| *V*BCP | -0.2021  -0.1158 | -0.1180  -0.0627 | -0.0934 | -0.2448 | -0.1330 | -0.0774 | -0.2424  -0.3700  -0.0141 | -0.1465  -0.0070 | -0.0759 |
| *H*BCP | -0.0086  -0.0040 | -0.0059  -0.0081 | -0.0228 | -0.0194 | 0.0033 | -0.0145 | -0.0143  -0.0527  0.0010 | 0.0004  0.0004 | -0.0167 |
| Interaction | Fe4-OS  Fe4-OS | Fe4-ON  Fe4-ON | Fe4-Cl | Fe4-OS | Fe4-ON | Fe4-Cl | Fe18-OS  Fe20-OS  O16-SS | Fe20-ON  O9-ON | Fe20-Cl |
| Bond Type | donor-acceptor | donor-acceptor | donor-acceptor | donor-acceptor | donor-acceptor | donor-acceptor | donor-acceptor | donor-acceptor | donor-acceptor |

|  |  |  |
| --- | --- | --- |
|  |  |  |
| (a) | (b) | (c) |
|  |  |  |
| (d) | (e) | (f) |
|  |  |  |
| (g) | (h) | (i) |

Figure 4. The AIM molecular graphs of the (a) SO42-/Fe3O4; (b) NO3-/Fe3O4; (c) Cl-/Fe3O4; (d) SO42-/Fe6O8; (e) NO3-/Fe6O8; (f) Cl-/Fe6O8; (g) SO42-/Fe9O12; (h) NO3-/Fe9O12; (i) Cl-/Fe9O12 complexes using the UB3LYP/6-31G wave function.

According to Bianchi et al., the donor-acceptor bond is characterized by relatively low *ρ*BCP, *G*BCP, and *V*BCP values, as well as a positive ∇2*ρ*BCP and negative *H*BCP that are very close to zero, and the parameters associated with donor-acceptor bonds have values similar to those of the metallic bond but are less shifted toward the ionic interaction [51]. The positive ∇2*ρ*BCP and nearly zero *H*BCP values are established for all of the A/(Fe3O4)n complexes, implying the presence of a donor-acceptor type interaction between the anions and nanoparticles. The results demonstrate that *ρ*BCP values at bond paths of SO42- with the Fe3O4 nanoparticle are more than that NO3- anion, and for NO3- anion, they are greater than that Cl- anion. The obtained *ρ*BCP values also relate to the interaction energies, thermodynamic findings, and reactivity parameters. Adsorption of anions on bigger nanoparticles (Fe6O8 and Fe9O12) is similar to that of Fe3O4 nanoparticles.

The isodensity boundary surface plots of FMOs are critical because they reveal the electron-withdrawing (oxidation) and accepting (reduction) sites, respectively [39, 52]. Figures 5 and 6 show the boundary surfaces of the α-HOMO and α-LUMO border orbitals of the A/(Fe3O4)n complexes, respectively.

|  |  |  |
| --- | --- | --- |
|  |  |  |
| (a) | (b) | (c) |
|  |  |  |
| (d) | (e) | (f) |
|  |  |  |
| (g) | (h) | (i) |

Figure 5.Isodensity boundary surface plots of the α-HOMO frontier orbitals of the (a) SO42-/Fe3O4; (b) NO3-/Fe3O4; (c) Cl-/Fe3O4; (d) SO42-/Fe6O8; (e) NO3-/Fe6O8; (f) Cl-/Fe6O8; (g) SO42-/Fe9O12; (h) NO3-/Fe9O12; (i) Cl-/Fe9O12 complexes obtained at the UB3LYP/6-31G level of theory.

|  |  |  |
| --- | --- | --- |
|  |  |  |
| (a) | (b) | (c) |
|  |  |  |
| (d) | (e) | (f) |
|  |  |  |
| (g) | (h) | (i) |

Figure 6. Isodensity boundary surface plots of the α-LUMO frontier orbitals of the (a) SO42-/Fe3O4; (b) NO3-/Fe3O4; (c) Cl-/Fe3O4; (d) SO42-/Fe6O8; (e) NO3-/Fe6O8; (f) Cl-/Fe6O8; (g) SO42-/Fe9O12; (h) NO3-/Fe9O12; (i) Cl-/Fe9O12 complexes obtained at the UB3LYP/6-31G level of theory.

The isodensity boundary surface plots in Figure 5 reveal that the charge density of each atom to the HOMO of A/(Fe3O4)n complexes is not uniform. For all complexes, the charge density around the bond axes of the anion-nanoparticle complexes is greater than that on the outer edges of the anion and nanoparticle, and that its contribution on the bond axes of the Fe3O4 complexes is greater. The LUMO orbital of the A/(Fe3O4)n complexes, on the other hand, is shown to be confined (≥ 90%) at the nanoparticles (Figure 6), suggesting them as probable reduction sites. These findings are compatible with the bonding energies, global reactivity parameters, and AIM studies (Tables 4, 5 and 8).

**4. Conclusions**

The electronic structures and stability of three different sizes of iron oxide amorphous nanoparticles (Fe3O4, Fe6O8, and Fe9O12) and SO42-, NO3-, and Cl- anions were studied using the DFT calculations. Using the Fukui functions, the most reactive atomic positions on nanoparticles and anions were predicted. The binary complexes were then built and fully optimized. The results revealed that for the SO42- and NO3- complexes, the distance between the most reactive atomic sites of the interacting moieties decreases whereas it increases for Cl- anion. The interaction energies indicated that small-size nanoparticles (Fe3O4) have greater tendency to adsorb anions than larger ones. Furthermore, the small nanoparticles showed a better interaction with SO42- anion than NO3- and Cl-. Therefore, it is expected that purification process of SO42- anion with iron oxide nanoparticles is favorable. The thermochemistry analysis demonstrated that as the size of the nanoparticles grows the absolute value of Δ*G*ad decreases and Δ*G*ad of A/Fe9O12 complexes is positive, indicating that the adsorption process becomes thermodynamically impossible, which is consistent with the results obtained for interaction energy. The interaction energies, Gibbs free energies, and global reactivity parameters showed that small nanoparticles are suitable for selective separation of the anions from mineral anionic pollutants and wastewater. According to the suggested AIM criteria, the interaction between the anions and nanoparticlesis a donor-acceptor type interaction, in which, the SO42- anion forms stronger bonds with the nanoparticles than NO3- and Cl-. The boundary surfaces of the FMOs of examined complexes demonstrated that variances in electronic structures are the basis of discrepancies in anion-nanoparticle interactions and bond strength.

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