# Understanding the adsorption interaction between Hg(II) and nano zinc oxide: A theoretical study

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**ABSTRACT**

The adsorption of mercuric ions ($Hg^{2+}$) on nano zinc oxide (ZnO-NPs) structure was studied using the Monte Carlo simulation and the density functional theory (DFT) methods. The obtained results have shown that the adsorption process is thermodynamically favorable. The mercuric ions are strongly adsorbed on the ZnO-NPs structures due to the formation of the chemical bonds resulted from the positive overlap between *p*-orbitals of the adsorbate species and the *p*-orbitals of the zinc atoms in the structure of ZnO-NPs.

## 1. Introduction

Environmental pollution induced by heavy metals released from industrial production has become a serious worldwide concern over the past few decades. Heavy metals are dangerous to the ecology and human health even at low concentration because they are not biodegradable and can be accumulated in the living organisms. Among the heavy metals, mercury is a widespread environmental pollutant and exhibits high degreee of toxicity. The potential sources of mercury ions in wastewater include hydroelectric, mining, manufactoring pigments and paper industries [1]. Nowadays, numerous methods such as ion exchange, chemical precipitation, adsorption, membrane filtration, electrodeposition and etc. have been used for the removal of heavy toxic metal ions, in particular, mercuric ions ($Hg^{2+}$) in the wastewater [2]. Among these methods, adsorption is recognized as an effective and economic method due to its flexibility in design, easy operation and low cost. Several adsorption materials are used for removal of heavy metal ions from solution including activated carbon [3,4], zeolites [5,6], bentonite [7], agricultural and biological waste [8,9] and etc. Inherent disadvantages of these materials are their low capacities and small selectivity. In recent years, researchers have been focused on the novel adsorbents – nanomaterials. At nanoscale, materials show unique characteristics and possess a large surface area. Variety of nanomaterials such as carbon nanotubes [10], $TiO_2$[11], $Fe_2O_3$ [12] and etc. have been investigated for their application towards the removal of toxic metals. Recently, some studies have showed that ZnO nanoparticles (ZnO-NPs) could be used as an effective adsorbent for adsorption of heavy metal ions from solutions. Seela *et al.* [13] has showed that the $Zn^{2+}$, $Cd^{2+}$ and $Hg^{2+}$ adsorption capacities of ZnO-NPs at 303 K and pH = 5.5 are significantly higher than these of activated carbon and have been determined to be 357, 384 and 714 mg $g^{-1}$, respectively. Compared to other nanostructured materials, ZnO-Nps also exhibit higher ability to absorb heavy metal ions. The adsorption capacities of $Cd^{2+}$ on nano ZnO, nano $TiO_2$, nano $Fe_2O_3$ are determined to be 119.1; 53.5 and 71.4 mg $g^{-1}$, respectively [14]. In addition, it is reported that ZnO-Nps are capable of adsorbing heavy metals from solution containing several ions such as ($Cd^{2+}$, $Cu^{2+}$, $Ni^{2+}$) [14].

Although a number of experimental works have shown that ZnO nanomaterials are effective materials for removal heavy metal ions, the theoretical study on the nature and the adsorption mechanisms of positively charged metal ions on ZnO-Nps is still quite rare.

The purpose of this work is to study the adsorption process of mercuric ions ($Hg^{2+}$) on the nanostructured ZnO, figure out the interaction between the adsorbate and the adsorbent using computational methods.

## 2. Models and Computational Methods

### 2.1. Models

In the previous theoretical studies related to the electronic structure and gas sensing properties of ZnO-NPs, variety of models of the nanosystem has been used such as: ZnO clusters, ZnO nanowires, ZnO nanotubes, ZnO nanosheets or bulk crystal [15,16].
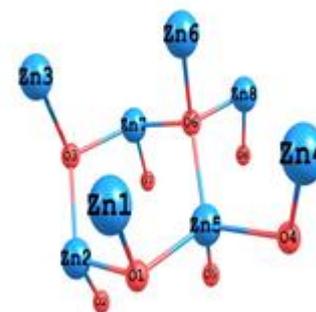


**Figure 1. The model of the ZnO-NPs and the schematic numbering of the atoms.**

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In this work, the model of nano ZnO has been constructed based on the bulk crystal structure of the wurtzite ZnO, which is one of the most stable form of ZnO. The model containing 8 zinc atoms and 8 oxygen atoms is presented in Figure 1.

## 2.2. Computational methods

The adsorption process of $Hg^{2+}$ was studied in two steps: i) The Monte Carlo (MC) simulation was used to generate adsorbed configurations according to a statistical mechanical ensemble. Here, the forces acting on the adsorbte molecules are mainly electrostatic and van de Waals (vdW) forces considerable from relatively far distances. In this first step, the adsorption process is initially considered as physisorption. In the MC simulation computations the Universal forcefield was used. The number of cycles was 5 and the number of steps per cycle was 50000. The electrostatic forces were calculated via group-based truncation method, while the vdW interactions were included via atom-based truncation method with cutoff distance is 12.5 Å; ii) The adsorbded configurations with the minimum energies obtained from MC simulation were subsequently optimized using density functional theory (DFT) in the generalized gradient approximation (GGA). The Perdew, Burke, and Ernzerhof (PBE) gradient-corrected functional [17] was used to calculate the exchange correlation energy. The double numerical plus d-function (DND) basis set was used for valence electrons, while core electrons are 'frozen' in their atomic state by using norm-conserving pseudo-potentials. The equilibrium structures were performed when the forces acting on the dynamic atoms all were smaller than 0.004 Ha/Å.

The adsorption energy ($E_{ads}$) was defined as:

$$E_{ads} = E_{adsorbate-substrate} - (E_{adsorbate} + E_{substrate})$$

$E_{ads}$ is an important criterion to estimate the adsorption ability of the adsorbent ZnO-NPs. Additionally, a significant change in the distance between atoms attributed to the charge transfer between the atoms was analyzed. Moreover, to evaluate the interation between adsorbate and adsorbent, the Mayer bond orders were also discussed.

## 3. Results and Discussion

From MC simulation calculations we obtained several preferred adsorbed configurations. After optimization we got three configurations which have structures illustrated on Figure 2.
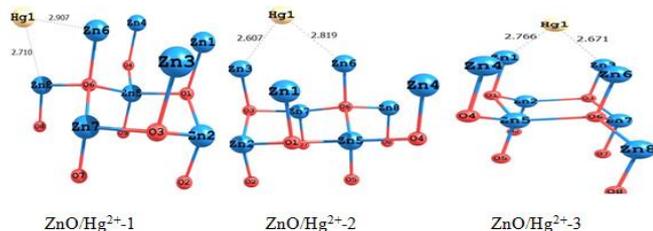


**Figure 2. The optimized adsorbed structures of $Hg^{2+}$ on ZnO-NPs.**

The calculated adsorption energies corresponding to the formation of the adsorbed configurations and the minimum distance from the adsorbate to the adsorbent are presented in Table 1.

**Table 1. The calculated parameters for $Hg^{2+}$/ZnO adsorbed configurations.**

| Configurations | $E_{ads}$, kJ.mol$^{-1}$ | $d_{min}$, Å |
|---|---|---|
| $Hg^{2+}$/ZnO-1 | -637.76 | 2.710 |
| $Hg^{2+}$/ZnO-2 | -645.29 | 2.607 |
| $Hg^{2+}$/ZnO-3 | -652.09 | 2.671 |

For all cases, the $E_{ads}$ values are very negative which demonstrate that the adsorption process of $Hg^{2+}$ on ZnO-NPs is thermodynamically favorable. The most prefered adsorption site is where $Hg^{2+}$ interacts with two zinc atoms in the same layer: Zn3-Zn6 atoms in $Hg^{2+}$/ZnO-2 and Zn3-Zn1 atoms in $Hg^{2+}$/ZnO-3 configurations. The minimum distance from adsorbate molecule to the adsorbent is determenided to be equal to the distance from $Hg^{2+}$ ion to the Zn3 atom. In other words, the Zn3 atom may be considered as the most reactive site in the ZnO structure. This is confirmed by the calculated Fukui indices for the ZnO-NPs which are shown in Table 2.

**Table 2. Fukui indices for ZnO-NPs.**

| Atom | $f^-$ | Atom | $f^-$ | Atom | $f^-$ | Atom | $f^-$ |
|---|---|---|---|---|---|---|---|
| Zn1 | 0.110 | Zn3 | 0.139 | Zn5 | 0.005 | Zn8 | 0.071 |
| O1 | 0.020 | O3 | 0.022 | O5 | 0.069 | O8 | 0.080 |
| Zn2 | 0.038 | Zn4 | 0.125 | Zn6 | 0.107 | Zn7 | 0.035 |
| O2 | 0.071 | O4 | 0.051 | O6 | -0.005 | O7 | 0.063 |

Fukui indices are useful parameters to predict the reactive sites of a chemical compound. The positively charged mercury ion is a electrophile reagent. Thus, it will attack the atoms with the higher Fukui indices $f^-$. Clearly, from Table 2, these atoms are zinc atoms Zn1, Zn3, Zn4 and Zn6.

Further, to figure out the nature of the interaction between the $Hg^{2+}$ ions and the ZnO-NPs adsorbent, the population analysis is evaluated. The obtained results for the adsorbed configuration with the lowest adsorption energy ($Hg^{2+}$/ZnO-3) are summarized in Table 3.

**Table 3. The calculated charge on atoms (q, e) and the bond order between atoms of the ZnO-NPs and the $Hg^{2+}$/ZnO-3 systems.**

| Parameter | ZnO-NPs | $Hg^{2+}$/ZnO-3 |
|---|---|---|
| q(Zn1), e | +0.545 | +0.539 |
| q(Zn3), e | +0.525 | +0.690 |
| BO$^*$(Zn1) | 1.31 | 1.50 |
| BO$^*$(Zn3) | 1.06 | 1.38 |

Notes: *- the total bond order of the atom with other atoms in the systems

There has been a significant change in the charge on Zn1 and Zn3 atoms before and after adsorption. In addition, the charge of mercuric ion is strongly reduced from +2 to +0.503. This fact denotes the electron transfer from the adsorbent to the adsorbate. Furthermore, the total bond order of Zn1 and Zn3 atoms with other atoms in the nanostructured ZnO increases from 1.31 and 1.06 to 1.50 and 1.38, respectively. In particular, the bond order between Zn1 atom and $Hg^{2+}$ is 0.38 and between Zn3 and $Hg^{2+}$ is 0.48. Consequently, the adsorption of mercuric ion on ZnO-NPs can be considered as chemisorption. To find out the characteristic of the bond formed between the zinc atoms and the mercuric ion, we have analyzed the component of the molecular orbitals of the $Hg^{2+}$/ZnO-3 adsorbed configuration (see Figure 3)
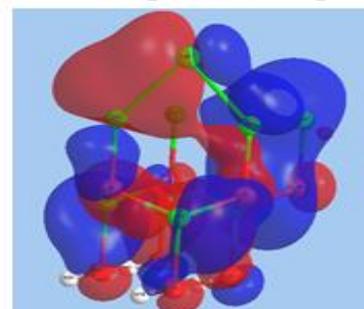


**Figure 3. The HOMO-26 orbital of the $Hg^{2+}$/ZnO-3 at isovalue 0.008 au.**

The expression of the wave function corresponding to this orbital is:

$\Psi = 0.13\ p_y\ (Zn3) - 0.13\ p_x\ (Zn3) - 0.11\ p_z(Hg1) - 0.11\ p_y(Hg1) + 0.06\ p_x\ (Zn1) - 0.06\ p_z\ (Zn3) + \sum C_i\Phi i$

where $C_i$ is the coefficient of other atomic orbitals $\varphi_i$ and $C_i < 0.06$.

Clearly, p-orbitals of $Hg^{2+}$ atom positively overlap with the p-orbitals of zinc atoms in the nanostructured ZnO-NPs resulting in formation of bonds between $Hg^{2+}$ and ZnO-NPs. This is in a good agreement with the above mentioned discuss according to that the adsorption of $Hg^{2+}$ on ZnO-NPs is chemical in nature.

## 4. Conclusion

In this work, Monte Carlo simulation and Density functional theory methods were performed to investigate the adsorption of mercuric ions on nanostructured ZnO-NPs. The calculated results show that the adsorbing process is thermodynamically favorable and can be considered as chemisorption. The bonds between $Hg^{2+}$ and ZnO-NPs are result of the overlaps between p-orbitals of the adsorbate atom and zinc atoms. This work will be helpful to understand the mechanism of adsorption of mercuric ion on nano zinc oxide and to design new materials that have higher heavy metal adsorption abilities.

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