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Global Reactivity Descriptors and Thermal Analyses of Polyethylene Terephthalate Interacted with Cd and Pb

Medhat Ibrahim

Molecular Spectroscopy and Modeling Unit, Spectroscopy Department, National Research Centre, 33-El-Bohouth Str. 12622 Dokki, Giza, Egypt

Abstract

Polyethylene terephthalate (PET) is one of the most commonly produced synthetic plastics worldwide. According to its cost effective and easy handling it is a subject of extensive work in both theoretical and experimental aspects. In this work a model is designed to describe the possible interaction between PET and di-hydrated Cd and di-hydrated Pb. The scheme of interaction is described then the global reactivity descriptors are calculated at density functional theory DFT at B3LYP with SDD basis set. Thermochemical parameters including enthalpy; entropy; free energy; heat capacity and heat of formation will be calculated at PM6 semi-empirical level of theory. Results indicated that, hydrated Pb and Cd could be coordinated with PET which indicated that ability of PET to remediate Cd and Pb from the environment. It could be concluded that, PET is an effective tool to remediate di-hydrated Cd and di-hydrated Pb from wastewater.

Keywords: PET; Cd; Pb; DFT and Thermochemical parameters

1. Introduction

Because plastic materials are strong, flexible, and inexpensive to produce, they are used extensively in both industry and daily life [1]. A synthetic plastic that is made most frequently nowadays is polyethylene terephthalate (PET) [2]. It is the most popular thermoplastic polymer resin in the polyester family, It is used to make garment fibers, food and drink containers, thermoforming, and engineering resins when combined with glass fiber [3-4]. High strength and toughness, a high glass transition temperature, remarkable mechanical capabilities, chemical resistance, and exceptional dimensional stability are just a few of the distinctive qualities and attributes that make PET an aromatic and semi-crystalline polymer [5-7]. The USEPA reported that 29.1% of PET bottles and jars were recycled in 2018. Even while this recycling percentage is significantly greater than the 8.7% global plastic recycling rate, the volume of PET produced highlights the need for a significant improvement in recycling rates [8]. It was suggested that its broad range of application modeling may be used to regulate the amount of lead in the environment. Modeling is a type of computer-based activity where the provided structure is optimized. Modeling at various levels and theories can yield some significant parameters [9–10]. For many chemical systems, modeling may be a helpful technique for clarifying important physical, chemical and structural parameters [11–13]. Several recycling techniques, such as primary, secondary, tertiary, and quaternary recycling, have been investigated. Reintroducing plastic trash into manufacturing lines is known as primary recycling; however, this process necessitates extremely low contamination levels, making it impossible to recycle domestic plastic garbage without extensive processing [14]. Waste plastic is separated and processed using mechanical techniques like melting and grinding in secondary recycling, which is the most popular kind of plastic recycling [15]. The breakdown of polymer backbones to create monomers, oligomers, and other useful intermediates is known as tertiary recycling, or chemical recycling. The capacity to completely close the plastic recycling loop without sacrificing the material's desired qualities is tertiary recycling's primary benefit [16]. Quaternary recycling, also known as energy recovery, offers a last resort for recovering plastics by burning discarded plastic to produce electricity or heat [17]. For the purpose of purifying wastewater that contains dyes, radionuclides, and heavy metals, PET waste can be transformed into activated carbon [18–20]. PET is also a great option for adsorbent feedstock due to its stable chemical and physical characteristics, even after several applications [21]. An innovative recycled PET/tannin nanofiber was created to effectively remove lead II from water [22]. Despite this, there are a lot of opportunities for using recycled PET nanofibers for metal adsorption, which has never been done before. If tannins are combined with PET to create PET/tannin nanofibers for the adsorption of lead (II), this might be further improved [23].

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

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2. Calculation Details

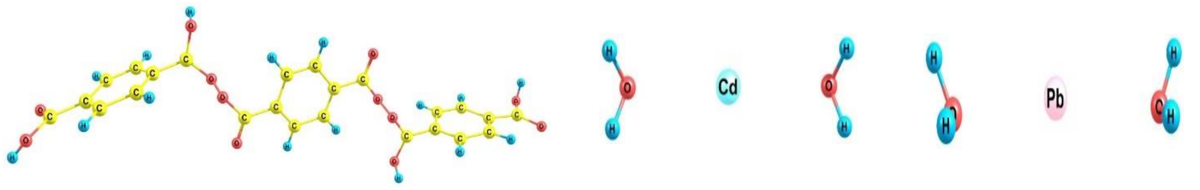
A model molecule for PET is constructed then possible interaction with di-hydrated Cd and Pb were studied using the GAUSSIAN 09 software package [24] implemented at the Molecular Modeling and Spectroscopy Laboratory, Centre of Excellence for Advanced Science, National Research Centre, Egypt. The molecular structures were optimized and calculated using Density Functional Theory (DFT) with Becke's three-parameter exchange and Lee-Yang- Parr correlation functional (B3LYP) [25-27], employing the SDD basis set. The reactivity of functionalized PET was analyzed through electronic descriptors, global reactivity descriptors. Such reactivity indices are the electron affinity (A), ionization energies (I), electrophilicity index (ω), nucleophilicity index (ε), chemical potential (μ), electronegativity (χ), hardness (η), and softness (S). these parameters could be calculated from a so called applied Koopmans' theorem which depends mainly on the frontier molecular orbitals HOMO and LUMO [28-29]. Thermochemical parameters such as Enthalpy; Entropy; Free energy; Heat capacity and Heat of formation as a function of temperature using PM6 level of theory [30]. The calculations were conducted using SCIGRESS Softcode [31] Which is also implemented at Molecular Modeling and Spectroscopy Laboratory, Centre for Excellence for Advanced Science, National Research Centre, Egypt.

3. Results and discussion

Before discussing the obtained results it is important that, the process of building of the studied model molecules are described. Figure 1 presented the studied model molecules, whereas Figure 1-a presnted the PET model which consists of three PET units; then Figure 1-b, which indicated that di-hydrated cadmium Cd.$2H_2O$ and finally Figure 1-c indicated that, di-hydrated Lead (Pb.$2H_2O$).

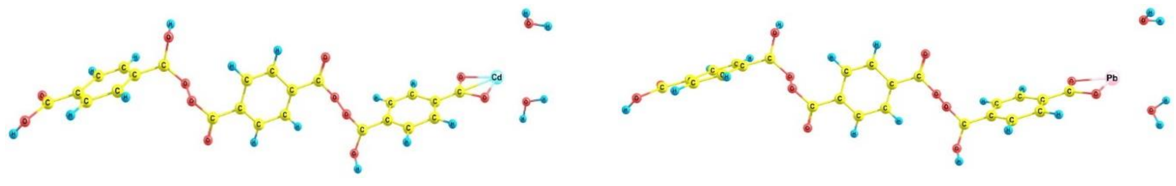
Figure 2 presented model molecules for di-hydrated cadmium interacts with PET through the hydrogen of the carboxyl group, forming a one-and-a-half linkage, resulting in (PET·Cd·$2H_2O$) as shown in Figure 2-a. then di-hydrated lead interacts with PET through the hydrogen of the carboxyl group, also forming a one-and-a-half linkage, resulting in (PET·Pb·$2H_2O$) as indicated in Figure 2-b.

Another model indicated in Figure 3-a in which di-hydrated cadmium interacts with two PET models through two hydrogen of two carboxyl resulting in (2PET.Cd.$2H_2O$). Figure 3-b indicated that, the di-hydrated lead interacts with two PET models through two hydrogen of two carboxyl, resulting in (2PET.Pb.$2H_2O$). Models in Figures 2 and 3 indicated a stable structure which is an indication for possible remediation of Pb and Cd with PET.



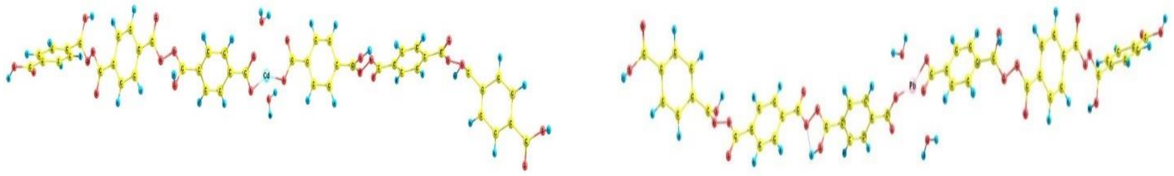
(a) **(b)** **(c)**

Figure 1. Model molecules for the studied structures (a) PET model; (b) Di-hydrated Cadmium (Cd.$2H_2O$); and (c) Di-hydrated Lead (Pb.$2H_2O$).



(a) **(b)**

Figure 2. Model molecules for the studied structures are as follows: (a) Di-hydrated cadmium interacts with PET through the hydrogen of the carboxyl group, forming a one-and-a-half linkage, resulting in (PET·Cd·$2H_2O$); (b) Di-hydrated lead interacts with PET through the hydrogen of the carboxyl group, also forming a one-and-a-half linkage, resulting in (PET·Pb·$2H_2O$).



(a) **(b)**

Figure 3. Model molecules for the studied structures (a) Di-hydrated cadmium interacts with two PET models through two hydrogen of two carboxyl resulting in (2PET.Cd.2H2O); and (b) Di-hydrated lead interacts with two PET models through two hydrogen of two carboxyl, resulting in (2PET.Pb.2H2O).

Regarding the optimized structures in Figure 2 and 3, both Cd and Pb could interact with PET as bidentate complex with carboxyl group as in Figure 2. Another scheme of interaction is indicated in Figure 3 as each metal (Cd and Pb) interacted as unidentate complex with two carboxyl groups located in two PET models. The existence of optimized structures for both scheme indicated that both Cd and Pb could be coordinated with PET as one unit and/or two PET units.

Table 1 presented the global reactivity descriptors of PET, Cd.2H_2O, Pb.2H_2O, PET.Cd.2H_2O, 2PET.Cd.2H_2O, PET.Pb.2H_2O and 2PET. Pb.2H_2O.

Global reactivity descriptors are a set of parameters based on HOMO and LUMO energies that can be calculated to provide further insights on the reactivity of the structures under study [32]. The calculate values that represent the global reactivity descriptors are ionization potential (I) which is the amount of energy required to release the least bound electron from its occupied orbital [33]; electron affinity (A) which represents the amount of energy difference between the lowest states of both a neutral atom and its corresponding negative ion [34]. Chemical hardness (η) is another important parameter which is considered as a measure of the resistance to change in the electron distribution of atoms, ions, and molecules [35]. The electronic chemical potential (μ) is an indicator for a reaction taking place, such that a molecule with a high μ is considered a good electron donor, while that with a low μ is a good electron acceptor [33]. Absolute chemical softness (S) is the opposite to hardness, and it refers to the capacity to attract electron, such that the higher S, the more the reactivity of the molecule [36]. Electrophilicity index (ω) is an important descriptor of electrophilic nature of molecules, representing a measure of energy reduction when electrons flow from a donor to an acceptor, such that the molecule with higher ω will react as an electrophile, while the molecule with the lower ω will react as a nucleophile [37]. One last descriptor is electronegativity (χ) which is the measure of the tendency of the molecule to attract electrons [38].

Table 1. Global reactivity descriptors including Ionization Potential (I); Electronic Affinity (A); Chemical hardness (η); Electronic chemical potential (μ); Absolute softness (S); Electrophilicity index (ω) and Electronegativity (χ) for 1- PET; 2-Cd.2H_2O; 3- Pb.2H_2O; 4- PET.Cd.2H_2O (alpha); 5- PET.Cd.2H_2O (beta); 6- 2PET.Cd.2H_2O; 7- PET.Pb.2H_2O (alpha); 8- PET.Pb.2H_2O (beta) and 9- 2PET. Pb.2H_2O.

	(I)	**(A)**	**(η)**	**(S)**	**(ω)**	**(χ)**
1	5.046	4.771	0.137	7.262	87.498	4.908
2	5.079	0.261	2.409	0.415	1.480	2.670
3	2.692	1.917	0.387	2.580	6.856	2.305
4	6.585	3.308	1.638	0.610	7.466	4.946
5	3.658	3.402	0.128	7.794	48.576	3.530
6	3.997	3.756	0.120	8.304	62.406	3.876
7	3.788	3.190	0.299	3.343	20.359	3.489
8	5.952	3.201	1.375	0.727	7.615	4.577
9	4.002	3.799	0.101	9.852	74.946	3.900

As demonstrated in table 1, before interaction, the ionization potential of Pb.2H_2O was the lowest indicating that it is more reactive than Cd.2H_2O, while upon interaction the ionization potential of PET.Cd.2H_2O (beta) was the lowest, revealing that it is more reactive than the other interactions. In terms of η, the structure with the highest η upon interaction was PET.Cd.2H_2O (alpha) indicating that it is the most stable and less reactive, while the least stable, hence more reactive, structure was 2PET. Pb.2H_2O. The obtained values of S demonstrated the same result in which 2PET. Pb.2H_2O had the highest value of S indicating that it is the most reactive structure while PET.Cd.2H_2O (alpha) was the least reactive. The PET.Cd.2H_2O (alpha) structure is also considered a good electron acceptor as evidenced by its lowest value of μ, while the PET.Pb.2H_2O (alpha) structure with its highest value of μ is considered a good electron donor in comparison to other structures. This result was supported by the calculated values of χ which revealed that PET.Cd.2H_2O (alpha) with its highest of χ has the highest tendency of to attract electrons while PET.Pb.2H_2O (alpha) has the least tendency.

Thermochemical parameters for PET are studied, it is described as an important factor indicating the stability of PET specially after interacting with the studied hydrated Cd and Pb.

The studied thermochemical parameters have been individually established as in the following.

Enthalpy is a measure of energy in a thermodynamic system; thermodynamic quantity equivalent to the total heat content of a system [39]. Entropy is a scientific concept that is most commonly associated with a state of disorder, randomness, or uncertainty [40]. The change in the free energy is the maximum amount of work that the system can perform in a process at constant temperature, and its sign indicates whether the process is thermodynamically favourable or forbidden [41]. Heat Capacity is a physical property of matter, defined as the amount of heat to be supplied to an object to produce a unit change in its temperature [42]. Heat of Formation is the amount of heat absorbed or evolved when one mole of a compound is formed from its constituent elements, each substance being in its normal physical state (gas, liquid, or solid), usually the conditions at which the compound is formed are taken to be at a temperature of 25 °C [43].

Table ۲ presented, the thermochemistry of PET molecule for Enthalpy, Entropy, Free Energy, Heat Capacity and Heat of Formation at Temperature from 200 (K) to 500 (K). Results indicated that all the studied thermal parameters are increased with increasing temperature up to 500 K. Regarding the same thermochemical parameters for PET interacted with Cd and Pb.

Table 3 presented the thermochemistry for PET·Cd·2H_2O, results show an increase in thermal parameters with a noticeable increase as a function of temperature. The thermochemistry for PET·Pb·2H_2O, is tabulated in table 4 almost comparable with those obtained for PET·Cd·2H_2O with the same behaviour.

Table 5 showed the thermochemistry of 2PET.Cd.2H_2O, in which Cd is interacted with two models of PET. A noticeable increase in the calculated parameters is regarded. The same behaviour is regarded as tabulated in table 6 corresponding for the 2PET. Pb.2H_2O molecule.

Collecting the results of the calculated thermochemical parameters, one can conclude that, the PET could interact with di-hydrated Cd and Pb forming a stable structure this in turn could be an indication for the ability of PET to be used in the environment to remediate these metals from wastewater.

Table 2. Thermochemistry of PET molecule for Enthalpy (Kcal/mol), Entropy (Cal/mol/k), Free Energy (Kcal/mol), Heat Capacity (Cal/mol/k) and Heat of Formation (Kcal/mol) at Temperature from 200 (K) to 500 (K)

T, K	Enthalpy	Entropy	Free energy	Heat capacity	Heat of formation
200	11.391	196.668	-293.811	92.039	-369.798
250	16.424	219.059	-275.379	109.235	-364.765
300	22.305	240.459	-258.041	125.896	-358.884
350	28.997	261.060	-241.751	141.600	-352.191
400	36.445	280.928	-226.475	156.086	-344.744
450	44.584	300.086	-212.173	169.256	-336.605
500	53.349	318.544	-198.811	181.130	-327.840

Table 3. Thermochemistry of PET·Cd·2H_2O molecule for Enthalpy (Kcal/mol), Entropy (Cal/mol/k), Free Energy (Kcal/mol), Heat Capacity (Cal/mol/k) and Heat of Formation (Kcal/mol) at Temperature from 200 (K) to 500 (K)

T, K	Enthalpy	Entropy	Free energy	Heat capacity	Heat of formation
200	13.810	222.701	-295.348	112.580	-397.129
250	19.935	249.956	-270.590	132.335	-391.003
300	27.031	275.779	-247.159	151.366	-383.907
350	35.053	300.475	-224.989	169.297	-375.885
400	43.937	324.177	-204.029	185.824	-367.001
450	53.610	346.945	-184.231	200.826	-357.328
500	63.995	368.816	-165.548	214.332	-346.943

Table 4. Thermochemistry of PET·Pb·2H_2O molecule for Enthalpy (Kcal/mol), Entropy (Cal/mol/k), Free Energy (Kcal/mol), Heat Capacity (Cal/mol/k) and Heat of Formation (Kcal/mol) at Temperature from 200 (K) to 500 (K)

T, K	Enthalpy	Entropy	Free energy	Heat capacity	Heat of formation
200	13.884	223.116	-189.325	115.461	-297.886
250	20.172	251.096	-162.891	135.973	-291.597
300	27.469	277.649	-137.819	155.747	-284.301
350	35.729	303.076	-114.046	174.426	-276.041
400	44.888	327.511	-91.518	191.682	-266.882
450	54.871	351.009	-70.189	207.368	-256.899
500	65.599	373.602	-50.012	221.493	-246.171

Table 5. Thermochemistry of 2PET.Cd.2H_2O molecule for Enthalpy (Kcal/mol), Entropy (Cal/mol/k), Free Energy (Kcal/mol), Heat Capacity (Cal/mol/k) and Heat of Formation (Kcal/mol) at Temperature from 200 (K) to 500 (K)

T, K	Enthalpy	Entropy	Free energy	Heat capacity	Heat of formation
200	24.821	363.608	-737.041	202.219	-913.478
250	35.836	412.618	-694.169	238.218	-902.463
300	48.618	459.132	-653.683	272.770	-889.681
350	63.077	503.643	-615.469	305.151	-875.222
400	79.090	546.364	-579.437	334.918	-859.209
450	96.522	587.398	-545.499	361.928	-841.777
500	115.240	626.813	-513.571	386.251	-823.061

Table 6. Thermochemistry of 2PET. Pb.2H_2O molecule for Enthalpy (Kcal/mol), Entropy (Cal/mol/k), Free Energy (Kcal/mol), Heat Capacity (Cal/mol/k) and Heat of Formation (Kcal/mol) at Temperature from 200 (K) to 500 (K)

T, K	Enthalpy	Entropy	Free energy	Heat capacity	Heat of formation
200	25.362	378.860	-709.725	205.549	-883.733
250	36.531	428.559	-667.478	241.055	-872.563
300	49.445	475.555	-627.645	275.222	-859.649
350	64.019	520.423	-590.108	307.349	-845.075
400	80.138	563.426	-554.767	336.958	-828.957
450	97.669	604.694	-521.532	363.867	-811.425
500	116.480	644.309	-490.318	388.122	-792.614

Reaction mechanism: The reaction mechanism which is conducted in this work could be indicated also in terms the studied molecular modeling level of theory. Each metal (Cd and/or Pb) is going to be hydrated with two water molecules. Then each hydrated metal is interacting with two chains of PET is indicated in Figure 4. More precisely, each metal is coordinated with to hydrogen bonding resulting from two carboxyl groups, each group is a terminal of PET chain. In this sense the interaction between Cd and/or Pb as di-hydrated form with PET is described in terms molecular modeling.

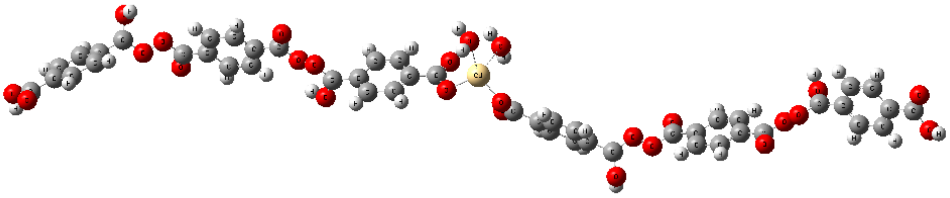


Figure 4. Model molecule for the reaction mechanism in which di-hydrated metals (Cd.2H_2O and/or Pb.2H_2O) is interacting with two chains of PET forming (2PET.Cd.2H_2O and/or 2PET.Cd.2H_2O)

4. Conclusions

Molecular modeling at DFT: B3LYP/SDD show the ability to describe the possible interaction between PET and hydrated Cd and Pb.

PET is reactive as indicated by the calculated reactivity descriptors and thermochemical parameters.

It is worth to mention that, the calculated thermochemical parameters indicated that, the studied PET interacted with hydrated Cd and Pb are chemically stable. This leads to that conclusion that, PET weather single and/or double molecule is interacted with Cd and/or Pb in hydration form with forming thermal stability compound.

The studied PET in terms the reactivity descriptors and thermochemical parameters is stable structure could be used to interact with heavy metals specially cd and Pb.

PET which is cheap and easy handling structure could be of concern in environmental applications. This paves the way toward application of PET in the remediation of Cd and Pb from wastewater.

5. Conflicts of interest

The authors declare that they have no conflict of interest.

6. Formatting of funding sources

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