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Comparative study of Zn(II) and Cd(II) ions adsorption on charged carbon nano tubes: molecular dynamics approach

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Abstract A comparative study was performed on adsorption process of Zn(II) and Cd(II) ions using charged carbon nano tubes (CNTs). The results show that the adsorption behavior of Zn(II) and Cd(II) ions have different patterns. To understand the reason for this difference, the ion–water complex properties and the reduced density of water around CNT were studied. The results reveal that the water molecules make high-, low-, and bulk regions around CNTs, which can affect the ion movement toward CNT. The ion–water complex characteristics during the adsorption demonstrated that the Cd(II)–water complex has a large number of exchange events between 4 and 8 coordinate numbers where Zn(II) has only 6 coordinate numbers during the adsorption process. The Cd(II)–water complex was found less stable and therefore has faster translational dynamics. These properties help cadmium ion to be adsorbed faster into CNT despite its heavier weight.

Keywords Molecular dynamics simulation · Adsorption · Zinc ion · Cadmium ion · Carbon nanotubes

1 Introduction

Carbon nano tubes (CNTs) have received great attention for their application in adsorption process. The investigations have approved that CNTs can be used in adsorption and storage process of hydrogen and methane (Kostov et al. 2002; Schimmel et al. 2003; Shokri et al. 2007), carbon dioxide and monoxide (Alexiadis and Kassinos 2008; Gu et al. 2008), natural organics (Lu and Su 2007), DNA (Lv 2011), hydrocarbons (Wesołowski et al. 2011) and many other materials.

During the recent years, many experimental investigations have shown that one of the most interesting applications of CNTs is the adsorption of heavy metal ions. CNTs have shown good ability in adsorption of heavy metal ions as Cd^{2+} (Gao et al. 2009; Wang et al. 2010; Li et al. 2003; Liang et al. 2004), Cu^{2+} (Gao et al. 2009; Wang et al. 2010; Li et al. 2003; Chen et al. 2009; Pyrzynska and Bystrzejewski 2010; Vukovic et al. 2010), Ni^{2+}(Gao et al. 2009; Liang et al. 2004; Lu and Chiu 2006; Chen and Wang 2006), and Zn^{2+}(Chen and Wang 2006; Lu and Liu 2006; Ansari Dezfoli et al. 2012). Experimental investigations show that many parameters like solution pH, ion properties and CNT characteristics can change the adsorption properties (Ansari Dezfoli et al. 2012; Shamspur and Mostafavi 2009; Pillay et al. 2009; Sheng et al. 2010; El-Sheikh et al. 2010) but, in order to fully understand the adsorption process of heavy metal ions on CNT, some analytical methods are necessary. In our previews works (Ansari Dezfoli et al. 2012; Ansari et al. 2013), we used molecular dynamics simulation in order to describe the adsorption of Zn(II) ion in an aqueous solution using charged CNT. This paper is an extension of our previews works, employing molecular dynamic simulation to make a comparison between the adsorption process of Zn(II), and Cd(II) ions from water using charged CNT. The selection of Zn(II), and Cd(II) was due to the difference in their atomic mass and radius. The analysis of these results helps to understand the dynamic properties of heavy metal ions adsorbed on the CNT.

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Table 1 Parameters used in modeling interaction energy

Symbol	Unit	Value
SPC model water molecules (DAngelo et al. 2008)		
r_{OH}	(nm)	1.0
θ_{HOH}	(^{o})	113
ε_{OO}	(kcal/mol)	0.15
σ_{OO}	(nm)	0.315
ε_{HH}	(kcal/mol)	0.0
σ_{HH}	(nm)	0.0
q_O	Electron unit	−0.82
q_H	Electron unit	0.41
k^{bond}	(kcal/(mol $\dot{A}^2$))	529.58
k^{angle}	(kcal/mol rad^2)	38.0
CNT (Ansari Dezfoli et al. 2012)		
ε_{CC}	(kcal/mol)	3.4
σ_{CC}	(nm)	0.055
q_C	Electron unit	CNT(I) = −0.01 CNT(II) = −0.02
Metal ions		
ε^a_{Zn-Zn}	(kcal/mol)	0.0125
σ^a_{Zn-Zn}	(nm)	1.96
q_{Zn}	Electron unit	+2
ε_{Cd-Cd} (Johnson et al. 2006)	(kcal/mol)	0.047
σ_{Cd-Cd} (Johnson et al. 2006)	(nm)	2.75
q_{Cd}	Electron unit	+2

[a] AMBER force field

2 Simulation details and potential models

The simulation was carried out using an in-house computer program written in FORTRAN language. A system consisting of one cadmium or zinc ion, water molecules, and a (4,4) charged CNT was considered. The CNT location was fixed during the simulation time. The length of CNT was 24.7 $\dot{A}$ and its diameter was 5.5 $\dot{A}$. It was located in the center of a periodic computational box with dimensions of $24.7 \times 24.7 \times 24.7\ \dot{A}^3$. This CNT was made of 160 carbon atoms having the charge of −0.01e or −0.02e where in this paper were named CNT(I) and CNT(II) respectively.

The MD code runs 5×10^4 times for either CNT(I) or CNT(II). The first 5×10^3 times assign to guarantee equilibrium condition between ion, water molecules, and CNT. In equilibrium condition, the interaction between CNT and ion is not considered. The next iterations are used to calculate the adsorption properties.

The equation of motion was applied on the system in the Cartesian coordinate:

$$m_i \ddot{r}_i = F_i \tag{1}$$

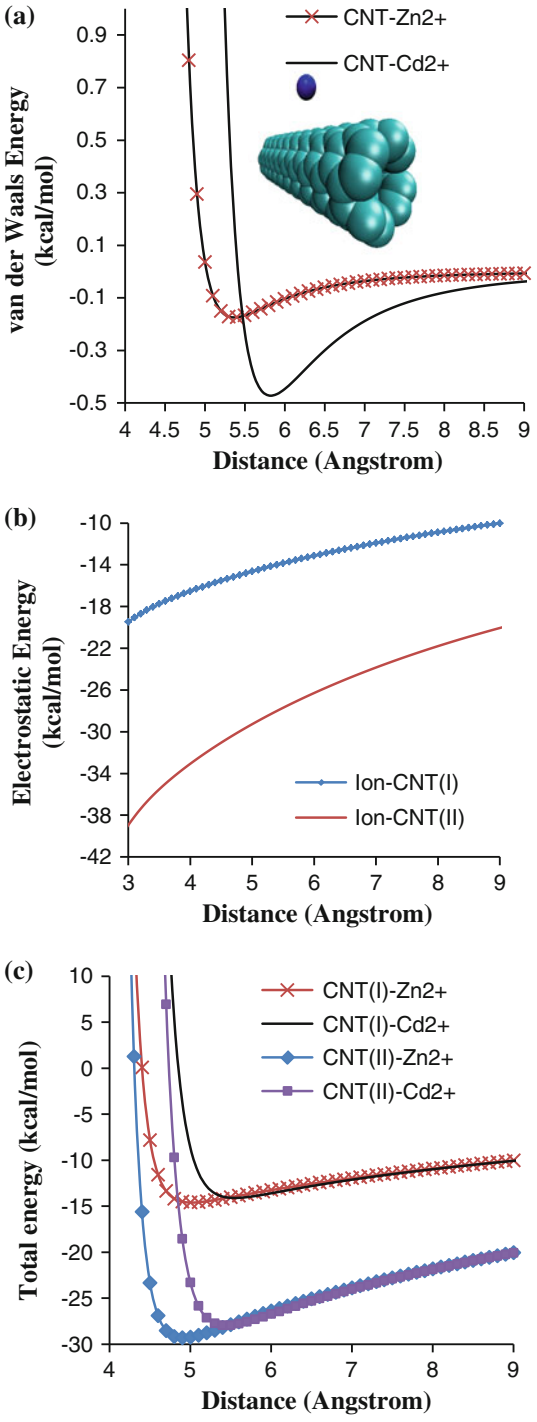

Fig. 1 Interaction energy between metal ions and CNT

where m_i is the mass of ion or molecule I, and F_i is the force acting on ion or molecule i defined as (Allen and Tildesley 1987):

$$F_i = -\frac{\partial}{\partial r} U \tag{2}$$

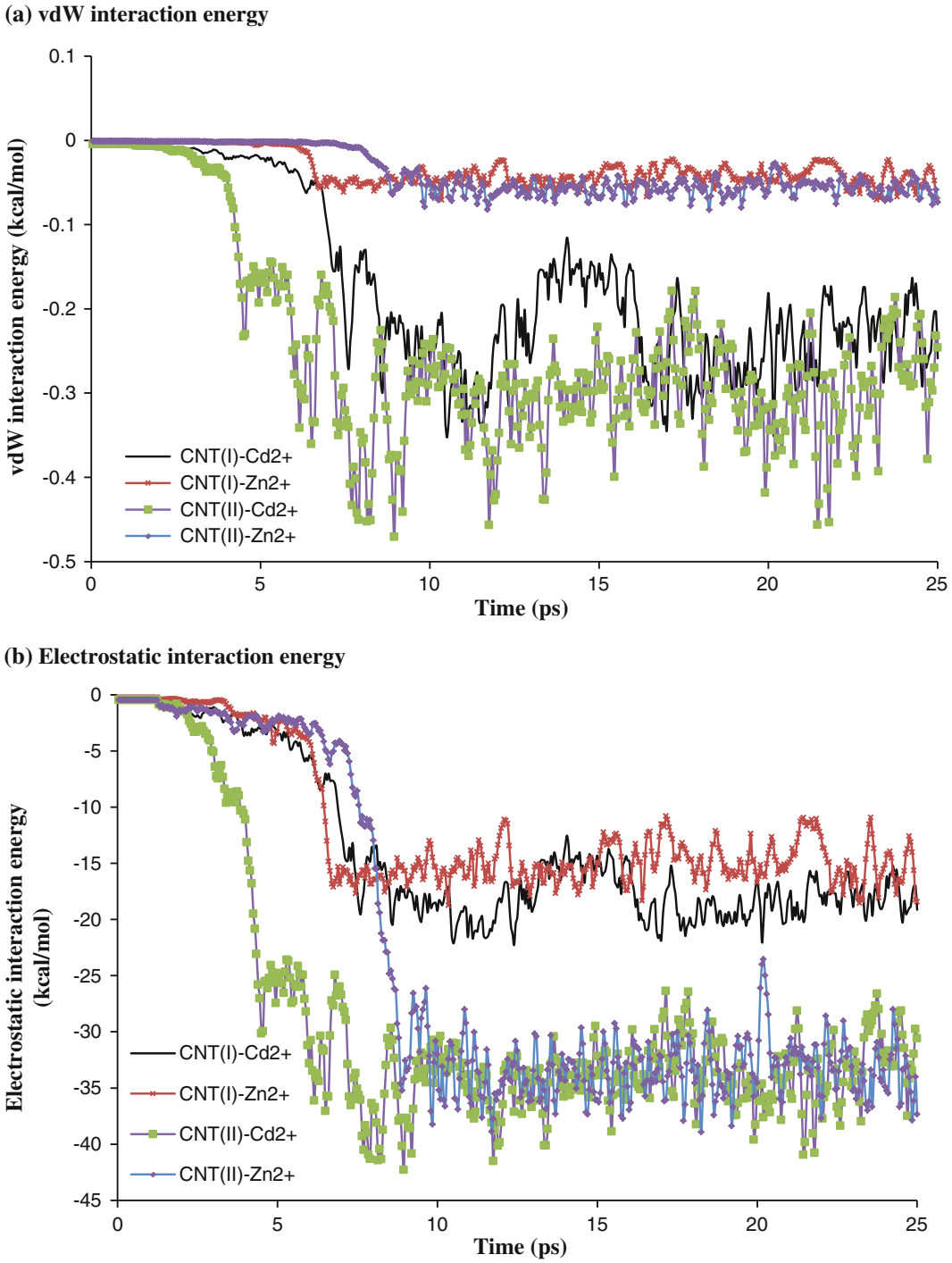

Fig. 2 The interaction energies between CNT and ion

U is the interactions potential. In this paper, we choose the flexible SPC model for water molecules. The interaction potential for flexible SPC model is expressed as follows:

$$U_{Total} = U_{bond} + U_{angle} + U_{vdw} + U_{coulomb} \tag{3}$$

where U_{bond}, and U_{angle} are the bond strength and angle bending energy, respectively. They are defined as (Allen and Tildesley 1987):

$$U_{bond} = \sum_{bond} K^{bond}\left(r_{O-H} - r_{O-H}^{eq}\right)^2 \tag{4}$$

$$U_{angle} = \sum_{angle} K^{angle}\left(\theta_{H-O-H} - \theta_{H-O-H}^{eq}\right)^2 \tag{5}$$

where k_i is the (bond or angle) force constant, $r_{O-H}$is the bond length, r_{O-H}^{eq} is the equilibrium bond length, θ_{H-O-H}

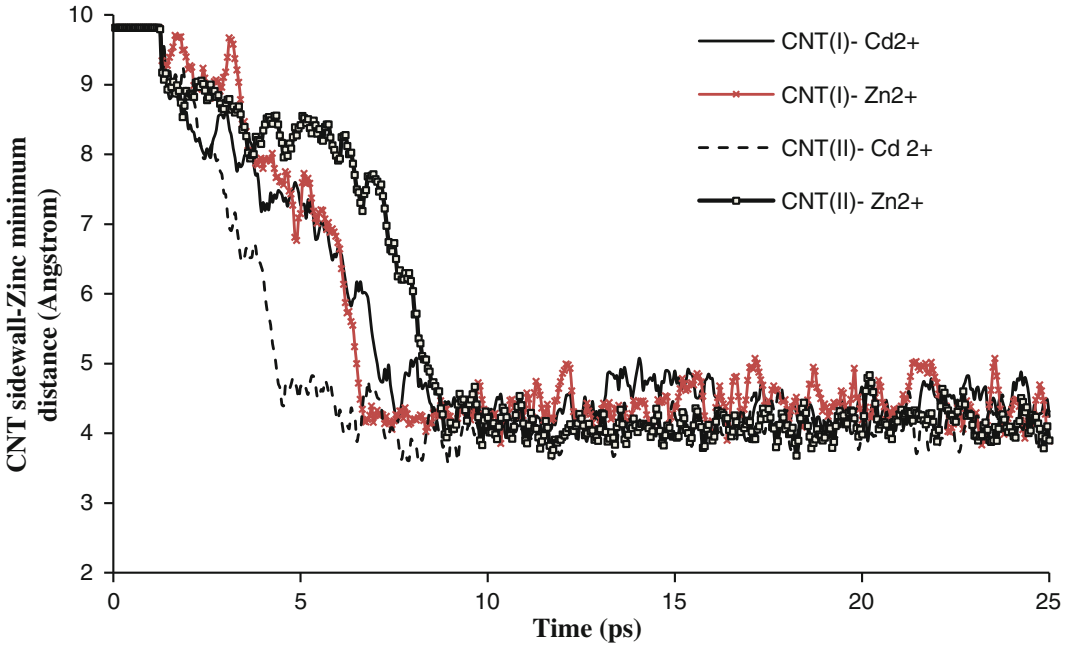

Fig. 3 The distance between ions and CNT wall side as a function of simulation time

is the angle between H–O–H, and $\theta^{eq}_{H-O-H}$is the equilibrium angle between H–O–H. The last two terms in Eq. 3 describe the van der Waals (vdW) and electrostatic non-bonded interactions, respectively:

$$U_{vdw} = \sum_i \sum_{j>i} \varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \quad (6)$$

$$U_{coulomb} = \sum_i \sum_{j>i} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad (7)$$

In this paper a simple Lennard-Jones 12-6 potential form was used to simulate vdW interaction. ε and σ are the well-depth and diameter of the potential (Allen and Tildesley 1987). The parameters q_i and q_j are charges of atoms i and j, which are located at center of the atoms.

For computation of ε and σ between unlike atoms, the Lorentz–Bertholet mixing rule can be used (Allen and Tildesley 1987):

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}, \quad \sigma_{ij} = \frac{\left(\sigma_i + \sigma_j\right)}{2} \quad (8)$$

The Beeman algorithm was used to integrate the equations of motion (Andersen 1983). Our code supports NVT (Isothermal) ensemble and uses Berendsen thermostat method to account for the temperature of the system (Berendsen et al. 1984). In Berendsen thermostat method, the particle velocity of system at each step is re-scaled by a factor λ. The λ factor is defined as Berendsen et al. 1984:

$$\lambda = \left[1 + \frac{\Delta t}{\tau_t} \left(\frac{T}{T_0} - 1 \right) \right]^{\frac{1}{2}} \quad (9)$$

where τ_t is the user defined time constant (typically 0.5–5.0 ps), T the current temperature, T_o the desired temperature and Δt the time step. The temperature was set to 298 K. The potential parameters and partial charges used in the simulation are listed in Table 1.

3 Results and discussion

3.1 Interaction energies

Figure 1 shows the vdW, the electrostatic and the total interaction energies between heavy metal ions and CNTs with respect to the distance between ion center and CNT centerline when ions are close to the center of CNT. The trend of total energy, as the sum of the vdW and the electrostatic energies, is the same as the vdW interaction energy. In large distances, the total interaction energy causes attractive force, but in short distances, the total interaction energy causes repulsive force. Thus, the total energy curves can be divided into two separate components: attractive and repulsive. The distance at which the total energy becomes minimum, is the equilibrium distance between the metal ion and CNT. Figure 1 reveals that the equilibrium distance between CNTs and Zn(II) is smaller than the equilibrium distance between CNTs and Cd(II).

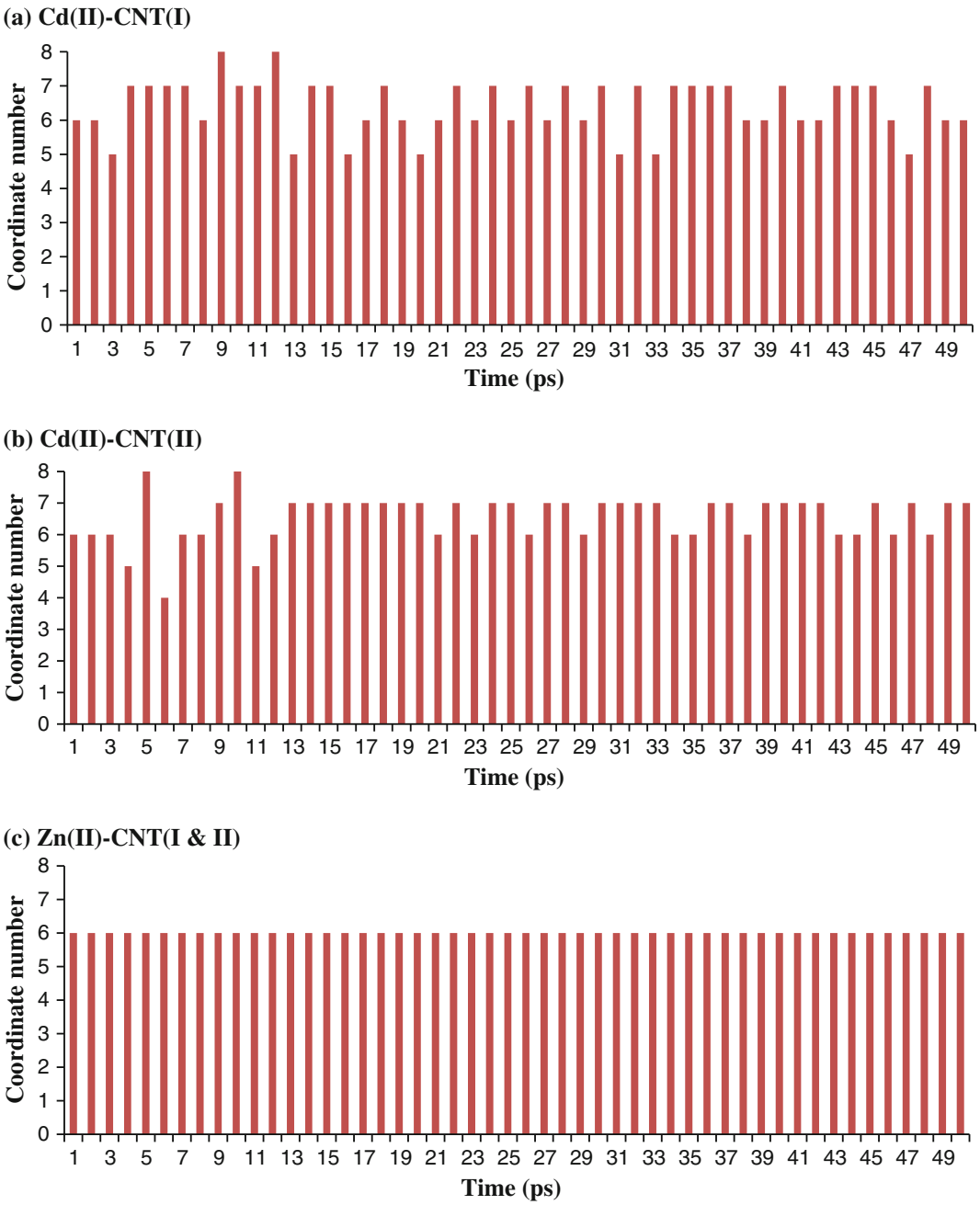

Fig. 4 Cd(II) and Zn(II) hydration numbers as a function of simulated time

For more insight into adsorption process, overview on the interaction energy between ions and CNT is necessary. The interaction energy between ion and CNT is defined as (Ansari Dezfoli et al. 2012):

$$E_{CNT-ion} = E_{Total} - E_{water-water} - E_{water-ion} - E_{water-CNT} \quad (10)$$

The interaction energies between ions and CNT are shown in Fig. 2. The results show that the electrostatic energy is higher than the vdW interaction energy. Thus, the electrostatic energy has major role in adsorption process. This energy is because of different attractive forces between ions with positive charge and CNT with negative sites.

3.2 Adsorption history

Figure 3 demonstrates the adsorption process history. The minimum distance between zinc ion and CNT is 4.3 $\dot{A}$ for CNT(I) and, 4.1 $\dot{A}$ for CNT(II). In addition, the minimum

Table 2 The coordination number distribution (CND) probability of Zn(II) and Cd(II)

Heavy metal ion	M^{2+}–$(H_2O)_4$ cluster (%)	M^{2+}–$(H_2O)_5$ cluster (%)	M^{2+}–$(H_2O)_6$ cluster (%)	M^{2+}–$(H_2O)_7$ cluster (%)	M^{2+}–$(H_2O)_8$ cluster (%)
Adsorption process (this study)					
Cd^{2+}	0	14	34	48	4
Cd^{2+}	2	4	34	56	4
Zn^{2+}	0	0	100	0	0
Zn^{2+}	0	0	100	0	0
Bulk water					
Cd^{2+} (Chillemi et al. 2005)	0	0	68	31.55	0.45
Cd^{2+} (DAngelo et al. 2008)	0	0	17.5	81.7	0.8
Zn^{2+} (Mohammed et al. 2005; Wu et al. 2010)	0	0	100	0	0

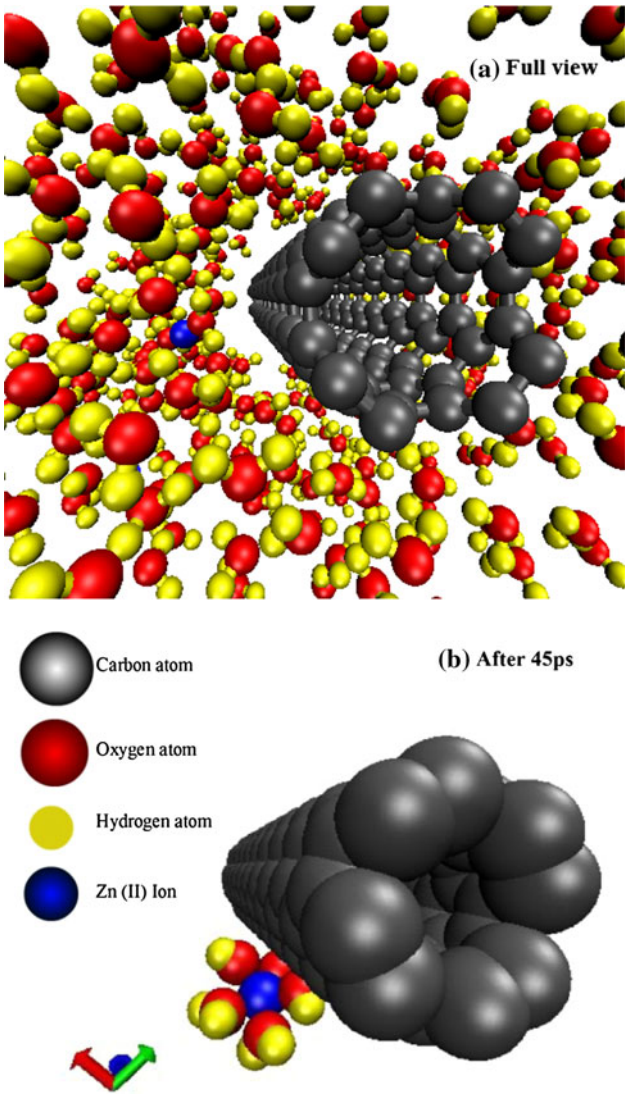

Fig. 5 MD simulation snapshots of Zn(II)–water cluster during the adsorption process on CNT. **a** Full view **b** after 45 ps

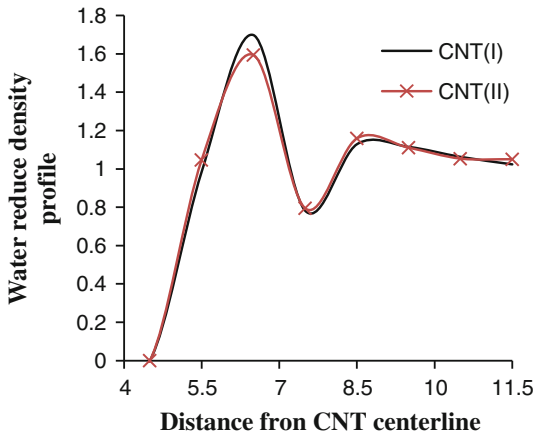

Fig. 6 The water reduced density profile around CNT(I) and CNT(II)

distance between cadmium ion and CNT is 4.5 *Å* for CNT(I) and, 4.2 *Å* for CNT(II).

The Cd(II) is about 1.7 times heavier than Zn(II). Therefore, when both Cd(II) and Zn(II) are affected by equal attractive forces from CNT, the zinc ion gets more accelerated. Figure 3, however does not show this difference in adsorption history of Cd(II) and Zn(II) on CNT(I). In addition, despite more attractive force between CNT(II) and Zn(II), Fig. 3 shows that the adsorption of Zn(II) on CNT(II) has a lower rate than CNT(I) between 4 and 9 ps. For Cd(II), the adsorption rate increased with increasing the CNT negative surface charge. The water–ion complex properties and water reduced density around CNT may express these phenomena.

3.3 Ion–water cluster

The zinc or cadmium ions can be presented as M^{2+}–$(H_2O)_6$, M^{2+}–$(H_2O)_7$, M^{2+}–$(H_2O)_8$, and M^{2+}–$(H_2O)_9$ clusters in

bulk water (Chen and Wang 2006). Figure 4 demonstrates the coordination number for Zn(II) and Cd(II) during the adsorption process. For Zn(II), the coordination number 6 is only observed during simulation time, but for Cd(II) the number of coordinate number varied between 4 and 8. The results reveal that the Cd^{2+}–$(H_2O)_4$, Cd^{2+}–$(H_2O)_5$, Cd^{2+}–$(H_2O)_6$, Cd^{2+}–$(H_2O)_7$, and Cd^{2+}–$(H_2O)_8$ constitute 0, 14, 34, 48, and 0.04 % of the simulation time for CNT(I) and 0.02, 0.04, 34, 0.56, and 0.04 % of the simulation time for CNT(II) respectively. Table 2 gives the coordination number distribution (CND) probability of Zn(II) and Cd(II) complex during adsorption process and compared these value with the CND probability of ion in bulk water. The results show that the coordinate number of Zn(II) was not influenced by adsorption process but the presence of Cd^{2+}–$(H_2O)_n$ cluster is reduced in the form of Cd^{2+}–$(H_2O)_6$ in adsorption process.

These results prove that Cd(II)–water cluster is less stable because of a larger number of exchange events between four and eight coordinated complexes. The order of stability of ion–water complex can be expressed as $Zn_{CNT(I)} = Zn_{CNT(II)} > Cd_{CNT(I)}) > Cd_{CNT(II)}$. The investigation shows that an ion

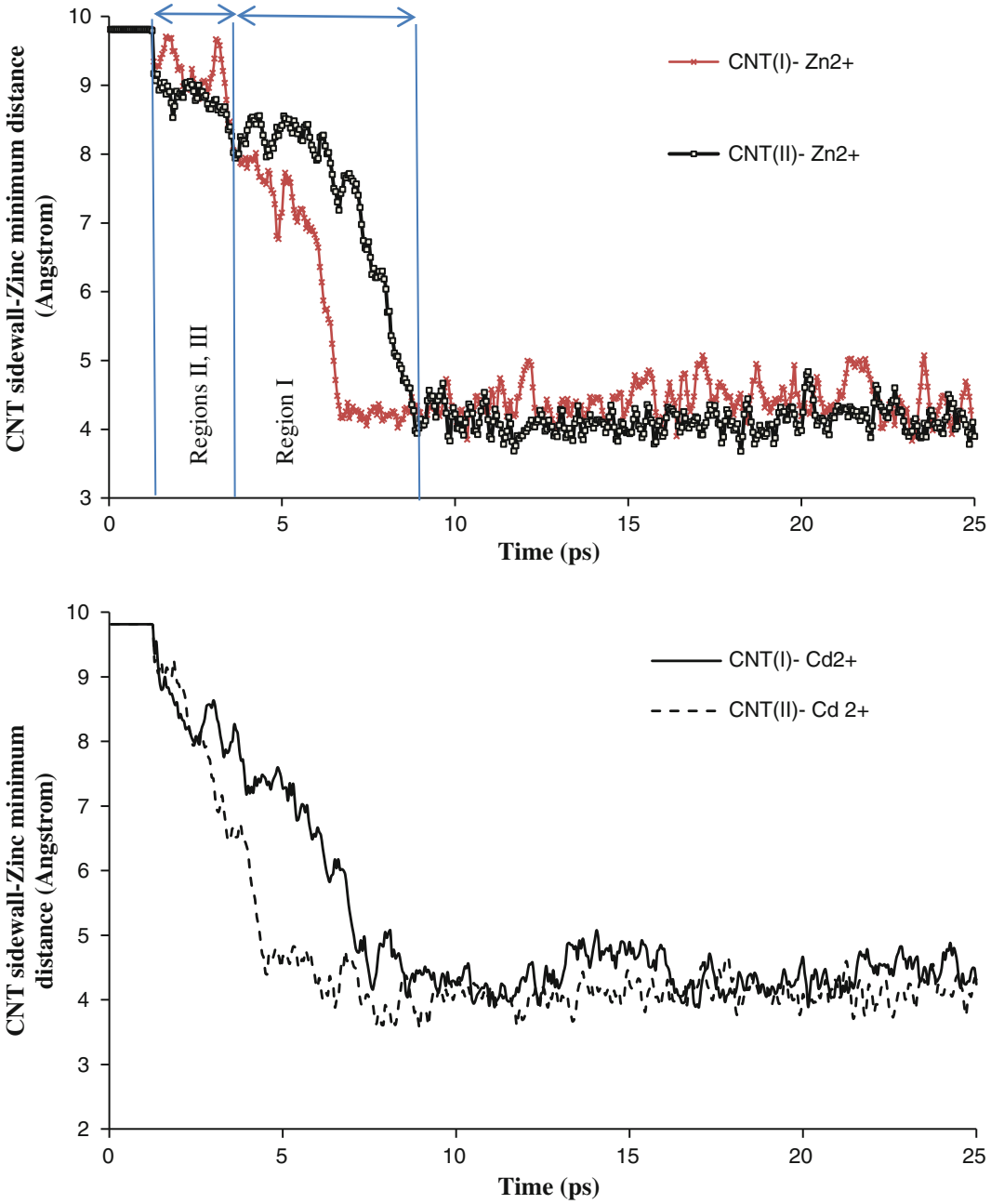

Fig. 7 Ion adsorption behavior around CNT(I) and CNT(II)

with less stable cluster demonstrated a higher translational dynamics (DAngelo et al. 2008). This higher translational dynamics helps ion move easier from water when attracted to CNT. That is why the Cd(II) with higher weight has an adsorption behavior like Zn(II) when adsorbed on CNT(I).

Figure 5 shows a configuration of the Zn(II)–water complex during adsorption on CNT(I). The results indicate that the ions are adsorbed to CNT with their cluster.

Figure 6 demonstrates the water radial density distribution around CNT(I) and CNT(II). The results indicate that a high-density region is located in water–CNT interface. It will be expected that water molecules in high-density region around CNT(II) have less flexibility as compared with CNT(I) as a results of stronger attractive force between CNT and water molecules. In our previous work, we defined three different regions of water molecules around CNTs, as:

Region I: the high water density region.

Region II: the low water density region.

Region III: the bulk water region.

We can use these regions for comparison between Zn(II) adsorption to CNT(I) and (II). In Region III, the water molecules have the same behavior like bulk water. In this region Zn(II) is adsorbed to CNT(II) fester than CNT(I) due to strong attractive force.

In Region (II), the water molecules have little effect on Zn(II) adsorption. Therefore in this region, the Zn(II) is also adsorbed to CNT(II) faster than CNT(I) because of higher attractive force.

In Region (I), Zn(II) adsorption is affected entirely by water molecules because of high water density, low flexibility of water molecules around CNTs, and low translational dynamics of Zn(II)–water complex. Thus in this region, the Zn(II) is adsorbed to CNT(I) faster than CNT(II) despite the stronger attractive force between Zn(II) and CNT(II). This different Zn(II) adsorption behavior is shown in Fig. 7. Because of high translational dynamics of Cd(II)–water complex, in all water regions around CNT, the rate of Cd(II) adsorption on CNT(II) is higher than CNT(I). It means that the attractive force can affect Cd(II) more than water regions around CNT.

4 Conclusion

The adsorption process of Zn(II) and Cd(II) from aqueous solution using charged CNT was investigated using molecular dynamic simulation. It was found that both ions can be adsorbed to CNT. The simulation results show that with increasing the CNT surface negative charge, the rate of adsorption of ions is changed. The results reveal that only Cd(II) adsorption rate was increased with increasing the net CNT surface charge from −0.01 to −0.02e, but Zn(II) adsorption rate was decreased. In order to fully understand the adsorption process, we studied the ion–water complex properties and water molecules regions around charged CNT. The results demonstrate that both ion–water complex properties and water regions around CNTs have direct effect on adsorption process. The most important factor for Cd(II) adsorption on CNT is CNT surface charge. Water characteristics such as water regions can influence Zn(II) adsorption strongly.

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