



Original Research Article

The effect of doping graphene with silicon on the adsorption of cadmium(II): theoretical investigations

Mohammad Reza Jalali Sarvestani

Young Researchers and Elite Club, Yadegar-e-Imam Khomeini (RAH) Shahr-e-Rey Branch, Islamic Azad University, Tehran, Iran

ARTICLE INFORMATION

Received: 1 April 2020

Received in revised: 28 April 2020

Accepted: 1 May 2020

Available online: 21 July 2020

DOI: [10.48309/JMNC.2020.4.2](https://doi.org/10.48309/JMNC.2020.4.2)

KEYWORDS

Cd (II)

Graphene

Adsorption

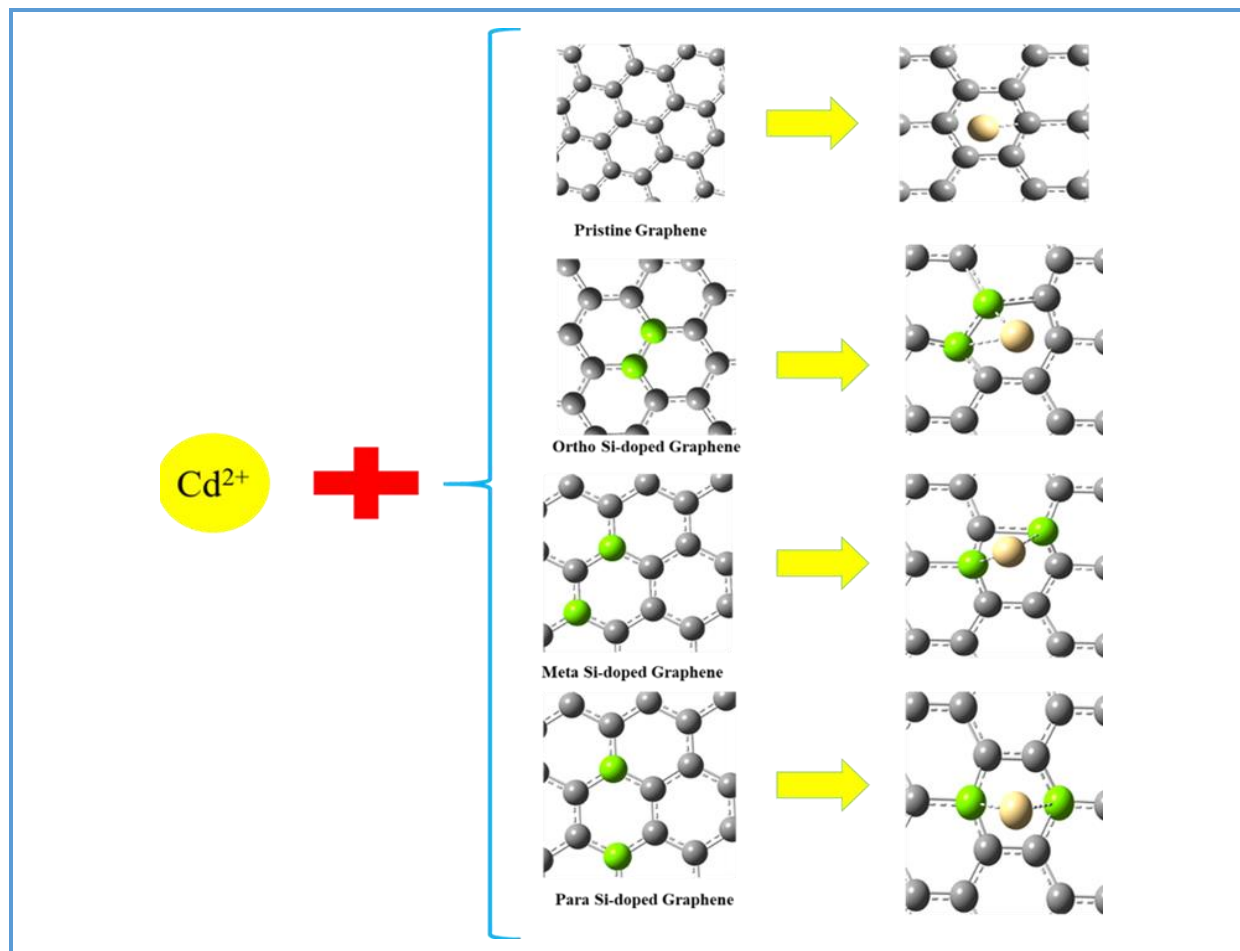
Silicon

Detection

ABSTRACT

In this research, the influence of doping graphene with silicon on the adsorption of Cd^{2+} was investigated using the infrared (IR), natural bond orbital (NBO) and frontier molecular orbital (FMO) computations. The thermodynamic parameters including Gibbs free energy changes (ΔG_{ad}), enthalpy variations (ΔH_{ad}) and thermodynamic constant (K_{th}) revealed that, the Si impurity made the cadmium adsorption more spontaneous, exothermic, irreversible, and experimentally feasible. The effect of temperature and geometrical situation of silicon impurities at three ortho, meta and para conditions were also evaluated. The results indicated that, the adsorption efficiency was higher at room temperature and doping graphene with silicon at the ortho position. The NBO results demonstrated that, the cadmium interaction with both pristine and Si-doped graphenes was chemisorption, which was due to formation of the covalent bonds with SP^3 hybridization in all of the evaluated configurations. The applicability of the pristine and Si-doped graphenes as an electrochemical sensing material for detection of the cadmium was also assessed by the FMO parameters including, bandgap, electrophilicity, and maximum transferred charge capacity. The ortho silicon doped graphene was found to be the best recognition element for the Cd(II) as the bandgap experienced the sharpest increase from 1.82 eV to 7.74 eV in the case of this adsorbent.

Graphical Abstract



Introduction

Cadmium is a toxic, mutagenic, carcinogenic, and teratogen heavy metal that is used in various industries including, the production of paints, batteries, plastics, alloys, and metal plating [1–4]. Consequently, the wastewaters of the mentioned industries are one of the main sources of the environmental pollution with cadmium. In addition, the combustion of the coal and fossil fuels has been the main source of air contamination with this toxic element [5–7]. According to the world health organization (WHO), the concentration of cadmium in the blood must not be higher than 0.005 ppm. This is due to the fact that, even ultra-trace amounts

of cadmium can cause severe health problems such as digestion impairment, nausea, headache, bone degradation, convulsions, shock, muscle cramps, blood damages, vomiting, diarrhea, hypertension, salivation, renal and liver failure. Therefore, developing novel methods for removal and detection of this hazardous metal is very important [8–11]. To date, different techniques including ion exchange, electrochemical methods, filtration, reverse osmosis, precipitation and adsorption for removal of cadmium. Amongst the aforementioned methods, adsorption is more suitable because of its easy handling, low cost, and being eco-friendlier. However, for the adsorption method, finding an economical

adsorbent with high adsorption capacity, good selectivity, enough reusability and applicability in harsh conditions is still a big challenge [11–13].

Furthermore, cadmium determination is conventionally done using the inductively coupled plasma mass spectrometry, flame atomic absorption spectrometry, electrothermal atomic absorption spectroscopy, atomic fluorescence spectrometry and high-performance liquid chromatography which are expensive, time-consuming and demanding large amounts of toxic organic solvents [13–15]. Therefore, designing a thermal or electrochemical sensor for cadmium measurement is of great importance as these types of sensors are portable, simple, rapid, selective, environmental friendly, economical and sensitive. However, the first step in fabricating a sensor is employing a sensing material with the proposed analyte [16–20].

Figure 1 demonstrates a carbon-based nanosheet with a hexagonal lattice. Graphene has a two-dimensional structure in which carbon atoms are connected to each other by the SP^2 bonds [21–23]. Graphene is a porous nanostructure with high specific surface area, excellent electrocatalytic activity and prominent electrical conductivity and these properties make it a suitable adsorbent and sensing material. Although the applicability of graphene in both fields has been widely evaluated by experimental and theoretical studies there only a few reports about the performance of silicon doped graphene as an adsorbent or a sensing material [24–27]. In this respect, applicability of silicon doped graphene as an effective adsorbent and sensor for cadmium (II) ion was investigated by NBO, IR and DFT studies for the first time in this research.

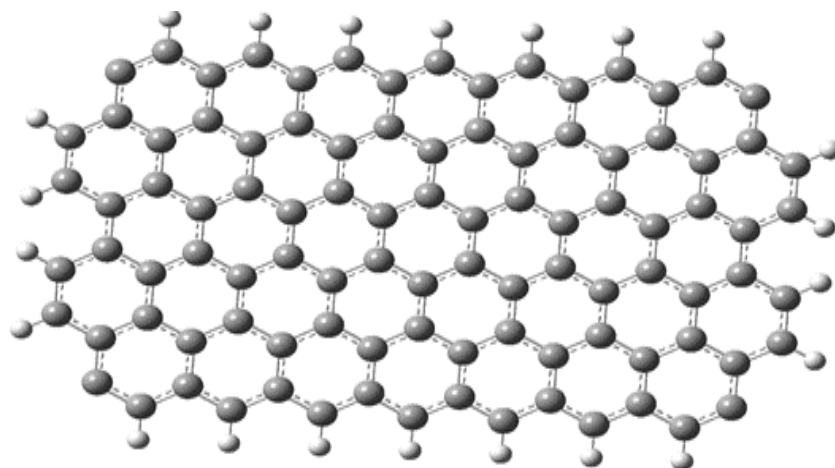


Figure 1. Graphene structure

Computational Details

The structures of pristine and Si-doped graphenes, cadmium (II) and their complexes were designed using the nanotube modeler 1.3.0.3 and Gauss View 6 software [25–27]. At

first, all of the designed structures were optimized geometrically. Then, IR, NBO and Frontier molecular orbital (FMO) computations were performed on them [23]. All of the calculations were performed by Gaussian 16 software using the density functional theory

(DFT) method using the exchange-correlation potential that constructed from Becke's three parameters functional for exchange (B3) along with the Lee-Yang-Parr parameterization for correlation (LYP) as implemented B3LYP method for pristine and silicon doped graphenes. for, the computations for cadmium and its complexes with the studied adsorbents were done by LANL2DZ (Los Alamos National Laboratory of Double Zeta) [20–22]. These basis sets were chosen because their results were in excellent accordance with the real experimental data. All of the calculations were performed in the aqueous phase in the temperature range of 298-398 at 10° intervals. The investigated process was as follows:



Equations 2-6 were used to calculate adsorption energy values (E_{ad}) and thermodynamic parameters including adsorption enthalpy changes (ΔH_{ad}), Gibbs free energy changes (ΔG_{ad}) thermodynamic equilibrium constants (K_{th}) and entropy changes (ΔS_{ad}) respectively [22–24].

$$E_{ad} = (E_{(\text{Cd-Adsorbent})} - (E_{(\text{Cd})} + E_{(\text{Adsorbent})})) \quad (2)$$

$$\Delta H_{ad} = (H_{(\text{Cd-Adsorbent})} - (H_{(\text{Cd})} + H_{(\text{Adsorption})})) \quad (3)$$

$$\Delta G_{ad} = (G_{(\text{Cd-Adsorbent})} - (G_{(\text{Cd})} + G_{(\text{Adsorbent})})) \quad (4)$$

$$K_{th} = \exp\left(-\frac{\Delta G_{ad}}{RT}\right) \quad (5)$$

$$\Delta S_{ad} = (S_{(\text{Cd-Adsorbent})} - (S_{(\text{Cd})} + S_{(\text{Adsorbent})})) \quad (6)$$

In the aforementioned equations, E is the total electronic energy of each structure, H denotes the sum of the thermal correction of enthalpy and total energy of the evaluated materials. G stands for the sum of the thermal correction of Gibbs free energy and total energy for each of the studied structures. R is the ideal gas constants, T is the symbol of the temperature and S is the thermal correction of entropy for each structure [21].

Frontier molecular orbital parameters including bandgap (E_g), chemical hardness (η), chemical potential (μ), electrophilicity (ω) and the maximum transferred charge (ΔN_{max}) were calculated using Equations 7-11 [20–24].

$$E_g = E_{LUMO} - E_{HOMO} \quad (7)$$

$$\eta = (E_{LUMO} - E_{HOMO})/2 \quad (8)$$

$$\mu = (E_{LUMO} + E_{HOMO})/2 \quad (9)$$

$$\omega = \mu^2/2\eta \quad (10)$$

$$\Delta N_{max} = -\mu/\eta \quad (11)$$

E_{LUMO} and E_{HOMO} in Equations 7 to 11 are the energy of the lowest unoccupied molecular orbital and the energy of the highest occupied molecular orbital respectively [24].

Results and Discussion

NBO and structural analysis

As seen in Figure 2, cadmium interactions with pristine and silicon doped graphenes were evaluated in different situations. Therefore, to express the results more conveniently, each structure is shown by an abbreviated name in tables and figures. The naming method was as follows:

The PG denotes the pristine graphene and PG-Cd is the cadmium complex with PG. The ortho doped silicon graphene is shown by OSDG abbreviation and OSDG-Cd is considered for cadmium complex with OSDG. The MSDG stands for meta silicon doped graphene and MSDG-Cd denotes cadmium complex with MSDG. The PSDG is para silicon doped graphene and the complex of this adsorbent with cadmium is shown by PSDG-Cd abbreviation.

The presented optimized structures in Figure 2 showed tangible deformations have occurred in the structure of adsorbents when cadmium is adsorbed on their surface, especially for the Si-doped graphenes. These deformations can be due to the formation of

some chemical bonds between cadmium and the studied adsorbents [14]. Therefore, in order to obtain more information about the adsorption mechanism NBO computations were employed. As demonstrated in Table 1, in the case of pristine graphene a monovalent bond with $SP^{2.94}$ Hybridization is formed between the cadmium and one of the carbon atoms of graphene. However, when silicon impurities are inserted in the structure of graphene the adsorption process becomes stronger because two monovalent bonds are formed between the adsorbate and adsorbents. All of the formed bonds are monovalent with SP^3 hybridizations and their energy is highly negative. The next matter that can be realized from Table 1 is that the energy of bonds created between cadmium and Si-doped graphenes is more negative than the ones with pristine graphene which indicates cadmium interaction with silicon doped graphene is more favorable [15]. Furthermore, among the Si-doped adsorbents, OSDG has the lowest bond energies which can be related to the better interaction of Cd^{2+} with this nanostructure. For verifying the NBO results accuracy the calculated values of total

electronic energy and adsorption energy were also given in Table 1. As it is obvious, the adsorption energy values for all of the configurations are lower than -200 kJ/mol which indicates Cd^{2+} interaction with all of the studied adsorbents are experimentally possible and the interactions are chemisorption in all of the conformers. However, by a more precise look at the provided data in Table 1, it can be understood that cadmium complexes with Si-doped graphenes have lower total electronic and adsorption energies than the Cd^{2+} derived product with the pristine graphene and these parameters become lower and lower by decreasing the distance of Si atoms in PSDG-Cd to OSDG-Cd conformers. Therefore, silicon impurities can catalyze the cadmium adsorption and OSDG is the best adsorbent for the removal of Cd^{2+} [16]. The dipole moments of the studied structure are also presented in Table 1. As it is clear when cadmium adsorbs on the surface of the adsorbents this parameter increases sharply. Therefore, Cd^{2+} derived products with graphenes have strong solvation in polar solvents than the pure adsorbent without cadmium [17–19].

Table 1. The NBO and structural parameters for cadmium (II) and its complexes with nano-adsorbents

	Bond length (Å)	Bond order	Occupancy	Hybridization	Bond energy (a.u.)	Total electronic energy (a.u.)	Adsorption energy (kJ/mol)	The lowest frequency (cm ⁻¹)	Zero-point energy (kJ/mol)	Dipole moment (deby)	
Cd (II)	---	---	---	---	---	-5410.971	---	0.00	394.356	0.00	
PG	---	---	---	---	---	-821.649	---	66.326	331.080	0.00	
PG-Cd	Cd-C	2.1	1	1.99	$Sp^{2.94}$	-0.448	-6232.800	-474.709	65.139	343.740	7.66
OSDG	---	---	---	---	---	---	-1317.856	---	78.827	285.22	0.00
OSDG-Cd	Cd-Si	1.44	1	1.94	$Sp^{3.02}$	-0.750	-6729.320	-1295.214	77.891	304.110	2.12
	Cd-Si	1.51	1	2.03	$Sp^{2.93}$	-0.632	-6729.429	---	101.098	299.960	8.91
MSDG	---	---	---	---	---	---	-6729.429	---	101.098	299.960	8.91
MSDG-Cd	Cd-Si	1.69	1	1.93	$Sp^{2.99}$	-0.512	-1318.089	-971.406	43.916	306.770	13.36
	Cd-Si	1.73	1	2.04	$Sp^{2.98}$	-0.604	-6729.378	---	80.313	296.900	4.09
PSDG	---	---	---	---	---	---	-6729.378	---	80.313	296.900	4.09
PSDG-Cd	Cd-Si	2.03	1	1.96	$Sp^{2.91}$	-0.478	-1318.109	-783.310	57.326	303.480	10.21
	Cd-Si	2.3	1	1.98	$Sp^{3.04}$	-0.501	-1318.109	-783.310	57.326	303.480	10.21

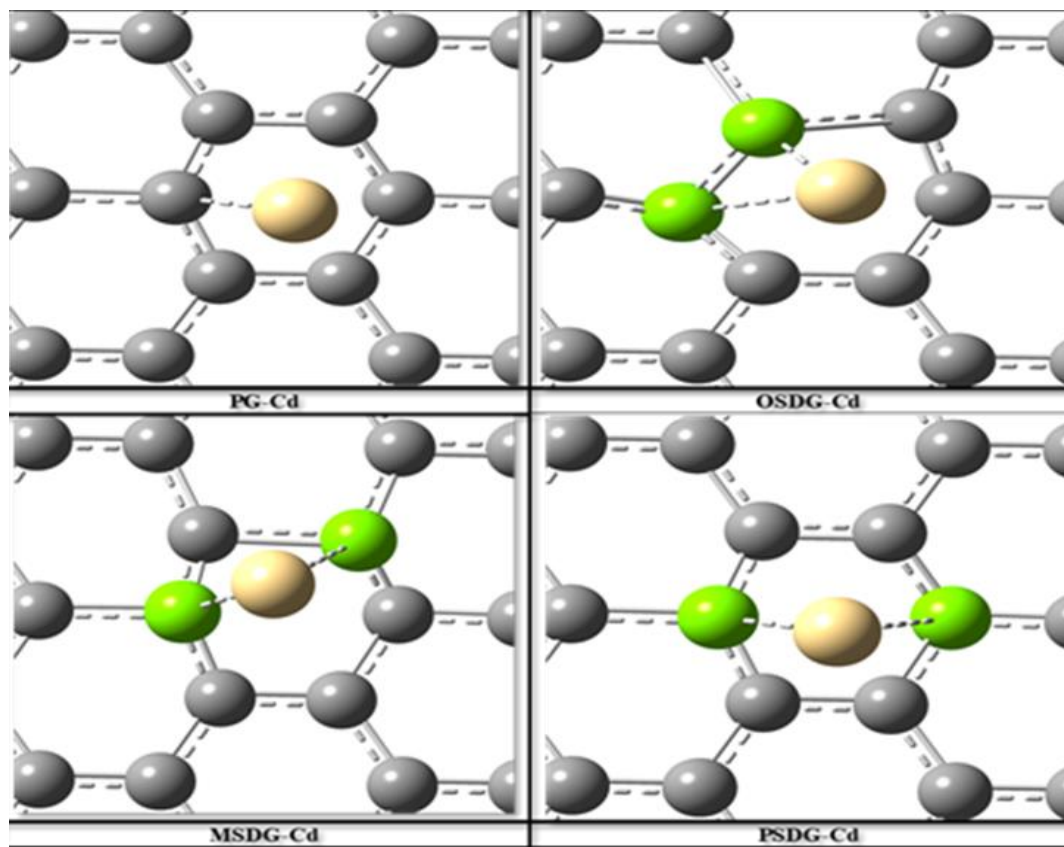


Figure 2. Optimized structures of Cd (II) complexes with pristine and Si-doped graphenes

Thermodynamic studies

The calculated adsorption enthalpy changes are presented as a function of temperatures in [Figure 3](#). As can be seen, the adsorption process is exothermic in all of the configurations because of the obtained highly negative ΔH_{ad} values. The next point that is obvious from [Figure 3](#) is that by increasing the temperature ΔH_{ad} experience a surge in all of the configurations and 298 K is the optimum temperature for the adsorption process. Owing to the exothermic nature of cadmium interaction with the adsorbents especially the Si-doped ones it can be deduced that silicon doped graphenes are appropriate sensing materials for developing new thermal sensors for detection of cadmium [24]. In thermal sensors, the desired analyte usually is involved

in a highly exothermic or endothermic interaction with the recognition element that is immobilized on the surface of a transducer and the variation in the temperature of the environment is recorded by a highly sensitive thermistor and it is used as a signal for determination the concentration of analytes. Among the investigated nanostructures OSDG seems to be the most suitable sensing material because the cadmium interaction with this nanosheet is the most exothermic [21].

The values of ΔG_{ad} and the logarithm of K_{th} are depicted as a function of temperature in [Figures 4](#) and [5](#). As it is obvious cadmium adsorption on the surface of pristine graphene is spontaneously and irreversibly. However, when silicon impurities are inserted in the structure of graphene the Spontaneity and irreversibility of the adsorption process

improved significantly and this enhancement got sharper by lowering the Si atoms distance from PSDG to OSDG. The next matter that is clear in Figures 4 and 5, by increasing of temperature, cadmium interaction with all of the adsorbent got weaker [20–22].

Adsorption entropy changes values were calculated by Equation 6 and the results are

given in Figure 6. As can be seen, this parameter is negative at all of the temperatures therefore, cadmium interaction with all of the nanostructures is inappropriate due to the aggregation in Cd^{2+} complexes with the nano-adsorbents [24].

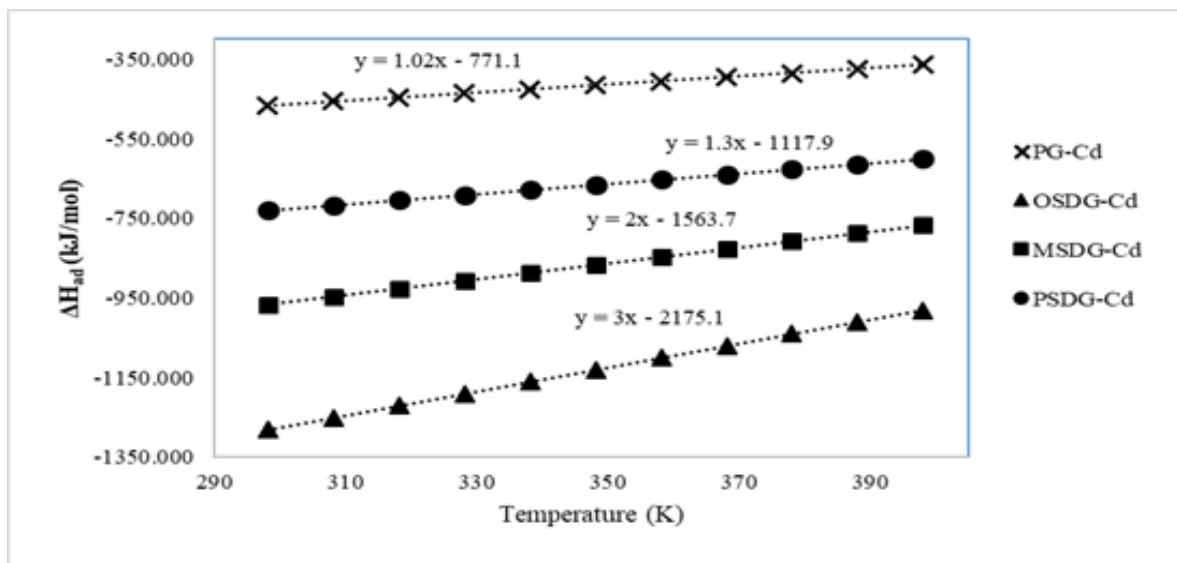


Figure 3. ΔH_{ad} values as a function of temperature in the temperature range of 298–398 K at 10° intervals

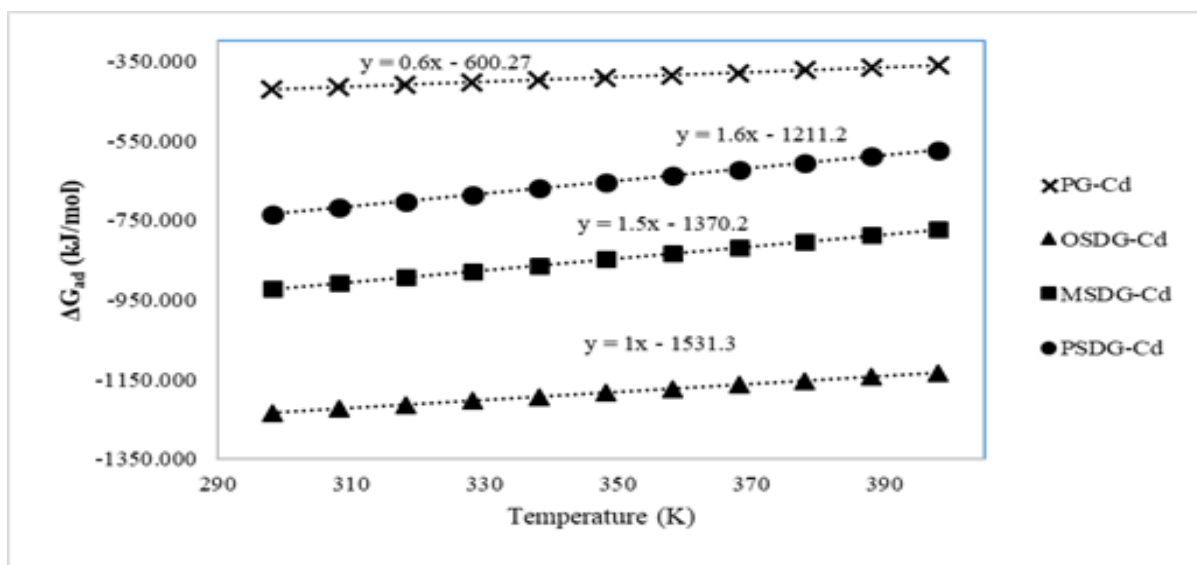


Figure 4. ΔG_{ad} values as a function of temperature in the temperature range of 298–398 K at 10° intervals

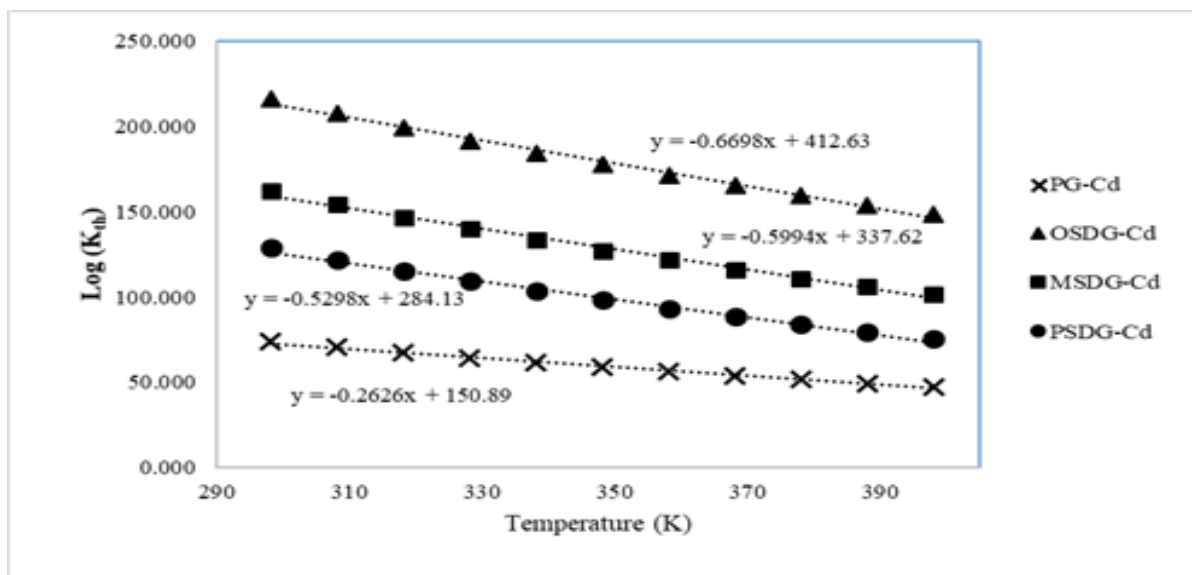


Figure 5. The logarithm of K_{th} values as a function of temperature in the temperature range of 298-398 K at 10° intervals

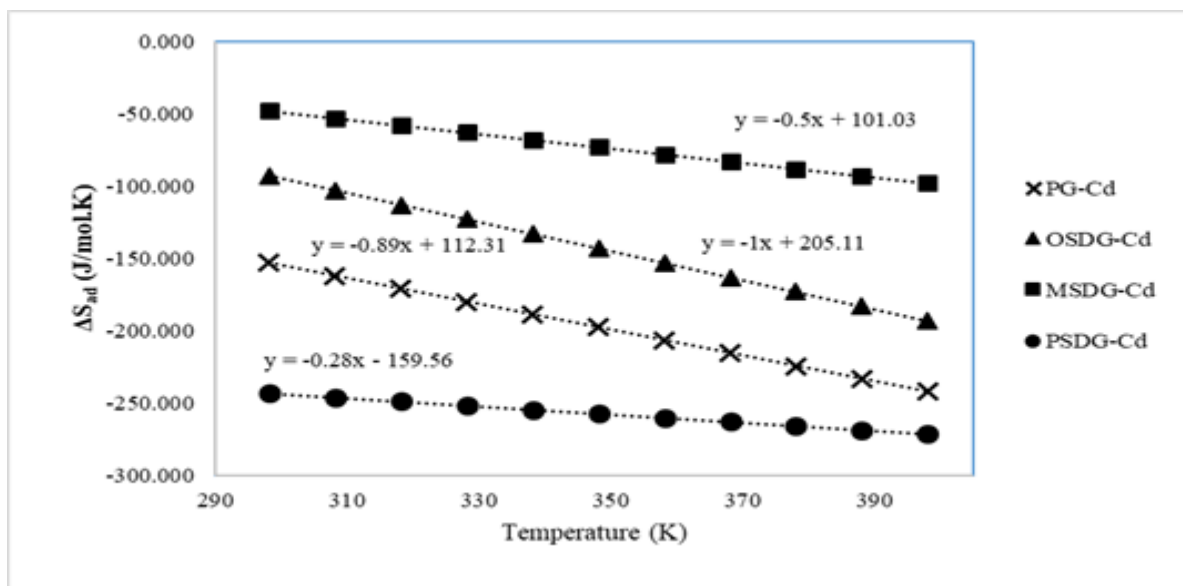


Figure 6. ΔS_{ad} values as a function of temperature in the temperature range of 298-398 K at 10° intervals

Frontier molecular orbital analysis

To evaluate the performance of pristine and Si-doped graphenes as an electrochemical sensing material for detection of Cd^{2+} , the bandgap, electrophilicity and maximum transferred charge capacity were calculated,

and the results are presented in Table 2. The E_g parameter has an inverse relationship with the conductivity. In other words, the molecules with low bandgap are more conductive than the compounds with high E_g values. As seen in Table 2, among the studied adsorbents, OSDG has the most conductivity. The sharpest change in E_g is

occurred for this nanostructure from 1.82 eV to 7.74 eV when cadmium adsorbs on its surface. Therefore, this adsorbent is the most suitable sensing material for developing new cadmium(II) electrochemical sensors because other nanostructures are less conductivity due to their high bandgap values and the changes of E_g are not so considerable [14–16]. The next matter that can be realized from Table 2 is that cadmium complexes with nano-adsorbents have lower E_g values than the pure nanostructures which indicates the conductivity declined when cadmium adsorbs on the surface of graphenes [15].

When two molecules reacting with each other, one of them plays the role of an electron acceptor and the other one plays the role of an electron donor. On the other hand, ω and ΔN_{\max} parameters that explain the tendency of a molecule towards electron. In fact, a compound with the high value of electrophilicity and maximum transferred charge capacity is a Lewis acid that tends to gain electron and the molecules with low values of ω and ΔN_{\max} are more eager to lose electron and playing the role of a Lewis base [19–22]. As can be seen in Table 2, the electrophilicity of cadmium is 25.32

which shows its high tendency to absorb electron (be an electron acceptor). However, the adsorbents have low ω and ΔN_{\max} values which implies both pristine and Si-doped graphenes can be an electron donor for cadmium. Therefore, electron transfer reactions can be done easily between cadmium and the adsorbents and the adsorbents especially the Si-doped ones are good electrochemical recognition elements for cadmium.

Chemical hardness and chemical potential are the admissible standards for estimating the reactivity of a compound. In fact, the soft materials with low η and high μ values are capable of doing necessary electron transmissions for a chemical reaction more conveniently than hard compounds with high η and low μ values. As seen in Table 2, chemical hardness of the studied adsorbents increased when Cd^{2+} adsorbs on their surface and chemical potential experienced a sharp increase during the process. Therefore, Cd-adsorbent complexes are less reactive compared with that of the pure nanostructures without cadmium [24].

Table 2. The calculated energy of HOMO and LUMO orbitals, bandgap, chemical hardness, chemical potential, electrophilicity and maximum transferred charge capacity for cadmium, adsorbents and their complexes

	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	η (eV)	μ (eV)	ω (eV)	ΔN_{\max} (eV)
Cd (II)	-29.100	-12.200	16.900	8.450	-20.650	25.232	2.444
PG	-3.990	-1.940	2.050	1.025	-2.965	4.288	2.893
PG-Cd	-14.090	-5.970	8.120	4.060	-10.030	12.389	2.470
OSDG	-3.170	-1.350	1.820	0.910	-2.260	2.806	2.484
OSDG-Cd	-13.230	-5.490	7.740	3.870	-9.360	11.319	2.419
MSDG	-5.560	1.250	6.810	3.405	-2.155	0.682	0.633
MSDG-Cd	-13.310	-6.120	7.190	3.595	-9.715	13.127	2.702
PSDG	-4.160	0.820	4.980	2.490	-1.670	0.560	0.671
PSDG-Cd	-13.110	-6.520	6.590	3.295	-9.815	14.618	2.979

Conclusions

Removal and detection of cadmium (II) even in ultra-trace amounts are of great importance.

In this respect, the effect of doping graphene with silicon in three ortho, meta and para situations on the adsorption of Cd^{2+} was

investigated by DFT, NBO and IR simulations, in this study. The calculated adsorption energy values, Gibbs free energy changes and thermodynamic equilibrium constants showed doping graphene with silicon make the adsorption process more spontaneous, non-equilibrium and experimentally favorable. The values of enthalpy changes showed that, both the pristine and Si-doped graphenes are suitable sensing materials for the construction of novel thermal sensors to cadmium determination and the adsorption process is exothermic. The impact of temperature on the adsorption process was studied by calculating the thermodynamic parameters in different temperatures. The results indicated that, 298.15 K is the optimum temperature. The NBO data revealed that, only one bond was formed between the pristine graphene and cadmium. However, Si-doped adsorbents formed two monovalent bonds with cadmium and the adsorption process was found to be chemisorption for all of the adsorbents. The bandgap, electrophilicity and maximum transferred charge capacity indicated ortho-silicon doped graphene is a suitable electroactive sensing material for designing electrochemical sensors for the determination of this toxic heavy metal. Some structural parameters including dipole moment, chemical hardness, geometrical variations were also discussed in detail.

Acknowledgments

The author would like to appreciate the Young Researchers and elite club of the Islamic Azad University of Yadegar-e-Imam Khomeini (RAH) Shahre-rey branch for supporting this project.

References

- [1]. Pal P., Pal A. *Int J Biol Macromol.*, 2017, **104**:1548
- [2]. Basu M., Guha A.K., Ray L. *Process Saf Environ Prot.*, 2017, **106**:11
- [3]. Lin j., Su B., Sun M., Chen B., Chen Z. *Sci Total Environ.*, 2018, **627**:314
- [4]. Fosso-Kankeua E., Mittal H., Waandersa F., Ray S. S. *J Indust Eng Chem.*, 2017, **48**:151
- [5]. Kataria N., Garg V.K. *Chemosphere.*, 2018, **208**:818
- [6]. Pyrzynska K. *J Environ Chem Eng.*, 2019, **7**:102795
- [7]. Kaushala S., Badrua R., Singha P., Kumarb S., Mittal S.K. *J Anal Chem.*, 2019, **74**:800
- [8]. Chen K., He J., Li Y., Cai X., Zhang K., Liu T., Hu Y., Lin D., Kong L., Liu J. *J Colloid Interface Sci.*, 2017, **494**:307
- [9]. Bhanjana G., Dilbaghi N., Kim K.H., Kumar S. *J Mol Liq.*, 2017, **242**:966
- [10]. Tabesh S., Davar F., Loghman-Estarki M.R. *J. Alloy Compd.*, 2018, **730**:441
- [11]. Awual M.R., Khraisheh M., Alharthi N.H., Luqman M., Islam A., Karim M.R., Rahman M.M., Khaleque M.A. *Chem Eng J.*, 2018, **343**:118
- [12]. Mohan C., Sharma K., Chandra S. *Anal Bioanal Electrochem.*, 2017, **9**:35
- [13]. Rezvani Ivani S.A., Darroudi A., Arbab Zavar M.H., Zohuri G., Ashraf N. *J Arab Chem.*, 2017, **10**:S864
- [14]. Aglan R.F., Hamed M.M., Saleh H.M. *J Anal Sci Technol.*, 2019, **10**:1
- [15]. Bakhshi F., Farhadian N. *Int J Hydrogen Energy.*, 2018, **43**:8355
- [16]. Farmanzadeh D., Abdollahi T. *Surf Sci.*, 2018, **668**:85
- [17]. Özkaya S., Blaisten-Barojas E. *Surf Sci.*, 2018, **674**:1
- [18]. Luo D., Zhang X. *Int J Hydrogen Energy.*, 2018, **43**:5668
- [19]. Esrafil M.D., Dinparast L. *J Mol Graph Model.*, 2018, **80**:25
- [20]. Janani K., John Thiruvadigal D. *Appl Surf Sci.*, 2018, **449**:829
- [21]. Ahmadi R., Jalali Sarvestani M.R. *Phys Chem Res.*, 2018, **6**:639

- [22]. Cortés-Arriagada D., Villegas-Escobar N. *Appl Surf Sci.*, 2017, **420**:446
- [23]. Jalali Sarvestani M.R., Ahmadi R. *J Water Environ. Nanotechnol.*, 2019, **4**:48
- [24]. Jalali Sarvestani M.R., Ahmadi R. *Asian J Nanosci Mater.*, 2020, **3**:103
- [25]. GaussView, Version 6.1, R. Dennington, Keith T. A., Millam J. M., Semiche Inc., Shawnee Mission, KS, 2016
- [26]. O'Boyle N.M., Tenderholt A.L., Langner K. *M. J Comp Chem.*, 2008, **29**:839
- [27]. Gaussian 16, 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.Petersson, G.A., Nakatsuji H., Li X., Caricato M., Marenich A.V., Bloino J., Janesko B.G., Gomperts R., Mennucci B., Hratchian H.P., Ortiz J.V., Izmaylov A.F., Sonnenberg J.L., Williams-Young D., Ding F., Lipparini F., Egidi F., Goings J., Peng B., Petrone A., Henderson T., Ranasinghe D., Zakrzewski V.G., Gao J., Rega N., Zheng G., Liang W., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Throssell K., Montgomery J.A., Peralta J.E., Ogliaro F., Bearpark M.J., Heyd J.J., Brothers E.N., Kudin K.N., Staroverov V.N., Keith T.A., Kobayashi R., Normand J., Raghavachari K., Rendell A.P., Burant J.C., Iyengar S.S., Tomasi J., Cossi M., Millam J.M., Klene M., Adamo C., Cammi R., Ochterski J.W., Martin R.L., Morokuma K., Farkas O., Foresman J.B., Fox D.J., Gaussian, Inc., Wallingford CT, 2016

How to cite this manuscript: Mohammad Reza Jalali Sarvestani*. The effect of doping graphene with silicon on the adsorption of cadmium(II): theoretical investigations. *Journal of Medicinal and Nanomaterials Chemistry*, 2(4) 2020, 280-290. DOI: [10.48309/JMNC.2020.4.2](https://doi.org/10.48309/JMNC.2020.4.2)