Volume 8, Issue 5, 2018, 3570 - 3574 ISSN 2069-5837

Biointerface Research in Applied Chemistry

www.BiointerfaceResearch.com

Original Research Article Open Access Journal

Received: 29.08.2018 / Revised: 28.09.2018 / Accepted: 06.10.2018 / Published on-line: 15.10.2018

# Interaction between nano silver and bacteria: modeling approach

**Noha M. Sabry [1], Sahar Tolba [2], Fagr Kh. Abdel-Gawad [1], Samah M. Bassem [1], Hossam F. Nassar [3], Gamila E. El-Taweel [1], Aly Okasha [4], Medhat Ibrahim [4]**

[1]Environmental Research Division, Centre of Excellence for Advanced Science, National Research Centre, 33 El-Bohouth St., 12622 Dokki, Giza, Egypt
[2]Department of Microbiology, Faculty of Science, Ain Shams University, Cairo, Egypt
[3]Environmental Sciences and Industrial Development Department, Faculty of Postgraduate Studies for Advanced Sciences (PSAS), Beni-Suef University, Beni-Suef, Egypt
[4]Spectroscopy Department, National Research Centre, 33 El-Bohouth Str. 12622 Dokki, Giza, Egypt

*corresponding author e-mail address: ***medahmed6@yahoo.com***

## ABSTRACT

A model molecule for bacteria is simulated in this work to study the mechanism of interaction between bacteria and silver nanoparticles. B3LYP/LANL1DZ quantum mechanical model was utilized to calculate the total dipole moment, HOMO/LUMO band gap energy and molecular electrostatic potential. Results indicated that silver in the form of $Ag.6H_2O$ interacts through hydrogen bond of both active sites of COOH and $NH_2$. The interaction could take place as adsorb state or complex state. The complex interaction led to the release of OH groups. Both interactions increased the reactivity which could result in further interaction with the surrounding environment. Both total dipole moment and HOMO/LUMO band gap energy indicated that the interaction throughout $NH_2$ is more probable in comparison with that through COOH.

**Keywords**: *B3LYP/LANL1DZ, silver nanoparticles, protein, bacteria, total dipole moment, band gap energy, electrostatic potential*.

## 1. INTRODUCTION

Early in 1959, the concept of nanotechnology was introduced [1]. This concept was subsequently followed by the establishment of the term "nanotechnology" which is referring to the engineering of different materials on the nano-scale level [2]. Nowadays, the materials in nanoscale are widely applied owing to their unique properties [3-5]. The biological activity of nano-scale materials dedicates them for many applications. Silver nanoparticles (AgNPs) show antibacterial activity [6], owing to their unique physical, chemical and biological characteristics and high surface area, which increases their specific biological activity to volume ratio [7-9]. It is stated that AgNPs show a bactericidal effect against several types of bacteria [10-12]. The potential impacts of AgNPs against several kinds of bacteria were reviewed [13]. Among their contradictory effects, AgNPs were found to be helpful to maintain the microbial community diversity in activated sludge [14]. Some bacteria such as *Pseudomonas aeruginosa* show great intrinsic antibiotic resistance which limits some effective antibiotics, but AgNPs have potential effects and could prevent infections of such bacteria due to its antibacterial activity [15]. Although the applications of AgNPs as biologically active nanomaterials have abundantly increased, alongside nano gold, the mechanism of interaction is still not fully known [16-17]. These findings resulted in many research studies reporting that AgNPs, among some other nano-scale materials, are considered as non-traditional antimicrobial agents [18-20]. Recently, the interaction between ZnO and bacteria is described as coordination between hydrated metal oxides and active sites of the protein [21]. Molecular modeling and/or molecular modeling with molecular spectroscopy are tools for understanding the mechanism of interaction in many biological systems [22-25].

Molecular modeling with different levels of theory is needed to understand the mechanism of interaction between nano-scale materials and bacteria. Accordingly, molecular modeling calculations at B3LYP/LANL1DZ are utilized to study the mechanism of interaction between AgNPs and bacteria. A model amino acid molecule is chosen as a building block for protein structure representing bacteria. The interaction is described in terms of three important physical parameters, namely total dipole moment (TDM), HOMO/LUMO band gap energy and molecular electrostatic potential (ESP).

## 2. EXPERIMENTAL SECTION

All the studied structures are calculated with Gaussian 09 [26] program at Spectroscopy Department, National Research Centre, Egypt. B3LYP/LANL1DZ [27-29] model is utilized to calculate TDM, HOMO/LUMO band gap energy and mapping molecular ESP.

## 3. RESULTS SECTION

**3.1. Building model molecules.** Silver is proposed to be hydrated with 6 water molecules as shown in figure 1-a, to form silver hexahydrate ($Ag.6H_2O$). The model for protein structure is indicated as shown in figure 2-a as amino acid monohydrate. The interaction between $Ag.6H_2O$ and the model molecule of bacteria is supposed to take place through the hydrogen bonding of the

active site COOH or $NH_2$. For the interaction between $Ag.6H_2O$ and protein, there are two schemes tried in this work. The first scheme is through weak interaction while the second one is through complex interaction. Both interactions took place between $Ag.6H_2O$ and H of COOH as indicated in figures 3 and 4, and H of $NH_2$ as indicated in figures 5 and 6 respectively. Figure 3 presents the optimized structure of amino acid monohydrate and $Ag.6H_2O$ through COOH as an adsorbed state. Figure 4 presents the optimized structure of amino acid monohydrate and $Ag.6H_2O$ through COOH as a complex. Figure 5 presents the optimized structure of amino acid monohydrate and $Ag.6H_2O$ through $NH_2$ as an adsorbed state. Figure 6 presents the optimized structure of amino acid monohydrate and $Ag.6H_2O$ through $NH_2$ as a complex state.

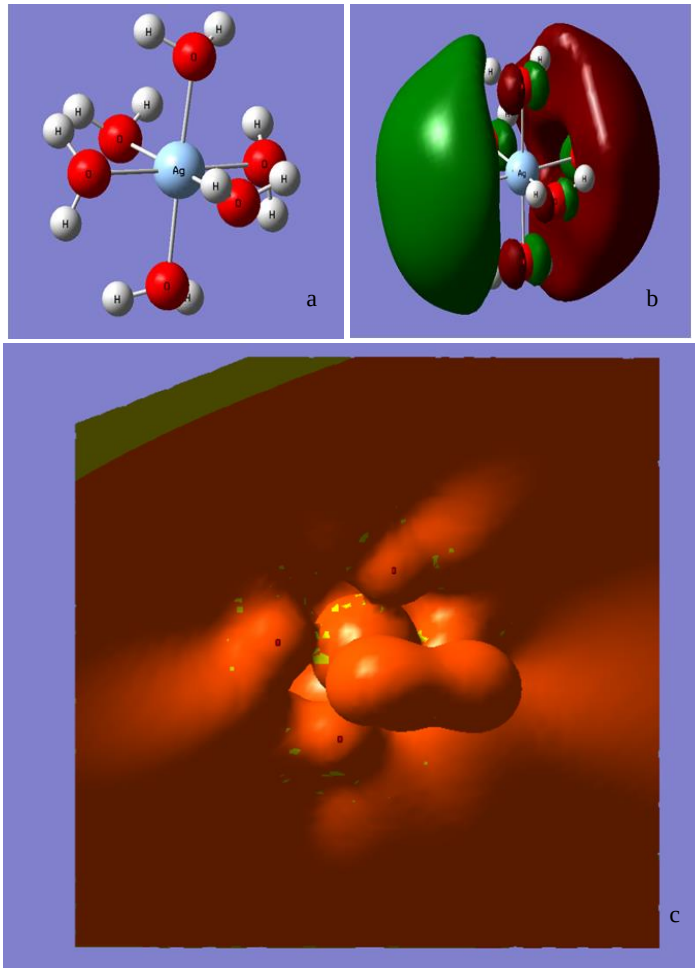


**Figure 1.** B3LYP/LANL1DZ optimized structure of a- $Ag.6H_2O$; b- HOMO/LUMO band gap energy of $Ag.6H_2O$ and c- Molecular electrostatic potential ESP of $Ag.6H_2O$.

**3.2. Calculated physical parameters.** In previous work, it is indicated that both TDM and HOMO/LUMO band gap energy are considered as indications for the chemical and biological reactivity of the chemical structure a given compound [30-31]. To describe a compound as reactive, its TDM is supposed to increase while its band gap energy is supposed to decrease.

Table 1 presents the B3LYP/LANL1DZ calculated TDM as Debye, HOMO/LUMO band gap energy as eV for the studied structures. Furthermore, HOMO/LUMO band gap energy for $Ag.6H_2O$; amino acid and the four model molecules of $Ag.6H_2O$/amino acid interactions are indicated in figures 1-b, 2-b. 3-b, 4-b, 5-b and 6-b respectively.

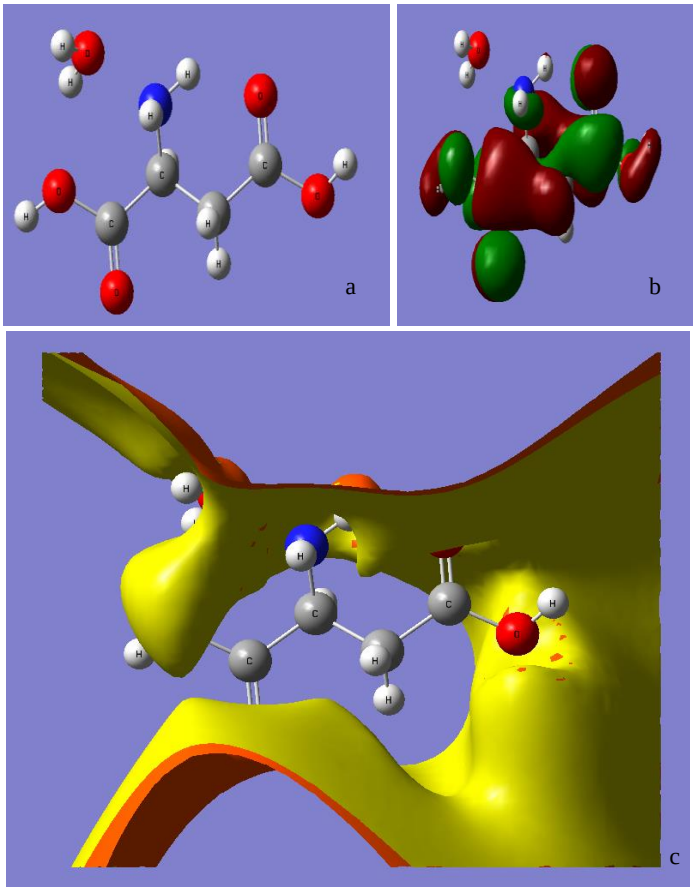


**Figure 2**. B3LYP/LANL1DZ optimized structure of a- amino acid monohydrate; b- HOMO/LUMO band gap energy of amino acid monohydrate and c molecular electrostatic potential ESP of amino acid monohydrate.

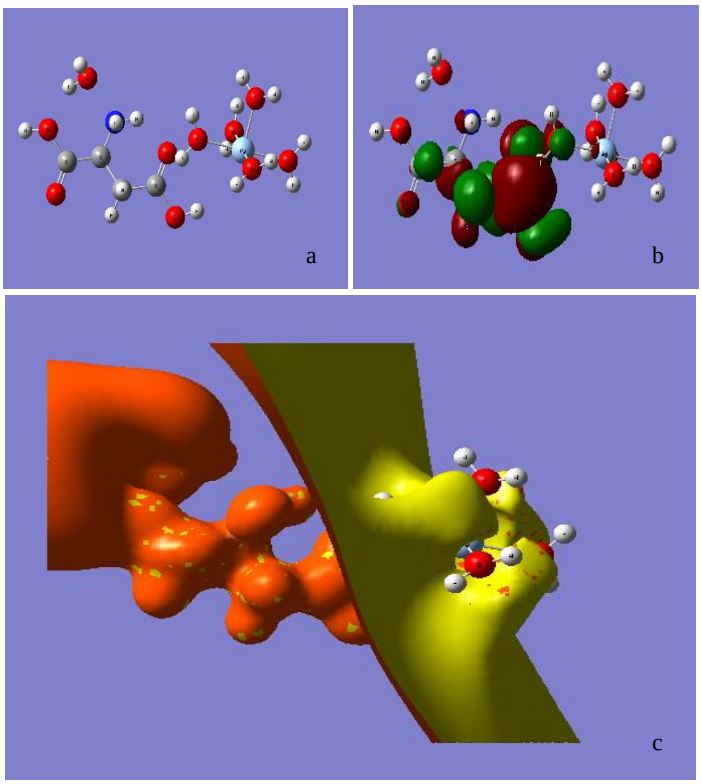


**Figure 3**. B3LYP/LANL1DZ optimized structure of a- amino acid monohydrate/$Ag.6H_2O$; b- HOMO/LUMO band gap energy of amino acid monohydrate/$Ag.6H_2O$ and c- molecular electrostatic potential ESP of amino acid monohydrate/$Ag.6H_2O$. The interaction took place through COOH as adsorb state.

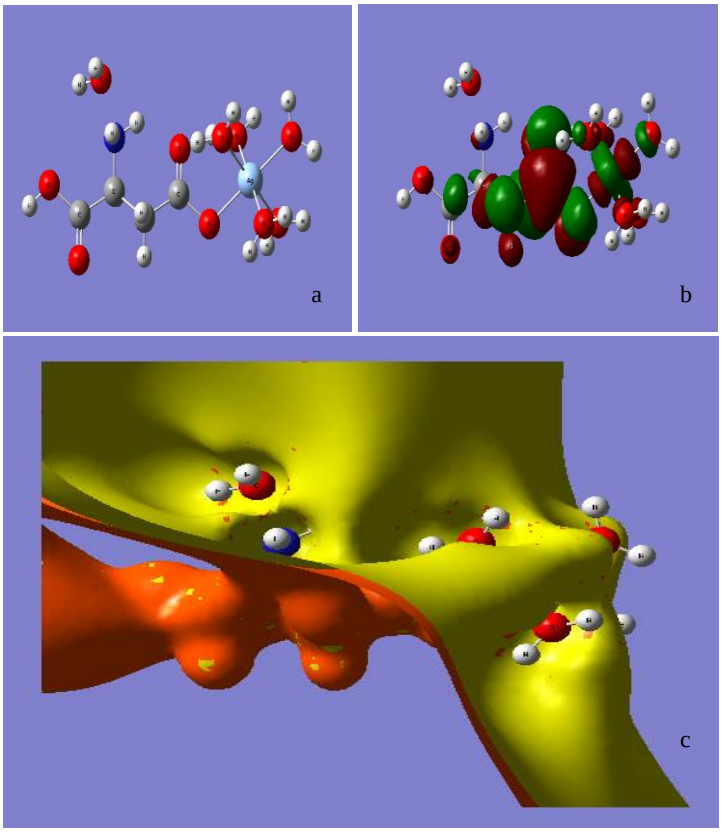


**Figure 4**. B3LYP/LANL1DZ optimized structure of a- amino acid monohydrate/Ag.6$H_2O$; b- HOMO/LUMO band gap energy of amino acid monohydrate/Ag.6$H_2O$ and c- molecular electrostatic potential ESP of amino acid monohydrate/Ag.6$H_2O$. The interaction took place through COOH as complex.

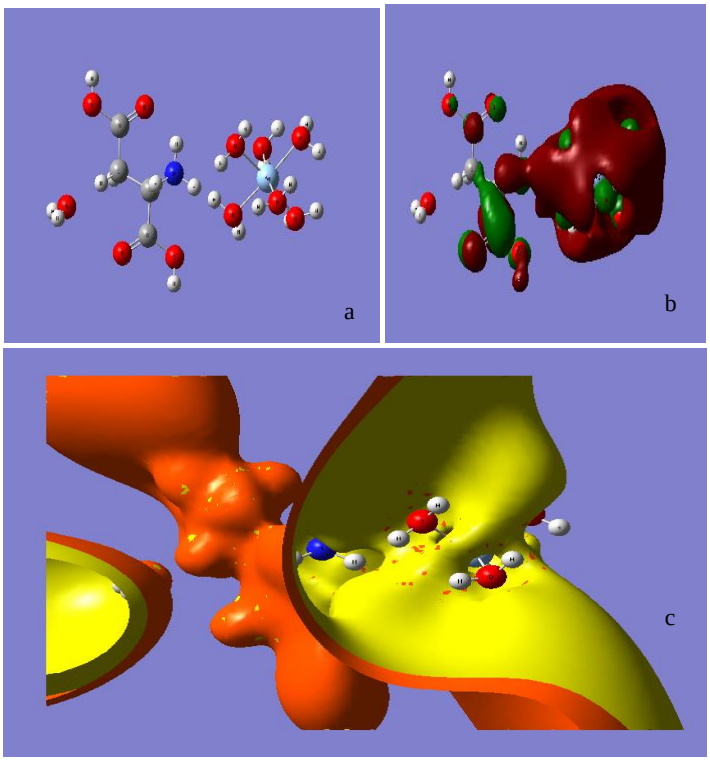


**Figure 5**. B3LYP/LANL1DZ optimized structure of a- amino acid monohydrate/ Ag.6$H_2O$; b- HOMO/LUMO band gap energy of amino acid monohydrate/Ag.6$H_2O$ and c- molecular electrostatic potential ESP of amino acid monohydrate/Ag.6$H_2O$. The interaction took place through $NH_2$.

As listed in table 1, Ag.6$H_2O$ has a TDM of 1.2037 Debye and band gap energy of 1.0555 eV. Amino acid is hydrated with one water molecule to form amino acid monohydrate which has a TDM of 1.4673 Debye and band gap energy of 2.0376 eV. As amino acid monohydrate and Ag.6$H_2O$ are interacted as an adsorb state through COOH, the TDM is increased to 5.3929 Debye while the band gap energy is decreased to 0.6144 eV. The same interaction took place as a complex with the release of OH group. The TDM is increased to 9.2151 Debye while the band gap energy is 1.9100 eV. Although the adsorbed state shows a lower band gap energy, the complex state shows a higher TDM. This indicates that the two schemes could take place for the interaction through COOH.

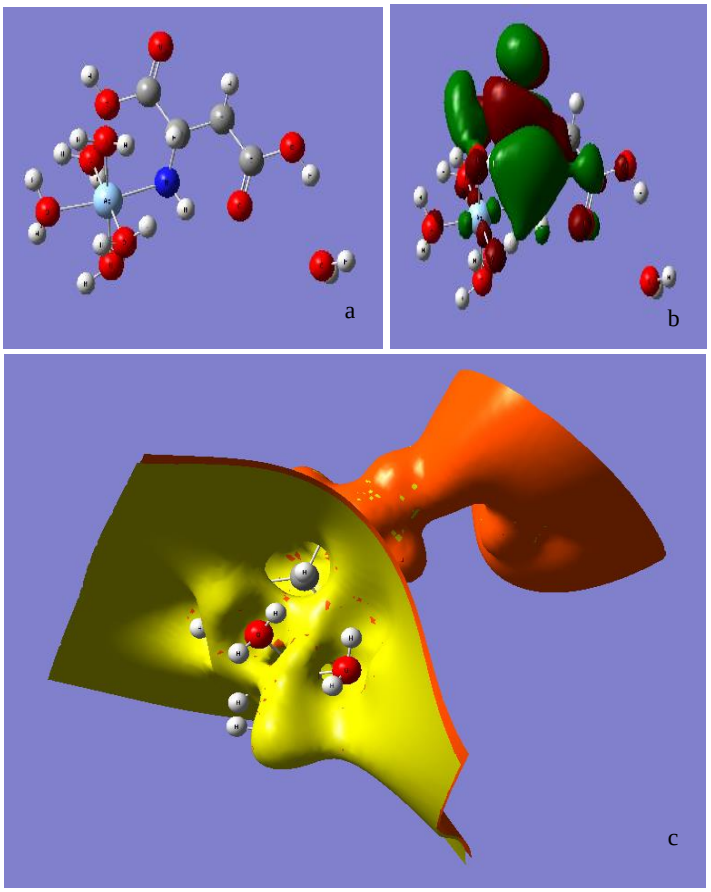


**Figure 6**. B3LYP/LANL1DZ optimized structure of a- amino acid monohydrate/ Ag.6$H_2O$; b- HOMO/LUMO band gap energy of amino acid monohydrate/Ag.6$H_2O$ and c- molecular electrostatic potential ESP of amino acid monohydrate/Ag.6$H_2O$. The interaction took place through $NH_2$ as a complex state.

When amino acid monohydrate is interacted with Ag.6$H_2O$ through $NH_2$ as adsorb state, the TDM measured 4.1538 Debye while the band gap energy measured 0.6746 eV. The interaction is then tried as a complex state in which the TDM slightly increased to 5.1691 Debye and the band gap energy also slightly increased to 0.7287 eV.

**Table 1**. B3LYP/LANL1DZ calculated total dipole moment as Debye, HOMO/LUMO band gap energy as eV for the studied structures.

| Structure | Total dipole moment | Band gap energy |
|---|---|---|
| **Ag.6$H_2O$** | 1.2037 | 1.0555 |
| **Amino acid monohydrate** | 1.4673 | 2.0376 |
| **Amino acid monohydrate/Ag.6$H_2O$ (COOH) adsorb** | 5.3929 | 0.6144 |
| **Amino acid monohydrate/Ag.6$H_2O$ (COOH) complex** | 9.2151 | 1.9100 |
| **Amino acid monohydrate/Ag.6$H_2O$ ($NH_2$) adsorb** | 4.1538 | 0.6746 |
| **Amino acid monohydrate/Ag.6$H_2O$ ($NH_2$) complex** | 5.1691 | 0.7287 |

Further confirmation for the interaction of the studied structures is needed, therefore the molecular ESP is calculated at the same level of theory.

It is stated that molecular ESP is displayed as the charge distribution revolving around a given structure in space. It is considered very important for describing then understanding both the electrophilic and nucleophilic attack sites for biological recognition [32]. Molecular ESP in this sense is considered as a tool necessary for the description of hydrogen bonding interactions [33].

The mapping of molecular ESP for $Ag.6H_2O$, amino acid and the four model molecules of $Ag.6H_2O$/amino acid interactions are indicated in figures 1-c, 2-c. 3-c, 4-c, 5-c and 6-c respectively.
To describe the figures of ESP, the values of the ESP at the studied surface are represented by colors. Potential is increased according to the following increasing orders:
red < orange < yellow < green < blue.

Blue is corresponding to the highest ESP energy and red indicates the lowest ESP energy [34]. In this sense as well, the intermediate colors represent intermediate ESP. As indicated in the mapping of ESP, the negative regions are mainly around the oxygen which is considered as sites for electrophilic attacks. On the other hand, the positive region is localized over the silver indicating that these sites are the more probable for nucleophilic attacks. These data are in good agreement with those presented in the last section for both TDM and HOMO/LUMO band gap energy, suggesting that $Ag.6H_2O$ is an active surface for interaction with protein throughout COOH and/or $NH_2$, with the interaction through $NH_2$ being the most probable. Data revealed that interaction between AgNPs and model molecule for bacteria increased indicating increasing the interaction with the surrounding molecules. If the interaction of AgNPs with bacteria is described as interaction with the active sites COOH and $NH_2$, the complex formation is blocking it, with the release of OH. Additionally, the adsorbed state inhibits the active site from making further interaction through it. While increasing TDM with decreasing band gap energy indicates that there is an increase in the ability of the structure for further interactions with the surrounding molecules. To understand this, it could be an indication for the possibility of degradation of protein as a result of future interactions with the surrounding media in the existence of water molecules.

## 4. CONCLUSIONS

Correlating both results, one can conclude that the interaction between silver and bacteria is more likely through the hydrogen bonding of $NH_2$ group. If the interaction is through complex state OH is released as a result of the interaction.

The TDM, HOMO/LUMO band gap energy, and molecular ESP results indicate that interaction between AgNPs and model molecule for bacteria increased the reactivity which may lead to the possible degradation due to the high rate of interaction. This is indicated through the higher TDM, lower band gap energy and high surface area with unique surface properties based on active sites indicated by molecular ESP mapping. The possible degradation of the model molecule under the influence of AgNPs could be further verified in the future with another molecular modeling study.

## 5. REFERENCES


[1] Gribbin J., Gribbin M., Richard Feynman: A Life in Science, *Dutton*, 170, 0452-2763, 1-4. **1997**.

[2] Papazoglou E.S., Parthasarathy A., Synthesis Lectures on Biomedical Engineering, *BioNanotechnology*, 2, 1-139, **2007**.

[3] Veissi Z., Afshar D., Ranjbar R., Shirazi M., Rezaei F., Mahboobi R., colleagues., Antimicrobial properties of ZnO nanoparticles, *J MDPI Tropical Med*, 17, 59, 1-4, **2012**.

[4] Bahnemann D.W., Kormann C., Hoffmann M.R., Preparation and characterization of quantum size zinc oxide: a detailed spectroscopic study, *J Phys Chem*, 91, 14, 3789-3798, **1987**.

[5] Schmid G., Large clusters and colloids – Metals in the embryonic state, *Chem Rev*, 92, 8, 1709-1727, **1992**.

[6] Alivisatos A.P., Perspectives on the physical chemistry of semiconductor nanocrystals, *J Phys Chem*, 100, 31, 13226-13239, **1996**.

[7] Gong P., Li H., He X., Wang K., Hu J., Tan W, e.a., 2007. preparation and antibacterial activity of Fe and Ag nanoparticles, *Nanotechnology*, 18, 604-611, **2007**.

[8] Oberdörster G., Oberdörster E., Oberdörster J., Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles, *Environmental health perspectives*, 113, 823, **2005**.

[9] Knetsch M., Koole L., New strategies in the development of antimicrobial coatings: the example of increasing usage of silver and silver nanoparticles, *Polymers-Basel*, 3, 340-366 **2011**.

[10] Antony J., Nivedheetha M., Siva D., Pradeepha G., Kokilavani P., Kalaiselvi S., Sankarganesh A., Balasundaram A., Masilamani V., Achiraman S., Antimicrobial activity of *Leucas aspera* engineered silver nanoparticles against *Aeromonas hydrophila* in infected Catla catla, *Colloid Surface B*, 109, 20-24, **2013**.

[11] Mahanty A., Mishra S., Bosu R., Maurya U., Netam S., Sarkar B., Phytoextracts-synthesized silver nanoparticles inhibit bacterial fish pathogen *Aeromonas hydrophila*, *Indian J Microbiol*. 53, 438-446, **2013**.

[12] Velmurugan P., Iydroose M., Lee S., Cho M., Park J., Balachandar V., Oh B., Synthesis of silver and gold nanoparticles using cashew nut shell liquid and its antibacterial activity against fish pathogens, *Indian J Microbiol*, 54, 196-202 **2014**.

[13] Zhiya S., Yang L., Potential impacts of silver nanoparticles on bacteria in the aquatic environment, *J Environ Manage*, 191, 290-296, **2017**.

[14] Zhiya S., Joy D.V-N., Jizhong Z., Yang L., Contradictory effects of silver nanoparticles on activated sludge wastewater treatment, *J Hazard Mater*, 341, 448-456, **2018**.

[15] Salomoni R., Léo P., Montemor A.F., Rinaldi B.G., Rodrigues M.F.A., Antibacterial effect of silver nanoparticles in Pseudomonas aeruginosa, *Nanotechnol Sci Appl*., 10, 115–121, **2017**.

[16] Durán N., Durán M., de Jesus M., Seabra A., Fávaro W., Nakazato G., Silver nanoparticles: a new view on mechanistic aspects on antimicrobial activity, *Nanomed-Nanotechnol*., 12, 789-799 **2016**.

[17] Mosselhy D., Abd El-Aziz M., Hanna M., Ahmed M., Husien M., Feng Q., Comparative synthesis and antimicrobial action of silver nanoparticles and silver nitrate, *J Nanopart Res*., 17, 473-482, **2015**.

[18] Rai M.K., Deshmukh S.D., Ingle A.P., Gade A.K., Silver nanoparticles: the powerful nanoweapon against multidrug-resistant bacteria, *J Appl Microbiol.*, 112, 5, 841-852, **2012**.

[19] Dakal T.C., Kumar A., Majumdar R.S., Yadav V., Mechanistic Basis of Antimicrobial Actions of Silver Nanoparticles, *Front Microbiol*., 7, 1831, **2016.**

[20] Tang S., Zheng J., Antibacterial Activity of Silver Nanoparticles: Structural Effects, *Adv Healthc Mater*., 7, 13, 1701503, **2018**.

[21] Sabry N.M., Tolba S., Abdel-Gawad F.K., Bassem S.M., Nassar H., El-Taweel G.E., Ibrahim M., On the Molecular Modeling Analyses of the Interaction between Nano Zinc Oxide and Bacteria, *Biointerface Research in Applied Chemistry*, 8, 3, 3294 -3297, **2018**.

[22] Mahmoud A.A., Osman O., Elhaes H., Ferretti M., Fakhry A., Ibrahim M.A., Computational Analyses for the Interaction Between Aspartic Acid and Iron, *J Comput Theor Nanosci*, 15, 470–473, **2018**.

[23] Abdel-Gawad F.K., Osman O., Bassem S.M., Nassar H.F., Temraz T.A., Elhaes H., Ibrahim M., Spectroscopic Analyses and Genotoxcity of Dioxins in the Aquatic Environment of Alexandria, *Marine Pollution Bulletin*, 127, 618-625, **2018**.

[24] Galal A.M.F, Shalaby E.M., Abouelsayed A., Ibrahim M.A., Al-Ashkar E., Hanna A.G., Structure and absolute configuration of some 5-Chloro-2-methoxy-N-phenylbenzamide derivatives, *Spectrochim Acta A.*, 188, 213-221, **2018**.

[25] Purwidyantri A., Chen C.H., Chen L.Y., Chen C.C,, Luo J.D., Chiou C.C., Tian Y.C., Lin C.Y., Yang C.M., Lai H.C., Lai C.S., Speckled ZnO Nanograss Electrochemical Sensor for Staphylococcus epidermidis Detection, *J Electrochem Soc*, 164, 6, 205-211, **2017**.

[26] Gaussian 09, Revision C.01, Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Mennucci B., Petersson G.A., Nakatsuji H., Caricato M., Li X., Hratchian H.P., Izmaylov A.F., Bloino J., Zheng G., Sonnenberg J.L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J.A., Peralta Jr.J.E., Ogliaro F., Bearpark M., Heyd J.J., Brothers E., Kudin K.N., Staroverov V.N., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J.C., Iyengar S.S., Tomasi J., Cossi M., Rega N., Millam N.J., Klene M., Knox J.E., Cross J.B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Martin R.L., Morokuma K., Zakrzewski V.G., Voth G.A., Salvador P., Dannenberg J.J., Dapprich S., Daniels A.D., Farkas Ö., Foresman J.B., Ortiz J.V., Cioslowski J., Fox D.J., Gaussian, Inc., *Wallingford* CT, **2010**.

[27] Becke A.D., Density functional thermochemistry. III. The role of exact exchange, *Chem. Phys*., 98, 5648, **1993**.

[28] Lee C., Yang W., Parr R.G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B*., 37, 2, 785, **1988**.

[29] Miehlich B., Savin A., Stoll H., Preuss H., Results obtained with the correlation energy density functionals of becke and Lee, Yang and Parr, *Chem. Phys. Lett*., 157, 3, 200, **1989**.

[30] Ibrahim M., El-Haes H., Computational Spectroscopic Study of Copper, Cadmium, Lead and Zinc Interactions in the Environment, *Int. J. Environ. Pollut*., 23, 417-424, **2005**.

[31] Ibrahim M., Mahmoud A.A., Computational Notes on the Reactivity of some Functional Groups, *J. Comput. Theor. Nanosci*., 6, 1523–1526, **2009**.

[32] Politzer P., Laurence P.R., Jayasuriya K., Molecular electrostatic potentials: an effective tool for the elucidation of biochemical phenomena, *Environmental health perspectives*, 61, 191, **1985.**

[33] Politzer P., Murray J.S., Molecular Electrostatic Potentials: Concepts and Applications, *J Theor Comput Chem*, 3, 649, **1996**.

[34] Şahin Z.S., Şenöz H.I., Tezcan H., Büyükgüngör O., Synthesis, spectral analysis, structural elucidation and quantum chemical studies of (E)-methyl-4-[(2-phenylhydrazono)methyl]benzoate, *Spectrochim. Acta A*, 143, 91, **2015**.