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A Nano Catalyst of CoFe2o4@ $B_{18}N_{18}$ as a Novel Material

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ABSTRACT

In this work the properties of CoFe2o4@ $B_{18}N_{18}$ have been illustrated as a novel catalyst to compare with well-known catalyst "Fe3O4@Silica".It has been shown that CoFe2o4 magnetite particle can be use as important catalyst inside the $B_{18}N_{18}$ ring. In our previous papers amazing result about the B_nN_n properties have been calculated, exhibited (Struct. Chem., 23, 551-580, (2012); J. Phys. Chem A, 117, 1670-1684, (2013); J. Phys. Chem. C, 114, 15315,(2010) and discussed. In present work it has been shown there is a non-covalent attraction between CoFe2o4 and $B_{18}N_{18}$ coated molecules. In the system of CoFe2o4@$B_{18}N_{18}$ catalyst, the magnetic nanoparticles (MNPs) as a core part causes important change in the electronic structure of $B_{18}N_{18}$ as a shell which some compounds are specific-sensitive functional groups for this system such as OH, CHO, NH_2 and were subjected to the some organic reaction. The Physical-chemistry properties such as energy densities, potential energy densities, electron densities, ELF, LOL, eta index, ellipticity of electron density and ECP for CoFe2o4@ $B_{18}N_{18}$ shell have been calculated and simulated in related reactions for those groups-functionalized. Our Calculation indicates that the $B_{18}N_{18}$ is much better surfaces for CoFe2o4 rather than silica surfaces.

Keywords: CoFe2o4, Nano-Particles, electron density, $B_{18}N_{18}$ nano-ring, Silica, SiO_2

INTRODUCTION

CoFe2o4 as the Cobalt ferrite crystallizes in a partially inverse spinel position represented as $(Co2x^{++}Fe^{3+}\ 1\text{-}x)(Co^{2+}\ 1\text{-}xFe^{3+}\ 1+x)O_4$ where x based on thermal[1] condition . It is ferri-magnetic with a Tc approximately 520 degree and exhibits a relatively magnetic hysteresis which distinguishes it from the other of the spinel ferrites[2, 3]. Magnetic measurements on nano-particles of cobalt ferrite dispersed in various solvents of organic compounds and nano-crystalline[2] powders prepared by hydroxide precipitation[3-5] have been investigated earlier. In magnetic fluids[3], it has been seen that for particles above three nanometer the saturation[3,4] magnetization remains constant at about 30 emu g^{-1} that is extensively less than the bulk[5] values.

Magnetic nanoparticles (MNPs) have shown exceptional potential for several biological and clinical applications[4, 5]. However, MNPs might be coated by the biocompatible shells for such applications. The aim of this study is to understand if and how the surfaces charges and coatings can affect the magnetic and electronic properties of Cobalt ferrite crystallizes. The role of the surfaces on the magnetic moments of a magnetic nano particle such as CoFe2o4 is an important issue, and various effects can contribute for making it deviate from the bulk value, including the charges, the nature of the coating, and also the synthetic technique. The electronic properties and ionic distribution of CoFe2o4 NPs were probed by X-ray[2-4] absorption spectroscopies X-ray-magnetic-circular-dichroism and X-ray-photoemission-spectroscopy-techniques known as the abbreviation XAC, XMCD and XPS respectively. Magnetite-particles[1-5] is also of interests in medicinal and industries application such as magnetic-resonance-imaging or {MRI}, organic catalyst and nanomaterial synthesize[6-8].

The overall magnetic behavior and the hyper-thermic properties were evaluated by magnetometers and molecular modeling measurements, respectively[7,8]. The results show that all of the investigated CoFe2o4 NPs have high magnetic anisotropy[6,9] energies, and the surfaces charges and coating do not influence appreciably their electronic and magnetic properties. In addition, the citrate shell improves the stability of the NPs in aqueous environment, making CoFe2o4 NPs suitable for biomedical applications. Magnetic nanoparticle exhibits several unique properties such as super-para-magnetism compared to bulk[9,6] material and particularly, are used in the field of biology[7-9] and medicines. Magnetic nanoparticle has attracted a great deal of research interests due to their distinctive properties and special application recently.

CoFe2o4, is a well-known hard magnetic material with very high cubic magneto-crystalline anisotropy, high coercively, and moderate saturation magnetization. These properties make it a promising material for high-density magnetic recording.

CoFe2o4 nanoparticles have been widely synthesized using several ways, same as sol-gel[9,10], micro-emulsion[11,12], chemical coprecipitation[11,12], hydrothermal synthesis and microwave[11-13] synthesis[14]. Among those methods, the sol-gel[9,10] routes are very attractive, within the main advantages including simple control for chemical composition[11]. Recently, in the sol-gel[9,10] synthesis of CoFe2o4 particles, the gels are built-up via physical and chemical binds between the chemical species[11-14]. It has been introduced a different sol-gel[9,10] routes @ polyacrylamide gel route for preparing CoFe2o4 nanoparticle. Due to lack of controls over the specific transformation of a nanoparticle, obviously super-paramagnetic particle has not been prepared from magnetite, i.e. Magnetite-nano-particle which generally loses their permanent magnetic properties in the lake of the external magnetic field[6-14].

The most applications require at least a magnetic-particle for dispersing in the non-magnetic matrixes. This matrix plays an important role for providing the meaning of particle dispersion for determining a physical property of a composite[10, 14]

The other important items of these matrixes are to act as a protection for magnetic nano-particles against oxidation or corrosion especially[13,14] in the metallic nano-particles[15-17]. Among oxide matrixes[15] such as alumina, silica[16], zeolites, titanic oxides, carbon-based, the silica[16] can be a general suitable materials for the matrixes because of inertness of the magnetic fields, its non-toxicity and easiness for forming cross lined networks structure[14-17]. Silica shells chemically is stable and can be rapidly functionalized in the bio-conjugation purposes, in other words is biocompatible therefore CoFe2O4 @SiO_2 as a silica coated magnetite composite nanoparticles have been synthesized by several groups[18-20].

Recently, silica coated magnetite functionalized by γ mercaptopropyl-tri-methoxysilane has been successfully used for extracting Pb^{2+}, Cd^{2+}, Na+, K+, Mg^2+, Hg^{2+} , and Cu^{2+}in the wide pH ranges from water[15-20]. The complex of metal- CoFe2o4@ SiO_2–NH_2 nanoparticles[1-4] could be recovered easily from aqueous through magnetic separation and reproduce readily by acid treatment. By this work it has been exhibited the amino-functionalized CoFe2o4@$B_{18}N_{18}$ magnetic nanoparticles compare to CoFe2o4@SiO_2 is much more effective as recyclable adsorbent for the removal of heavy and alkali/earth metal ions in water and wastewater treatments.

Catalysts has a very sensitive treatment in technology and modern sciences as they increase reaction yield via reducing the temperature in synthesis of the chemical product[21,22]. There are two basic types of catalysis, (1); "heterogeneous[22-23], where the reaction accomplishes on the surfaces and the catalysts are in the solid phase. (2) "homogeneous[23], where the catalyst is in one phase as reactant[21].

The heterogeneous[22] catalyst might be easily separated from the mixed solvent but because of their limited area of surfaces the reaction rate is restricted[22]. Meanwhile homogeneous[23] catalyst might react fast for providing a good rate (conversion rate) for the catalyst, but as they are solvable in the medium reaction, it might be a laboring processing for removing them of the reaction enviroment[23]. The problem in removing homogenous[23], catalysts from the reaction environment leads to problem of maintain the catalyzer for repeating[24]. The bridge between heterogeneous[22] and homogeneous[23] catalysts can be attained through the CoFe2o4 nanoparticle[25]. CoFe2o4 exclusively is useful and important as the magnetic nano-particle which exhibit strong magnetic-moment and are seldom sustained outside of an external magnetic field[25]. These kinds of nano-particle might be consist of several materials such as nickel, cobalt, iron oxides, ferrites[26,27] and also alloys such as platinum/iron[26]. CoFe2o4 MNPs of silica shells catalytic materials have the benefit for increasing surface area which causes for any increased reaction rate[28]. Moreover, nanoparticle might permit additional catalytic functionality because of their unique properties[29]. Several catalysis of magnetic nano-structure has been investigated up to now[30-32], such as preparation of nano-composite materials consist of magnetic-(core) nano-particle which has been coated by various shells of other catalytically[30] active nano-material[32].

Other type of catalysts that are interest for organic compounds involves the using of organic molecules which are enabling for preservation the materials in the end of any reactions for reuseing[31-32]. In this work we have investigated the catalysis's properties of CoFe2o4 nanoparticles @ $B_{18}N_{18}$ instead of SiO_2 for comparing in the area of chemical synthesizes.

Recently extensive theoretical and experimental studies have been accomplished on boron-nitride-fullerenes for understanding their relative stabilities and also size dependence of important physical properties[33-35]. $(BN)_n$ are iso-electronic with carbon species, making them the goal of various research area and enhanced[34] by this fact which B-N compounds have a stable crystalline phase near to graphite[36-38]. Electronic properties of different BnNn rings and cages have been investigated theoretically[39-45].Despite those experimental and theoretical works, the structural synthesized of B_nN_n rings and cages are still unknown.

Boron nitrides exist in several crystalline forms, such as hexagonal and cubic shapes. Due to the closely structures between C-C and B-N units, large efforts have been done recently to "BN" fullerenes, which has excellent properties like structural stability, heat resistance and insulation[46,47]. As the thermodynamic mechanism of BN growth (from nuclei) is still not well known for those nanotubes, a comprehensive theoretical simulation continue to attract enhanced attention[48]. Although those nanotubes are found to be non-chiral or chiral; however, most interests in the zigzag and armchair investigation are much less known about the chirality area of hexagonal boron nitride[49].

In our previous works[50-69], it has been exhibited the BN stabilities, NMR data, electronic properties, chemical phenomenon and the mechanism of tubes generating for the various structures of BN especially for the SWBNNT via a multi-walled nanotube including chirality m, n (with n = 3-4 and m=5-7). The diagram generation for nano-ring of the B_nN_n (n = 15, 16, 18 and 20) are shown in the references of[52-54]. In addition, we reported a unique stable structures[52-54] with combinations of five and six loops same as a quasi $B_3N_3H_6$ shape for $B_{15}N_{15}$ and $B_{18}N_{18}$, respectively. Those kinds of shapes have significant properties in the nano studies of CoFe2o4 @ $B_{18}N_{18}$ particles. The suitable stability and reasonable aromaticity of those structures have been confirmed by thermodynamic data, frequency optimization and NQR[52-54].

Hyperfine parameter and spin density, electrical potentials, electromagnetic properties and isotropic-fermi-coupling-constant[52-55] indicate the stability of those rings through using non-bonded interaction model between CoFe2o4 & $B_{18}N_{18}$. A novel amino functionalized CCoFe2o4 & $B_{18}N_{18}$ magnetic nano-material with the core-shell structures has been developed, for removing heavy metal ions from the aqueous media. The elasticity of electron density, electrical properties same as electron and energy densities, kinetic and potential energies of densities, ELF or LOL, eta index and ECP for CoFe2o4-$B_{18}N_{18}$ core-shell systems have been calculated and simulated in related reactions for Amino-functionalized CoFe2o4@ $B_{18}N_{18}$ core–shell magnetic. The amino-functionalized CoFe2o4 & $B_{18}N_{18}$ nano-adsorbent exhibited high adsorption affinities for aqueous Fe (iii), Pb (ii), Ni (ii), Cu (ii) and Zn (ii) ions, resulting from complexation by surface amino groups.

BACKGROUND & METHODOLOGY

Magnetic particles are suitable for aqueous transition and heavy metals due to thier unique advantages of quick separation and their high surface area under external magnetic fields[68-71]. The surface modification, adsorption affinity, including covalent binding and physical coating, has often been explored[70-75] for enabling specific complexation for further facilitates[72-76].

Recently it have been exhibited which the amino-functionalized molecules demonstrated outstanding abilities for removing a wide variety of transition heavy metal ions[77-79]. Both $B_{18}N_{18}$ & SiO_2 are stable under acidic conditions, as compared with some other materials and functions for protecting the inner magnetite core[80-82].

Although CoFe2o4@SiO_2 has recently been investigated for potential biomedical applications[82], there is no work about the CoFe2o4 @ $B_{18}N_{18}$.

In this study with the theoretical approaches magnetic nano adsorbent has been developed via covalently grafting amino groups over the surfaces of CoFe2o4@ $B_{18}N_{18}$ nanoparticles. Part of the systems including CoFe2o4 @ $B_{18}N_{18}$ nanoparticles has been simulated with QM/MM methods and the investigation carried out by the Monte Carlo calculations. In this study, various force fields are done via "Amber" and OPLS for comparing the calculated energy of the CoFe2o4 @ $B_{18}N_{18}$ nanoparticles. Furthermore, a Hyper-Chem professional release-7.01program is used for any further calculations.

For the non-covalent forces of $B_{18}N_{18}$ and CoFe2o4, the B3LYP &BLYP methods are unsuitable for describing van der Waals[83, 84] through medium-range interaction[84]. Therefore, the ONIOM* methods with three levels of tight (H), medium Hamiltonian (M), and low (L) calculations have been accomplished in these studies to estimate the non-bonded interaction between $B_{18}N_{18}$ and CoFe2o4.

The density functional method is used for the high level while the semi-empirical (pm_6) with pseudo=$Lanl_2$ and Pm_3MM for both of them respectively. Some accurate studies have indicated that in-accuracy of the low range exchange energies goes to the large systematic errors for the prediction of molecular properties[85-88].

Geometries optimization and electronic calculations have been accomplished using the m06 functional of DFT. These approaches are based

Table 1: All Electron Densities of non-bonded interactions for CoFe2o4@Silica shell [(a)], CoFe2O4@ $B_{18}N_{18}$ shell [(b)] and CoFe2o4 (isolate)[C]

Atoms of CoFe2o4	Density of all electron(10^{-3}) (a)	(c)	(b)	Density of alpha ((10^{-3}) (a)	(c)	(b)	Density of Beta ((10^{-3}) (a)	(c)	(b)	Spin Density (a)	(c)	(b)
Co(1)	0.30	0.12	0.36	0.15	0.06	0.18	0.15	0.06	0.18	0.0	0.1	0.0
Fe(2)	0.28	0.10	0.34	0.14	0.05	0.17	0.14	0.05	0.17	0.0	0.1	0.0
Fe(3)	0.14	0.12	0.32	0.07	0.06	0.16	0.07	0.06	0.16	0.0	0.0	0.0
O(1)	0.32	0.16	0.14	0.16	0.08	0.07	0.16	0.08	0.07	0.0	0.0	0.0
O(2)	0.18	0.12	0.24	0.09	0.06	0.12	0.09	0.06	0.12	0.0	0.0	0.0
O(3)	0.30	0.18	0.12	0.15	0.09	0.06	0.15	0.09	0.06	0.0	0.0	0.0
O(4)	0.12	0.18	0.22	0.06	0.09	0.11	0.06	0.09	0.11	0.0	0.0	0.0

on solution of the Kohn & Sham equation[89] in the plane-waves sets with projector-augmented-pseudo-potentials[90]. The Perdew &Burke & Ernzerhof PBE[90] exchange-correlation and generalized-gradient-approximation GGA[90] are also used for non-bonding calculation.

The charge transferring and electrostatics potentials derived charges were also estimated using the Merz & Kollman & Singh[91], chelpG[92] or chelp[93]. The charges calculation methods based on MESP or molecular-electrostatics-potentials fitting are not well suited for the larger systems whereas several of the inner-most points are located far away from the centers at which the MESP[93] are computed. In that position, variation of the inner-most atomic charges would not be towards the changing of the MESP[91] outside of the molecules.

The charge-density profiles of this study have been estimated from the first principle calculation through an averaging process as described in the references[90-95]. The interaction energies or adsorbents energies between metals and CoFe2o4 @$B_{18}N_{18}$ catalyst were done according to the equation as follows:
$\Delta Es(eV) = \{Ec - (\Sigma^{n}i=1(metal - CoFe_2o_4 - B18N18 - NH_2)_i + \Sigma^{m}_{j=1} (CoFe_2O_4)_j + \Sigma^{q}_{v=1} B18N18)_v) + \Sigma^{p}_{k=1} metal - ion)_k \} + E_{BSSE}$ ...(1): That is the adsorbents energies.

The electron-localization-function or ELF[96-98], localized-orbital-locator or LOL[96-98] , electron density of the Gradient-norm & Laplacian, values of orbitals wave- functions, electron spin densities, electrostatic-potentials from nuclear-atomic-charges,

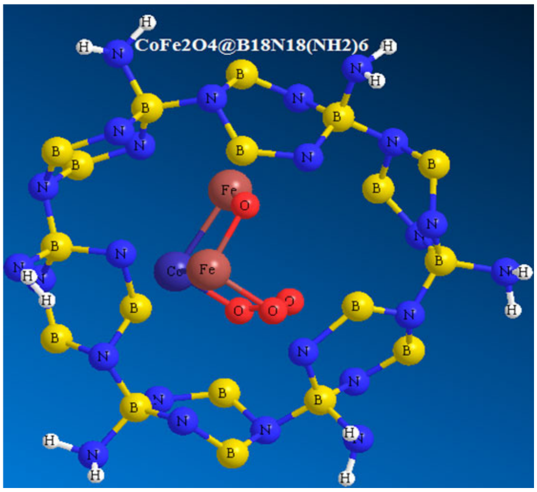

Fig. 1: the non-bonded interaction between CoFe2o4 and $B_{18}N_{18}$ shell

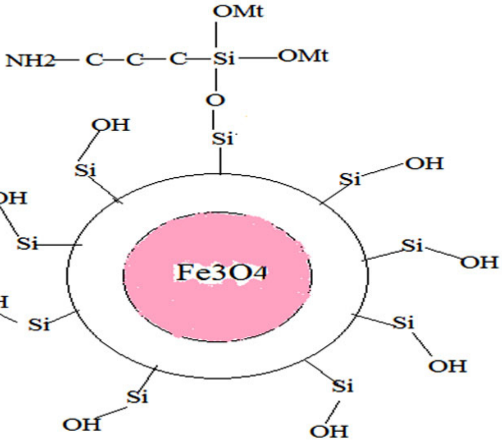

Fig. 2: the non-bonded interaction between Fe3O4 and silica shell for binding to 3-aminpropyltrimethoxysilane (APTMS)

Table 2: All Electron Energies of non-bonded interactions for CoFe2O4@Silica shell [(a)] ,CoFe2o4@$B_{18}N_{18}$ shell [(b)] and CoFe2O4 (isolate)[C]

Atoms of CoFe2o4	Lagrangian kinetic [G(r)]energy(10^{-3})			Hamiltonian kinetic [K(r)]energy(10^{-2})			Potential energy Density [U(r)](10^{-2})		
	(a)	(c)	(b)	(a)	(c)	(b)	(a)	(c)	(b)
Co(1)	0.32	0.14	0.30	0.60	0.58	0.54	-0.68	-0.52	-0.78
Fe(2)	0.33	0.12	0.31	0.62	0.66	0.62	-0.65	-0.64	-0.63
Fe(3)	0.23	0.16	0.30	0.38	0.72	0.68	-0.34	-0.37	-0.58
O(1)	0.28	0.21	0.14	-0.32	-0.5	-0.43	-0.24	-0.59	-0.50
O(2)	0.24	0.15	0.26	-0.14	-0.40	-0.46	-0.86	-0.68	-0.54
O(3)	0.16	0.15	0.18	-0.44	-0.39	-0.44	-0.33	-0.63	-0.55
O(4)	0.24	0.16	0.18	-0.14	-0.42	-0.42	-0.85	-0.63	-0.51

the exchange-correlation density, as well as total electrostatic potentials ESP), correlation-holes and correlation-factors, and the average local ionization energies using the Multi-functional-Wave-function analyzer have also been calculated in this study[96-98].

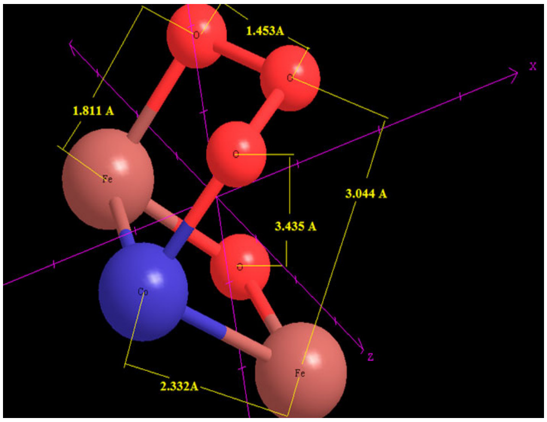

Fig. 3: the optimized of CoFe2o4 in $B_{18}N_{18}$ shell

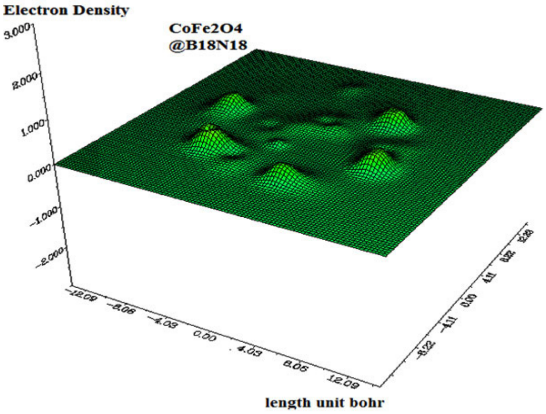

Fig.4: Shaded surface map for electron density of CoFe2o4-$B_{18}N_{18}$ shell

Density electron approach for interaction between MNPs and $B_{18}N_{18}$

The kinetic energies densities are not defined individually, since the expected values of the operators: $< \varphi |-\left(\frac{1}{2}\right)\nabla^2| \varphi >$ ...(2) can be estimated by integrating kinetic energy densities from those alternatives definitions. One of the usual used definitions is as follows: $k(r) = -1/2\ \Sigma_i \eta_i \varphi_i^* (r)\ \Delta^2\varphi_i(r)$ ... (3), the local kinetic energies given below guarantee[96-98] hence the physical data are more commonly used. The Lagrangian of kinetic energies densities, G(r)[97] are also known as positive definite kinetic energy densities.

$G(r) = 1/2\ \Sigma_i \eta_i \mid \nabla\ (\varphi_i)|^2 = 1/2\ \Sigma_i \eta\{[(\partial\ \varphi_i(r)\ /\ \partial(x)^2 + \partial\ \varphi_i(r)\ /\ \partial(y)^2 + \partial\ \varphi_i(r)\ /\ \partial(z)^2\}$ ...(4) K(*r*) *and* G(**r**) *are* directly related by Laplacian of electron density $\frac{1}{4}\nabla^2\rho(r) = G(r) - K(r)$

The electrostatic potential from nuclear/atomic charges can be calculated via: $V_{nuc}(r) = \Sigma_A Z_A / |r - R_A|$ where R_A and Z_A denote position vector and nuclear charge of atom A, respectively.

Becke and Edgecombe have noted that spherically averaged like-spin conditional pair probability have correlation with the Fermi hole and it has been suggested which the electron localization function (ELF)[98]. $ELF(r) = 1 / 1+[D(r) / D_{0(r)}]^2$ ...**(5)** where $D(r) = \frac{1}{2}\sum_i \eta_i\ |\nabla\varphi_i|^2 - \frac{1}{8}[\frac{|\nabla\rho|^2}{\rho(r)}]$ and $D_{0(r)} = 3/10\ (6\pi^2)^{2/3}\ [\rho\alpha(r)^{5/3} + \rho\beta\ (r)^{5/3}]$ ...(6) for close-shell system, since $\rho\alpha(r) = \rho\beta\ (r) = 1/2\rho$, *D* and *D*0 terms

Table 3: Laplacian, ELF, LOL and Local information entropy of non-bonded interactions for CoFe2o4@Silica shell [(a)] ,CoFe2o4@$B_{18}N_{18}$ shell [(b)] and CoFe2o4 (isolate)[C]

Atoms of CoFe2o4	Laplacian of electron density(10^{-1})			Electron localization function (ELF) (10^{-1})			Localized orbital locator (LOL)			Local information entropy(10^{-4})		
	(a)	(c)	(b)	(a)	(c)	(b)	(a)	(c)	(b)	(a)	(c)	(b)
Co(1)	-0.20	-0.26	-0.22	0.41	0.46	0.65	0.14	0.22	0.13	0.14	0.15	0.25
Fe(2)	-0.25	-0.24	-0.24	0.41	0.48	0.66	0.12	0.24	0.14	0.20	0.34	0.25
Fe(3)	-0.13	-0.27	-0.26	0.13	0.25	0.61	0.63	0.12	0.17	0.4	0.16	0.18
O(1)	0.79	-0.67	-0.55	0.13	0.17	0.25	0.32	0.25	0.25	0.13	0.12	0.10
O(2)	0.18	0.25	0.30	0.13	0.16	0.2 2	0.10	0.15	0.25	0.23	0.32	0.30
O(3)	0.84	0.14	0.25	0.16	0.15	0.26	0.31	0.12	0.25	0.32	0.20	0.31
O(4)	0.23	0.24	0.15	0.16	0.13	0.29	0.16	0.17	0.21	0.32	0.24	0.14

can be simplified as D(r) = $\frac{1}{2}\sum_i \eta_i \ |\nabla\varphi_i|\ ^2 - \frac{1}{8}[\frac{|\nabla\rho|\ ^2}{\rho(r)}]$, $D_{0(r)} = 3/10(3\pi^2)^{2/3}\rho(r)^{5/3}$.

In which the kinetic energies terms in *D*(**r**) is replaced by Kirzhnits types second-order gradients expansion, which are $1/2\ \Sigma_i\eta_i\,|\nabla\ \varphi_i|^2 \approx D_0(r) + 1/72\ |\nabla\ \rho\,|\,/\,\rho(r) + 1/6\ \nabla^2\rho(r)$ ...(7) so that ELF is totally independent from the wave-function, and then can be used for analyzing electron densities from X-ray diffraction data.

Localized orbital locator or LOL[98,99] is another item for locating high localization regions likewise ELF, which explained by Schmider & Becke[99] . LOL (r) = $\tau(r)\ /\ 1 + \tau(r)$, where $(r) = D_0(r)\,/\,1/2\,\Sigma_i\eta_i\,|\nabla\ \varphi_i|^2$, ...(8) $D_0(r)$ for spin-polarized system and close-shell system are defined in the same way as in ELF[98]. LOL have similar approaches compared to ELF.

Notice that evaluating ESP is much more time-consuming than evaluating other functions. The ESP evaluated under default value is accurate enough in general cases. Reduced density gradient (RDG) RDG are a pair of very important functions for revealing weak interaction region[96-98] for detail. RDG is defined as RDG (r) $1/2(3\pi^2)^{1/3}\,|\nabla\ \rho(r)|\ /\ \rho(r)^{4/3}$ ...(9)[96-98] . Fortunately, it is found that weak interaction analysis under pro-molecular density is still reasonable. Pro-molecular density is simply constructed by superposing electron densities of free-state atoms and hence can be evaluated extremely rapidly. Where is pre-fitted spherically averaged electrons densities of atom A.

RESULT AND DISCUSSION

This work basically focuses on the magnetic properties of CoFe2O4 in the non-bonded systems with $B_{18}N_{18}$ surfaces including "CoFe2o4@ $B_{18}N_{18}$". The CoFe2o4@$B_{18}N_{18}$ nano-adsorbent shown high adsorption affinities for aqueous Na+, K+, Mg2+, and the amino- CoFe2o4@SiO_2 exhibited high adsorbent for Fe (iii), Pb (ii), Ni (ii), Cu (ii) and Zn (ii) ions, resulting from complexation of the metals ion with the surface amino groups. The metal loaded CoFe2o4@ $B_{18}N_{18}$ nanoparticles could be recovered easily from aqueous solution by magnetic separation. The data have shown in ten figures and eight tables. As it is indicated in table1, LOL is low and constant for Both CoFe2o4@silica, $CoFe_2O_4$@$B_{18}N_{18}$ and CoFe2o4@ $B_{18}N_{18}$. ELF has a similar expression as LOL.

The non-bonded interactions are shown in figs1-3. As it is indicated in tables 1-4, the electrical properties can be obtained from changes in the non-bonded interactions. Potential energy densities, ELF, LOL, electron densities, energy densities, eta index and ECP are shown in tables1-4. The results of ELF and LOL indicate that the surfaces of silica and B18N18 are suitable to attach in aromatic and organic compounds in any scale from nano to micro or medium.

As it is shown in Figs.5-9, there are clear curves within a decreasing amount for electron

Table 4: Average local ionization energy and RDG of non-bonded interactions for CoFe2o4@Silica shell [(a)] ,CoFe2o4@$B_{18}N_{18}$ shell [(b)] and CoFe2o4 (isolate)[C]

Atoms of CoFe2o4	Reduced density gradient (RDG)(10^{-1})			Average local ionization energy		
	(a)	(c)	(b)	(a)	(c)	(b)
Co(1)	0. 4	0.5	0.5	0.4	0.4	0.5
Fe(2)	0.3	0.4	0.5	0.6	0.5	0.5
Fe(3)	0.4	0.5	0.5	0.4	0.4	0.5
O(1)	0.6	0.4	0.6	0.7	0.6	0.4
O(2)	0.3	0.4	0.5	0.3	0.5	0.4
O(3)	0.6	0.3	0.6	0.7	0.3	0.5
O(4)	0.4	0.3	0.5	0.3	0.4	0.5

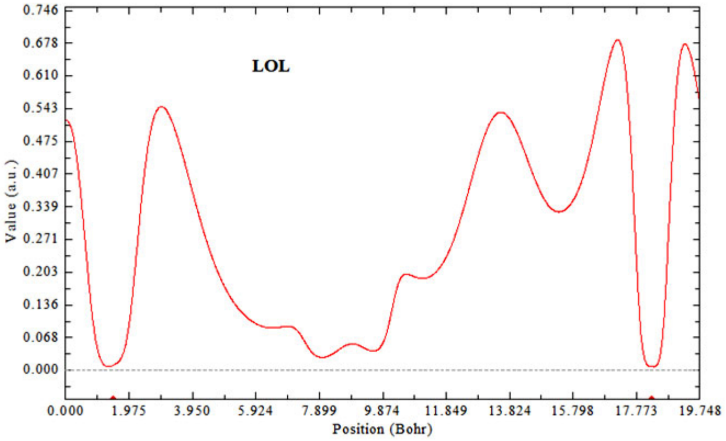

Fig. 5: LOL versus Position for $CoFe_2O_4@B_{18}N_{18}$

density, energy density, ELF and LOL. The interaction energy between two sides of CoFe2o4-silica and CoFe2o4-B18N18 are also calculated. The potential energy difference between the two parts, are depicted in table 2.

It has been exhibited the BN compounds such as $B_{18}N_{18}$ and amino-functionalized materials presented an ability for removing a wide range of earth/alkali. In contrast, the most usual used magnetic sorbents are based on iron oxide and unfortunately thus susceptible to leaching under acidic conditions. This problem will removed by replacing the $B_{18}N_{18}$ instead of Sio_2 as a shell of CoFe2o4. In addition, functional groups on the coating layer chemically adhering to the MNPs are also assailable to acid treatment. In contrast of SiO_2 rings which is stable under acidic conditions the $B_{18}N_{18}$ rings is independent from acidic situations and hence for $B_{18}N_{18}$ comparing to SiO_2, the functions is not needed as an ideal shell composite to protect the inner magnetite core. Although CoFe2o4@SiO_2 or Silica-coated core–shell magnetite nanoparticles have recently been investigated for potential biomedical applications, by this work we exhibit the $B_{18}N_{18}$ is much useful for removing the earth/alkali metal from the aqueous solution.

Relative adsorption energies of four alkali and alkali/metal ions on CoFe2o4@$B_{18}N_{18}$ have investigated. The adsorption data for Cu, Pb, Cd and so on were fitted to the Langmuir model according to the equation: $q_e = q_m c_e b/ 1 + c_e b$[101] where Ce (mmol/L) and qe (mmol/g) and are the aqueous concentration the adsorbed concentration at equilibrium adsorption, and, b and qm are the coefficient of affinity and the adsorption capacity respectively[101].

CONCLUSION

We think that $B_{18}N_{18}$ capabilities of magnetic substrates should be explored in the near future. Another interesting development is using the $B_{18}N_{18}$ on magnetic-nanoparticle enables effective removal of alkali -earth/alkali metals based on catalysts froms important pharmaceutical products in the drug nanotechnology. Our Calculations indicate that the $B_{18}N_{18}$ are suitable surfaces for CoFe2o4 such silica surfaces for removal metal ions such as Na+, Mg++,K+ and Ca++.

REFERENCES

1. Haneda, K.; Morrish, A.H. *J. Appl. Phys* **1998**, *63* (8) 4258.
2. Moumen,N.; Veillet, P. ; Pileni, M.P. *J. Magn. Magn. Mater*. **1995**, *149* , 67.
3. Blaskov, V.; Petkov, V.; Rusanov, V.; Martinez, L.M.; Martinez, B.; Munoz, J.S.; Mikhov, M. *J. Magn. Magn* **1996**, Mater. *162*,331.
4. Pillai, V.; Shah, D.O.; J. *Magn. Magn. Mater* **1996**, *163*,243
5. Davis, K.J.; Wells, S.; Upadhyay, S.V.;

Charles, S.W.; O'Grady, K.M.; El Hilo, M.; Meaz, T.; Morup, S. *J. Magn. Magn. Mater*. **1995**, 149 14

6. Ma, Ming; Zhang, Yu; Guo, Zhir4.ui; GU, Ning. *Nanoscale Research Letters* **2013**, *8* (1): 16. doi:10.1186/1556-276X-8-16.
7. Massart, R., *IEEE transactions on magnetics*, **1981**, *17,* 2, 1247–1248
8. Valter Ström, Richard T. Olsson, K. V. Rao, *J. Mater. Chem*., **2010**, *20,* 4168-4175
9. Shi, M.; Zuo, R. Z.; Xu, Y. D.; Jiang, Y. Z.; Yu, G. Y.; Su, H. L.; Zhong, J. G. *J. Alloy. Compd*. **2012**, *512*, 165170
10. Cui, H. T.; Jia, Y. Y.; Ren, W. Z.; Wang, W. H. *J. Sol-Gel Sci. Technol*. **2010**, *55*, 3640
11. Burianova, S.; Vejpravova, J. P.; Holec, P.; Plocek , J.; Niznansky, D.; *J. Appl. Phys*, **2011**, 110,073902.
12. Zhu, Z. G.; Li, X. Y.; Zhao, Q. D.; Shi, Y.; Li, H.; Chen, G. H.; J. *Nanopart. Res*, **2011**, *13* 21472155.
13. Zhang, Y.; Liu, Y.; Yang, Z.; Xiong , R.; Shi, J.; *J. Nano-part. Res*, **2011***, 13*, 45574563
14. Peng, J. H.; Hojamberdiev, M.; Xu, Y. H.; Cao, B. W.; Wang, J.; Wu, H.; *J. Magn. Magn. Mater*. **2011**, *323*, 133137
15. Yanase, A.; Siratori, K.; *J. Phys. Soc. Jpn.***1984***, 53*, 312
16. Pe´nicaud, M.; Siberchicot, B.; Sommers, C. B.; Ku¨bler, *J. Magn. Magn. Mater*, **1992**, 103, 212
17. Babes, L.; Denizot, B.; Tanguy, G.; Le Jeune, J.J.; Jallet P. *Journal of Colloid and Interface Science* , **1999***, 212* (2): 474–482
18. BERRY, C.; CURTIS, A S G. *J Phys D: Appl Phys*, **2003**, *36*: 198" 206.
19. RUUGE, E K.; RUSETSKI, A N. *J Magn Magn Mater*, **1993**, *122,* 335"339
20. POPE, N M.; ALSOP, R C.; CHANG, Y A.; SMITH, A K. *J Biomed Mater Res*, **1994***, 2:* 449"457.
21. Tago, T.; Hatsuta, T.; Miyajima, K.; Kishida, M.; Tashiro, S.; Wakabayashi, K.; *Journal of the American Ceramic Society*, **2002**, *85,* 9, 2188-2194.
22. Lei, Z.; Li, Y. L.; Wei, X. Y. *Journal of Solid State Chemistry*, **2008**, *181*, 3, 480-486.
23. Huang, C. Z. Hu, B.; *Spectrochim Acta Part B: Atomic Spectroscopy*, **2008**, *63*, 437-444.
24. Philipse, A.P. *J. Chem. Educ.* **2011**, *88*, 59–62.
25. Sheldon, R.A.; Downing, R.S. *Appl. Catal. A* **1999**, *189*, 163–183.
26. Cole-Hamilton, D.J. Homogeneous catalysis—New approaches to catalyst separation, recovery, and recycling. *Science* **2003**, *299*, 1702–1706.
27. Cornils, B.; Herrmann, W.A. *J. Catal.***2003**, *216*, 23–31
28. Johnson, B.G. Nanoparticles in catalysis. *Top. Catal.* **2003**, *24*, 147–159.
29. Laurent, S.; Forge, D.; Port, M.; Roch, A.; Robic, C.; Vander Elst, L.; Muller, R.N. *Chem. Rev.* **2008**, *108*, 2064–2110.
30. Kodama, R.H. Magnetic nanoparticles. *J. Magn. Magn. Mater.* **1999**, *200*, 359–372.
31. Chang, L.L.; Erathodiyil, N.; Ying, J.Y. *Acc. Chem. Res.* **2012**, *46*, 1825–1837.
32. Fujishima, A.; Zhang, X.; Tryk, D.A. *Surf. Sci. Rep.* **2008**, *63*, 515–582.
33. Wang, X.; Starz-Gaiano, M.; Bridges, T.; Montell, D. *Protoc, Exch,* 28, 2008.
34. Wei, S.; Wang, Q.; Zhu, J.; Sun, L.; Lin, H.; Guo, Z. *Nanoscale* **2011**, *3*, 4474–4502.
35. Yoon, T.-J.; Lee, W.; Oh, Y.-S.; Lee, J.-K. *New J. Chem.* **2003**, *27*, 227–229.
36. Yu, Zh.; Hu, M. L.; Zhang, C. X.; He, C. Y.; Sun, L. Z.; Zhong, J. *J. Phys. Chem. C* **2011**, 115, 10836.
37. Seifert, G.; Flower, P. W.; Mitchell, D.; Porezag, D.;Frauenheim, T. *Chem. Phys. Lett.* **1997**, 268, 352.
38. Alexandre, S. S.; Chacham, H.; Nunes, R. W. *Appl. Phys. Lett.***1999**, 75, 61.
39. Locke, I. W.; Darwish, A. D.; Kroto, H. W.; Prassides, K.;Taylor, R.; Walton, D. R. M. *Chem. Phys. Lett.* **1994**, 225, 186.
40. Behrman, E. C.; Foehrweiser, R. K.; Myers, J. R.; French, B. R.;Zandler, M. E. *Phys. Rev. A* **1994**, *49*, R1543.
41. Kaxiras, E.; Jackson, K.; Pederson, M. R. *Chem. Phys. Lett.* **1994**,225, 448
42. Zhao, J. X.; Ding, Y. H. *J. Phys. Chem. C* **2008**, 112, 5778.
43. Bagheri,S.; Moosavi,M.S..; Moradiyeh,N.; Zakeri,M.; Attarikhasraghi,N.; Saghayimarouf,N.; Niyatzadeh,G.; Shekarkhand,M.; Mohammad S. Khalilimofrad, Ahmadin,H.; Ahadi,M.; *Molecules* **2015**, *20*, 21636–21657;

44. Strout, D. L. *Chem. Phys. Lett*. **2004**, 383, 95.
45. Zope, R. R.; Dunlap, B. I. *Chem. Phys. Lett*. **2004**, 386, 403.
46. Zope, R. R.; Baruah, T.; Pederson, M. R.; Dunlap, B. I. *Chem.Phys. Lett.* **2004**, 393, 300.
47. Zheng, J. W.; Zheng, L. P.; Wu, P. *J. Phys. Chem.* C **2010**, 114,5792.
48. Chopra, N. G.; Luyken, R. J.; Herrey, K.; Crespi, V. H.; Cohen, M. L.; Louie, S. G.; Zettl, A. *Science* **1995**, 269, 966.
49. Blase, X.; Rubio, A.; Louie, S. G.; Cohen, M. L ì *Europhys. Lett.* **1994**, 28L, 335.
50. Monajjemi, M.; Lee, V.S.; Khaleghian, M.; B. Honarparvar, B.; F. Mollaamin, F. *J. Phys. Chem C*. **2010**, 114, 15315
51. Monajjemi, M, *Journal of Molecular Liquids*, **2017**, 230 , 461–472
52. Monajjemi,M.; Nayyer T. Mohammadian *J. Comput. Theor. Nanosci*. **2015,** 12, 4895-4914.
53. Monajjemi, M. *Struct Chem.* **2012**, 23,551–580
54. Monajjemi, M.; Boggs, J.E. *J. Phys. Chem. A*, **2013,** *117,* 1670 "1684
55. Mollaamin, F.; Monajjemi, M, *Journal of Computational and Theoretical Nanoscience***.** **2012**, *9 (4)* 597-601
56. Monajjemi, M.; Khaleghian, M, *Journal of Cluster Science.* **2011,** 22 (4), 673-692
318
57. Monajjemi, M.; Wayne Jr, Robert. Boggs, J.E. Chemical Physics. **2014**, *433*, 1-11
58. Monajjemi, M. Falahati, M.; Mollaamin, F.; *Ionics,* **2013**, *19*, 155–164
59. Monajjemi, M.; Mollaamin, F. *Journal of Cluster Science*, **2012**, *23*(2), 259-272
60. Tahan, A.; Monajjemi, M. *Acta Biotheor,* **2011,** *59*, 291–312
61. Mollaamin, F.; Monajjemi, M. *Physics and Chemistry of Liquids* .**2012**, *50,* 5, 2012, 596–604
62. Monajjemi, M.; Khosravi, M.; Honarparvar, B.; Mollaamin, F.; *International Journal of Quantum Chemistry***, 2011**, *111,* 2771–2777
63. Monajjemi, M*. Theor Chem Acc*, **2015**, 134:77 DOI 10.1007/s00214-015-1668-9
64. Monajjemi, M*. Journal of Molecular Modeling* , **2014**, *20*, 2507
65. Monajjemi, M.; Khaleghian, M.; Mollaamin, F. *Molecular Simulation*. **2010**, *36*, 11, 865–
66. Monajjemi, M. *Biophysical Chemistry*. **2015** .,*207*,114 –127
67. Jalilian,H.; Monajjemi, M. *Japanese Journal of Applied Physics*. **2015,** *54*, 8, 08510
68. S. Shin, J. Jang, *Chem. Commun*. **2007.,** 41., 4230.
69. L.C.A. Oliveira, D.I. Petkowicz, A. Smaniotto, S.B.C. Pergher, *Water Res*. **2004.,** 38
3699.
70. J. Hu, G. Chen, I.M.C. Lo, *Water Res.* **2005.,** 39., 4528.
71. C.T. Yavuz, J.T. Mayo, W.W. Yu, A. Prakash, J.C. Falkner, S. Yean, L. Cong, H.J.
Shipley, A. Kan, M. Tomson, D. Natelson, V.L. *Colvin, Science* **2006.,** 314 964
72. B. Hai, J. Wu, X. Chen, J.D. Protasiewicz, D.A. *Scherson, Langmuir* **2005.,***21*
3104.
73. J. Hu, M.C. Lo, G.H. Chen, Sep. *Purif. Technol*. **2007.,** 58 .,76.
74. Y.C. Chang, D.H. Chen, *J. Colloid Interface Sci.* **2005.,** 283 446.
75. J.F. Liu, Z.S. Zhao, G.B. Jiang, *Environ. Sci. Technol.* **2008.,** 42 ., 6949.
76. W. Yantasee, C.L. Warner, T. Sangvanich, R.S. Addleman, T.G. Carter, R.J.
Wiacek, G.E. Fryxell, C. Timchalk, M.G. Warner, *Environ. Sci. Technol*. **2007.,** *41*
5114.
77. M. Kumar, D.P.S. Rathore, A.K. Singh*, Talanta* **2000.,**51., 1187.
78. K.F. Lam, K.L. Yeung, G. McKay, *Environ. Sci. Technol*. **2007.,** *41* **.,**3329.
79. J. Li, X. Miao, Y. Hao, J. Zhao, X. Sun, L. Wang, *J. Colloid Interface Sci*. **2008.,.***318*
309.
80. Q. Liu, Z. Xu, J.A. Finch, R. Egerton, Chem. Mater. **1998.,** *10 .,*3936.
81. C.W. Lu, Y. Hung, J.K. Hsiao, M. Yao, T.H. Chung, Y.S. Lin, S.H. Wu, S.C. Hsu, H.M.
Liu, C.Y. Mou, C.S. Yang, D.M. Huang, Y.C. Chen, *Nano Lett.* **2007.,** *7* .,149.
82. P. Ashtari, X.X. He, K. Wang, P. Gong, Talanta **.,2005.,** *67* 548.
83. Zhao, Y.; Truhlar, D.G. *Theor Chem Account* ,**2008**, 120:215–241**,** DOI 10.1007/s00214-007-0310-x
84. Zhao, Y.; Truhlar, D.G, *Accounts of Chemical*

Research.**2008**, *41*, (2): 157-167.

85. Monajemi, M; Ketabi, S; Zadeh, MH; et al. *Biochemistry-Moscow* **2006**, *71* S1-S8
86. Grimme, S. *Angew Chem Int Ed,* **2006,** (45), 4460–4464, DOI: 10.1002/anie.200600448.
87. Schreiner, P.R.; Fokin, A. A.; Pascal, R. A Jr.; de Meijere, A. *Org. Lett,* **2006**, (8): 3635–3638.
88. Zhao, Y.; Truhlar, D.G. *Org. Lett***,** **2006**, (8):5753–5755.
89. Kohn, W.; Sham, LJ. *Phys. Rev,* **1965,** (140) A: 1133-1138.
90. Perdew, J .P. Burke, K.; *Phys. Rev. Lett.***1996**, (77): 3865-3868.
91. Besler, B.H.; Merz, K.M.; Kollman, P.A. *J. comp. Chem*, **1990**, (11): 431-439, DOI: 10.1002/jcc.540110404
92. Brneman, G.M, Wiberg, K.B. *J. Comp Chem*, **1990**, (11): 361
93. Chirlian, L.E.; Francl, M.M. *J.comp.chem,* **1987**, (8): 894-905, DOI: 10.1002/jcc.540080616
94. Martin, F.; Zipse, H. *J Comp Chem*. 2005, (26): 97 – 105.
95. Balderchi, A.; Baroni, S.; Resta, R. Phys. Rev. Lett, **1998**, (61): 173.
96. Lu, T.; Chen, F. *Acta Chim. Sinica*, **2011**, *69*, 2393-2406.
97. Lu, T.; Chen, F J. Mol. Graph. Model, **2012**, (38): 314-323.
98. Lu, T.; Chen F. *J. Comp. Chem*. **2012**, (33) 580-592.
99. Schmider and Becke, J. Mol. Struct. (THEOCHEM), 527, 51
100. Murray and coworkers, J. Mol. Struct. (THEOCHEM), 307, 55
101. Jiahong Wang, Journal of Colloid and Interface Science **2010.,***349.,* 293–299
102. Mollaamin, F.; Baei, M. T.; et al. *Russian Journal of Physical Chemistry A*, **(2008)** *82* , 13,2354-2361
103. Mollaamin , Fatemeh; *Journal of Computational and Theoretical nanoscience* **2012** 597-601
104. Mollaamin, F.; Varmaghani, Z.; *Physics and Chemistry of Liquids* **2011** *49* , 3 318- 336.
105. M. Monajjemi, Chemical Physics, 2013, 425, 29–45
106. M. Monajjemi, Macedonian Journal of Chemistry and Chemical Engineering, 2017, 36, 1,101–118 DOI: 10.20450/mjcce.2017.1134