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Application of quantum descriptors for predicting adsorption performance of starch and cyclodextrin adsorbents

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ABSTRACT

Adsorption trend of aromatic compounds on epichlorohydrin (EPI), 1,6-hexamethylene diisocyanate (HDI), and 4,4-methylene diphenyl diisocyanate (MDI) cross-linked starch and cyclodextrin adsorbents were comparatively studied by density functional theorem (DFT) based interaction descriptors and batch adsorption studies. The DFT quantum chemical descriptors predicted adsorption trend of MDI adsorbents > HDI adsorbents > EPI adsorbents. The values of the fractional number of electrons transferred (ΔN) for all the studied adsorbent–adsorbate pair were negative, indicating that the adsorbents were electron donors in the studied adsorption interaction. The batch adsorption performance for the studied cross-linked adsorbents was in agreement with the DFT predictions. Energy gap, chemical hardness, and softness showed good linear correlation ($R^2 = 0.8073 \pm 0.2259$) to the batch adsorption performance for most of the studied adsorbent–adsorbate pairs. The present study demonstrated that DFT quantum chemical parameters are suitable adsorption descriptors for predicting adsorption performance of cross-linked adsorbents.

1. Introduction

Adsorption has proved to be the procedure of choice for treating water pollution caused by polycyclic aromatic hydrocarbon (PAHs) and phthalate esters (Chen, Yuan, & Liu, 2011; Julinova & Slavik, 2012). However, cost limitation and biodegradability challenges of the common adsorbents have posed a serious set-back on the full utilization of adsorption technology for water treatment, thus creating the need to source for alternative adsorbents.

Starch and its derivative, cyclodextrin, represent cheap and environmentally safe precursors for the preparation of low-cost adsorbents that have proved to be useful for the removal of pollutants from wastewater (Datskevich, 2009; Guo, Li, Liu, Yin, & Li, 2009; Simkovic, Laszlo, & Thompson, 1996). Starch and cyclodextrin are amenable to a variety of chemical modifications which include: substitution, grafting, and cross-linking reactions to produce materials with novel properties (Ahmed, Tiwari, Imam, & Rao, 2012). Among these methods, cross-linking process has proved to be the most effective way of developing starch and cyclodextrin based adsorbents, because modification of these polysaccharides by cross-linking of the glucose chains of starch polymer or that of cyclodextrin molecules not only increases hydrophobicity, but also provides opportunity for tuning the sorption properties of the adsorbent as a function of the nature of the cross linking agent as well as degree of cross linking process (Crini, 2005).

The tunable adsorption properties of these cross-linked polymers have been utilized in the past by adopting different cross-linking agents like epichlorohydrin (EPI), hexamethylene diisocyanate (HDI), dimethyl diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), adipic acid, succinic anhydride, etc. with varying degree of success in terms of adsorption performance (Delval, Crini, Bertini, Filiatre, & Torri, 2005; Kwak, Lee, & Chang, 2011). Considering the array of cross-linking agents, polymer scientists face the challenge of selecting a suitable cross-linking agent that will be most effective for a given target pollutant. So far, the conventional approach for assessing the design and adsorption performance of these cross-linked polymer adsorbents has only been experimental studies. Based on this approach, the cross-linked polymers have to be synthesized using the various available cross-linking agents, characterized to confirm successful cross-linking process, and thereafter screened based on their respective adsorption performance. Apart from being laborious and time consuming, this approach is not cost effective, hence there is a need for theoretical/computational approach for predicting the likely adsorption

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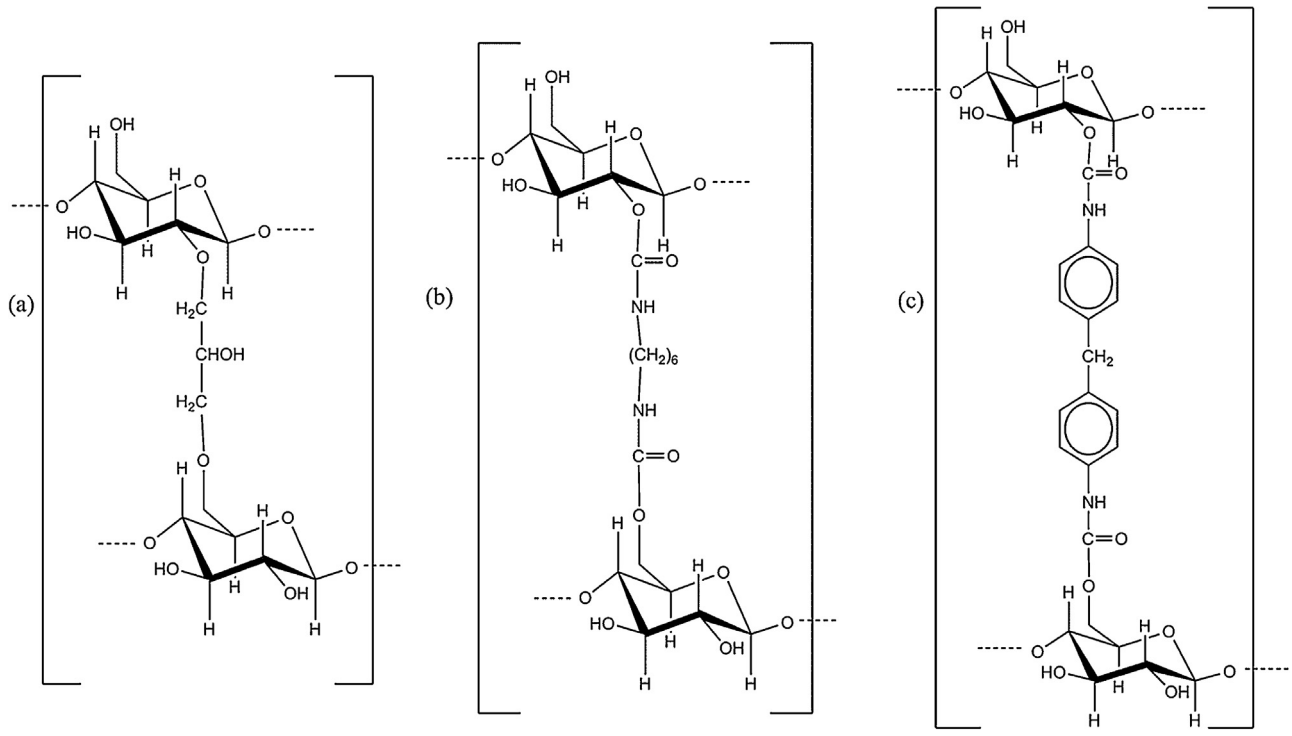

Fig. 1. Monomer structures of (a) EPI, (b) HDI, and (c) MDI cross-linked adsorbents.

potential and/or trend which can serve as a feasibility guide in choosing a suitable cross-linking agent in the application of cross-linked polymer adsorbents for water treatment.

The design and selection of adsorbents for a target adsorbate molecule is based on the adsorption isotherm, and this can be evaluated based on interaction potentials and structure/geometry of the adsorbent. The total potential between the adsorbate molecules and the adsorbent is the sum of the total adsorbate–adsorbate and the adsorbate–adsorbent interaction potentials. The adsorbate–adsorbent potential is considered more relevant because the adsorbent has only a secondary effect on the adsorbate–adsorbate interaction (Yang, 2003).

Density functional theorem (DFT) has become an attractive theoretical method for evaluation of molecular interaction, because it has proved to be adequate for pointing out the changes in electronic structure responsible for chemical interaction, otherwise known as quantum chemical descriptors. In addition to this, DFT gives exact values of these basic vital parameters for even huge complex molecules at low cost. DFT quantum chemical descriptors have been successfully applied in assessing adsorption (Rafati, Hashemianzadeh, & Nojini, 2008; Shirvani, Beheshtian, Parsafar, & Hadipour, 2010; Udhayakala, Rajendiran, & Gunasekaran, 2012).

This study was therefore designed to explore the relationship between DFT quantum chemical descriptors and adsorption performance of cross-linked starch and β-cyclodextrin polymer adsorbents for sorption removal of aromatic compounds in aqueous media. Also, this study assessed the applicability of these molecular interaction descriptors as reliable tool for predicting the adsorption performance of the cross-linked adsorbents.

2. Experimental methods

2.1. DFT computational studies

Monomer units of EPI, HDI, and MDI cross-linked polymer adsorbents (Fig. 1) were adopted as representative structural models for the adsorbents, while the full molecular structures of the adsorbates (acenaphthylene, phenanthrene, benzo[a]anthracene (BaA), and diethyl phthalate (DEP)) were adopted for the computational studies. All the quantum calculations with full-geometry optimizations were performed using Spartan 10v1.0.1. suite of programs. Geometry optimizations and calculation of energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), dipole moment, and QSAR volume of adsorbents and adsorbates were performed with the DFT method at B3LYP level of theory with the 6-31G basis set.

2.2. Preparation and characterization of the adsorbents

The cross-linked polymer adsorbents have been prepared in one step by reticulation of the precursors (starch or β-cyclodextrin) using different cross-linking agents: EPI, HDI, MDI. Each family of adsorbents was prepared by reacting a given mass of either of the precursors with various quantities of each of the cross-linking agents, to produce cross-linked adsorbents with varying degree of cross-linking. The nomenclature of the cross-linked polymers was described according to the nature of the precursor, type of cross-linking agent and the precursor/cross-linking agent ratio (which equally reflects the degree of cross-linking process achieved). For the synthesis of EPI cross-linked starch (EPICS: EPICS1, EPICS2, EPICS3, and EPICS 4) and EPI cross-linked β-cyclodextrin polymer (EPIBCD: EPIBCD1, EPIBCD2, EPIBCD3, and EPIBCD4) families of adsorbents, the synthetic method developed by Simkovic et al. (1996) was adopted. The synthetic method described by Ozmen and Yilmaz (2007) was adopted for the synthesis of HDI cross-linked starch (HDICS: HDIC1, HDICS2, HDICS3, and HDICS4), MDI cross-linked starch (MDICS: MDICS1, MDICS2, MDICS3, and MDICS4), HDI β-cyclodextrin polymer (HDIBCD: HDIBCD1, HDIBCD2, HDIBCD3 and HDIBCD4), and MDI β-cyclodextrin polymer (MDIBCD: MDIBCD1, MDIBCD2, MDIBCD3, and MDIBCD4) families of adsorbents, with increase in the ratios of the cross linking agents to improve the mechanical strength of the polymer adsorbents. (See Table S1 of supporting materials

for details of the quantities of the reactants and designation of the adsorbents.)

After the synthesis, the cross-linked polymers were separated by filtration, and thereafter washed copiously with distilled water, and further purified in a soxhlet unit using acetone for 12 h. The polymer was finally lyophilized, and kept in a desiccator prior to use to prevent re-absorption of water from laboratory environment.

Infra-red (FT-IR) spectra of the synthesized adsorbent were obtained using Perkin Elmer Spectrum 1 FTIR spectrophotometer, scanning from 4000 to 450 cm^{-1}, to confirm the presence of new functional groups introduced as a result of the cross linking process.

Elemental (carbon, hydrogen, and nitrogen) analysis was conducted using an Elementar (Germany) Vario Macro Cube analyzer. The oxygen content was determined by a mass balance. The percentage carbon content, H/C and (O + N)/C atomic ratios were calculated to evaluate the hydrophobicity, aromaticity and polarity of the adsorbents respectively.

2.3. Adsorption study

Batch adsorption experiments were carried out by agitating a 50 ml volume of simulated PAH or phthalate polluted water samples with desired dose of adsorbent (50 and 20 mg for PAHs and DEP, respectively) in 50 ml capacity glass stopped Erlenmeyer flasks covered with aluminum foil, at 170 rpm for 24 h at room temperature (25 ± 2 °C), using a horizontal shaker water bath. The initial concentrations of single solute solutions of acenaphthylene, phenanthrene, BaA and DEP were 1.2, 3.0, 0.01 and 4.2 mg/L, respectively. After equilibrium was attained, aliquot solutions were separated from the adsorbent by centrifugation at 4000 rpm for 15 min, and the equilibrium pollutant concentrations were determined by high performance liquid chromatography (HPLC) system (PerkinElmer Series 200 (USA) using Brownlee Analytical (PerkinElmer, USA) PAH reverse phase column (150 mm × 3.2 mm, 5 μm, 110 Å). Acenaphthylene and DEP were detected with UV detector while phenanthrene and BaA were detected by fluorescence detector (see supporting material for full description of HPLC analysis). All the adsorption experiments were performed in duplicates.

A blank study was done by adding a known mass of the adsorbent to a given volume of Milli-Q water free of organic traces to check whether the adsorbent could release PAHs in the aqueous solution. For every experiment, adsorbent free PAH solutions were subjected to the same experimental conditions to evaluate the loss of PAHs to factors, other than adsorption.

2.4. Data treatment

2.4.1. DFT computational study

Quantum chemical descriptors such as ionization potential (I), electron affinity (A), energy gap (ΔE), chemical hardness (η), softness (S), chemical potential (μ) and fractional number of electron transferred between the adsorbent and adsorbate (ΔN) were respectively calculated according to Eqs. (1)–(7) (Ebenso et al., 2010).

$$I = -E_{HOMO} \tag{1}$$

$$A = -E_{LUMO} \tag{2}$$

$$\Delta E = E_{HOMO} - E_{LUMO} \tag{3}$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} = \frac{I - A}{2} \tag{4}$$

$$S = \frac{1}{\eta} = \frac{2}{I - A} \tag{5}$$

$$\mu = -\frac{I + A}{2} \tag{6}$$

$$\Delta N = \frac{\mu_B - \mu_A}{2(\eta_A - \eta_B)} \tag{7}$$

where E_{LUMO} and E_{HOMO} are the energies of lowest unoccupied molecular orbitals and highest occupied molecular orbitals, respectively, generated from the DFT calculations, μ_A and μ_B are the chemical potentials of the adsorbent (A) and adsorbate (B), and η_A and η_B are chemical hardness of the adsorbent (A) and adsorbate (B).

2.4.2. Batch adsorption study

Adsorption capacities for each of the adsorbents q_e, and mean adsorption capacity for each family of the adsorbents $\bar{q}_{eA}$, were calculated according to Eqs. (8) and (9), respectively.

$$q_e = \frac{(C_o - C_e)V}{M} \tag{8}$$

$$\bar{q}_{eA} = q_{eA1} + q_{eA2} + q_{eA3} + q_{eA4} \tag{9}$$

where q_e is the equilibrium sorption capacity (mg/g); C_o and C_e (mg/L) are adsorbate concentrations before and after adsorption, respectively; V is the volume of the experimental solution (L); M is the mass of sorbent (g), $\bar{q}_{eA}$ is the mean adsorption capacity for each family of adsorbents (mg/g), q_{eA1}, q_{eA2}, q_{eA3}, and q_{eA4} are the sorption capacities of individual adsorbents that comprised each of the adsorbent families (A), thus A represents the following families of adsorbents: EPICS, HDICS, MDICS, EPIB CD, HDIB CD, and MDIBCD.

2.4.3. Study of relationship between the batch adsorption performance and the computational predictions

Linear correlation analysis was applied for evaluation of the relationship between the batch adsorption performances of cross-linked adsorbents and the DFT theoretical predictions.

The values of DFT based quantum chemical descriptors reflect the nature of the cross-linking process. Therefore, to evaluate the correlation for the effect of nature of cross-linking process for starch adsorbents, the mean adsorption capacities $\bar{q}_{eA}$, for EPICS, HDICS and MDICS for a given adsorbate, were linearly correlated with the respective values of DFT quantum parameters for these adsorbents. To evaluate the correlation for the DFT quantum prediction based on ΔE, the values of $\bar{q}_{eA}$ for EPICS, HDICS and MDICS for acenaphthylene was correlated with the values of ΔE for these adsorbents. The $\bar{q}_{eA}$ values for phenanthrene, BaA, and DEP were also similarly correlated with the ΔE of these adsorbents, to study the correlation between experimental adsorption of these pollutants and predicted trend based on energy gap. The same procedure was adopted for correlation of experimental adsorption and η, S and dipole moment predicted trend. The entire procedure was repeated for the study of β-cyclodextrin polymer adsorbents using the $\bar{q}_{eA}$ values for EPIBCD, HDIBCD and MDIBCD for a given adsorbate and the respective DFT quantum parameters.

To evaluate the correlation between theoretical prediction and experimental adsorption for the effect of degree of cross-linking process, the adsorption capacity q_e, for individual adsorbents was correlated with their respective values of arbitrary degree of cross-linking process for each family of adsorbents.

Table 1
DFT generated quantum chemical descriptors of the cross-linked adsorbents.

Adsorbents/adsorbates	EPI ads[a]	HDI ads	MDI ads	Acy[b]	Phe[c]	BaA	DEP
E_{HOMO} (eV)	−6.45	−6.63	−5.57	−5.81	−5.73	−5.32	−6.95
E_{LUMO} (eV)	1.06	0.81	−0.18	−1.89	−0.99	−1.55	−1.40
Ionization potential, I	6.45	6.63	5.57	5.81	5.73	5.32	6.95
Electron affinity, A	−1.06	−0.81	0.18	1.89	0.99	1.55	1.40
Energy gap, ΔE (eV)	7.51	7.44	5.39	3.92	4.74	3.77	5.55
Chemical hardness, η (eV)	3.76	3.72	2.70	1.96	2.37	1.89	2.78
Chemical softness S (eV^{-1})	0.27	0.27	0.37	0.51	0.42	0.53	0.36
Dipole moment (Debye)	3.30	6.54	6.71	0.34	0.04	0.07	3.40
QSAR volume ($\tilde{A}$)	NA[d]	NA	NA	171.66	201.68	253.06	232.46
Number of transferred electron, ΔN							
ΔN for Acy	−0.10	−0.08	−0.10	NA	NA	NA	NA
ΔN for Phe	−0.05	−0.04	−0.05	NA	NA	NA	NA
ΔN for BaA	−0.07	−0.05	−0.06	NA	NA	NA	NA
ΔN for DEP	−0.11	−0.10	−0.12	NA	NA	NA	NA

[a] Adsorbent.
[b] Acenaphthylene.
[c] Pheneanthrene.
[d] Not applicable.

3. Results and discussion

3.1. Investigation of adsorption interaction using DFT computational studies

The success of DFT based global and local quantum chemical descriptors in predicting the chemical interaction and selectivity profiles of several systems is one of the interesting applications of quantitative structure activity relationship (QSAR) (Todeschini & Consonni, 2000). The DFT descriptors relevant to adsorption interactions are E_{HOMO}, E_{LUMO}, ionization potential (I), electron affinity (A), HOMO–LUMO energy gap (ΔE), chemical hardness (η), softness (S), chemical potential (μ), dipole moment of the adsorbent molecules, and the fractional number of electrons transferred between the adsorbent and adsorbate (ΔN) (Ebenso et al., 2010; Peyghan, Baei, Moghimi, & Hashemian, 2013).

Molecular orbital energies give information about reactivity/stability of specific regions of the molecule. Among the molecular orbitals, a fundamental role is played by the frontier orbitals (HOMO and LUMO), which are responsible for the formation of many charge transfer complexes such as those involved in adsorption interactions. Except dipole moment, all other descriptors discussed in this study were based on molecular orbital energies (Eqs. (1)–(7)). Table 1 shows the computed values of these DFT molecular interaction parameters for the adsorbents.

E_{HOMO} is the energy of the highest energy level containing electrons in the molecule. Molecules with high HOMO energy values can donate electrons more easily compared to molecules with low HOMO energy values, and hence are more reactive. Therefore, the E_{HOMO} descriptor is related to ionization potential (Eq. (1)) which is a measure of nucleophilicity of a molecule. E_{LUMO} is the energy of the lowest energy level containing no electrons in the molecule. Molecules with low LUMO energy values are more able to accept electrons than those with high values. Hence, E_{LUMO} descriptor is related to electron affinity A (Eq. (2)). The high HOMO and low LUMO energy values of the studied adsorbents are potentials for good adsorption interaction. However, neither ionization potential nor electron affinity alone can adequately describe adsorption interaction, since adsorption involves electron donation, acceptance and sharing. Therefore, quantum descriptors that incorporate both E_{HOMO} and E_{LUMO} are considered more adequate for describing adsorption interaction.

ΔE is a vital stability index which measures the difference between E_{LUMO} and E_{HOMO} (Eq. (3)). Large values of ΔE translate to high stability of a molecule and consequently low reactivity, and vice versa. ΔE is an approximation of the lowest excitation energy of the molecule, and thus can be used for the definition of chemical hardness and softness.

In simple terms, chemical hardness is a measure of the resistance to change in electron distribution or charge transfer. In DFT context, chemical hardness is mathematically defined as:

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial^2 N_e}\right) = \frac{1}{2}\left(\frac{\partial \mu}{\partial N_e}\right) = \int h(r)dr = \frac{1}{2S}$$

where μ, $h(r)$ and S are electronic chemical potential, hardness density, and total softness, respectively (Todeschini & Consonni, 2000).

However, on the basis of frontier molecular orbitals, chemical hardness and softness can be approximated with Eqs. (4) and (5). Based on Eqs. (3)–(5), ΔE and η were expected to have positive correlation, while S was expected to have negative correlation with the adsorption performance of the adsorbents. Based on the computed values of ΔE, η, and S; the expected trend of adsorption performance is MDI adsorbents > HDI adsorbents > EPI.

Dipole moment has been established to have a positive correlation with adsorbent–adsorbate intereaction (Yang, 2003). Based on the values of the dipole moment generated from the DFT quantum calculations, the predicted adsorption trend is MDI adorbents > HDI adsorbents > EPI adsorbents. This trend was equally in agreement with those of ΔE, η, and S.

Global adsorption interaction, ΔN has been successfully applied in corrosion inhibition studies where it has proved to be very reliable for assessing and predicting adsorption interaction of the inhibitor molecules with steel surfaces (Ebenso et al., 2010). It has been established that a positive value of ΔN indicates that charge flows from adsorbate to adsorbent, thus the adsorbent acts as electron acceptor, whereas a negative value of ΔN indicates that charge flows from adsorbent to adsorbate and that adsorbent acts as electron donor. The calculated ΔN values (Table 1) for all the studied adsorbent–adsorbate pair were negative, thus indicating that the adsorbents were electron donors in the adsorption process. The computed ΔN values of the adsorbents predicted the adsorption interaction of MDI adsorbents > EPI adsorbents > HDI adsorbents for acenaphthylene and diethyl phthalates respectively, and EPI adsorbents ≥ MDI adsorbents > HDI adsorbents for phenanthrene and BaA.

However, the reliability of ΔN as adsorption interaction descriptor has been found to be dependent on the magnitude of the

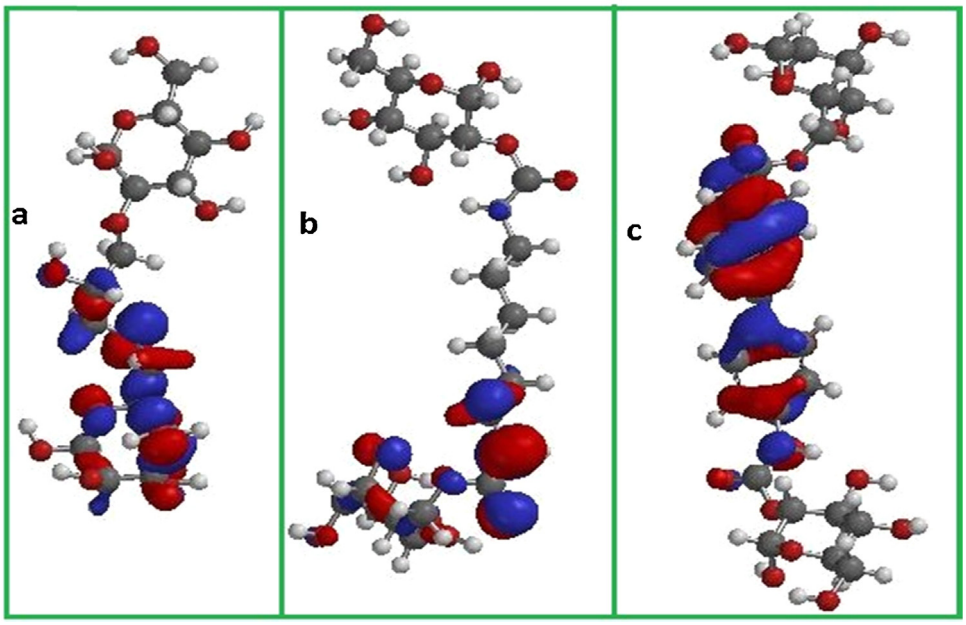

Fig. 2. Frontier molecular orbitals of E_{HOMO} of the monomer models of (a) epichlorohydrin (EPI) (b) 1,6-hexamethylene diisocyanate (HDI), and (c) 4,4-methylene diisocyanate (MDI) cross-linked adsorbents.

fraction of transferred electrons. For corrosion studies, it has been established that ΔN values are reliable as adsorption interaction descriptors when $\Delta N < 3.6$ (Ebenso & Obot, 2010). Hence, considering the very small values of ΔN for this study, it may not be a reliable adsorption descriptor. On the basis of frontier molecular orbital (FMO) theory (Musa, Kadhum, Mohamad, Rahoma, & Mesmari, 2010), it was observed that access to the HOMO orbitals (Fig. 2) of the cross-linked adsorbents were not the same, due to location and orientation of these orbitals. The orbitals of the MDI cross-linked adsorbents (MDICS and MDIBCD families) are more accessible due to their location on the cross-linker part of their representative model structure, while those of the EPI and HDI are substantially located on the glucose unit which forms part of the glucose chain of the polymer, and hence they are less accessible. Considering the foregoing, ΔN prediction of the adsorption interaction may not be reliable. Also, since the adsorbents were electron donors in the adsorption process, the chemical descriptors of electronegativity and chemical potential, that are based on electron acceptance were not considered as suitable descriptor.

Based on the values of the studied DFT molecular interaction descriptors, the predicted trend of adsorption interaction was MDI adsorbents > HDI adsorbents > EPI adsorbents.

Also, considering the adsorption schemes as shown in Fig. 3, increment in degree of cross-linking process leads to a corresponding increment in the number of interstitial spaces. Hence, the adsorption performance was expected to have a positive correlation with the degree of cross-linking process of the adsorbents.

However, prediction of adsorption performance based on interaction potentials assumes that the adsorbate molecules have uniform access to all the possible sorption/binding sites (Yang, 2003). Hence, surface area and pore characteristics equally play important contributory role in the real adsorption performance.

3.2. Characterization tests

3.2.1. Fourier transform infra red spectroscopy (FT-IR)

The IR spectra of both the pristine and cross-linked starch and cyclodextrin polymer adsorbents showed the characteristic peaks of anomeric C—H ring deformations (554, 596, 662, 596, 592, and 584 cm^{-1} for EPICS, HDICS, MDICS, EPIBCD, HDIBCD, and MDIBCD, respectively), in addition to normal C—O (1320–1000 cm^{-1}) and O—H (3500–3200 cm^{-1}) stretching vibrations of polymeric compounds especially polysaccharides, which implies that both the starch and cyclodextrin structural backbone was retained in the cross-linked polymer adsorbents. The presence of C—N (1247 and 1227 cm^{-1}) bands in the spectra of polyurethane based adsorbents (MDI and HDI cross-linked adsorbents) confirmed the successful introduction of nitro group into the starch and cyclodextrin polymer matrix. The spectra data of MDICS and MDIBCD polymer showed presence of aromatic C—H (3036 and 3041 cm^{-1} for MDICS and MDIBCD, respectively), C—C (1598 and 1405 cm^{-1} for MDICS and MDIBCD, respectively), and C—N stretch (1303 and 1318 cm^{-1} for MDICS and MDIBCD, respectively), C—H out of plane stretching (oops) vibration (819 and 746 cm^{-1} for MDICS and MDIBCD, respectively), and plane bending bands which confirmed the successful incorporation of aromatic group into the structural matrix of these adsorbents. The full details of the available peaks were shown by the FTIR spectra of each family of adsorbents (Fig. S1 of supporting documents).

3.2.2. Elemental composition

The elemental composition of the adsorbents is as shown in Table 2. The observed increment in carbon content in all the adsorbents with corresponding increment in the quantities of cross-linking agent translates to increment in the level of hydrophobicity of the adsorbents. This is in agreement with what has been reported by Ozmen and Yilmaz (2007). The data for the polyurethane based polymers showed increment in nitrogen content, and consequently the degree of cross-linking process as the quantity of cross linking agent was increased.

The (O + N)/C atomic ratios (Table 2), otherwise known as polarity coefficient of the polymers, is an important parameter to predict sorption (Chen, Yuan, & Liu, 2011; Olivella, Jové, & Oliveras, 2011). The values of the polarity coefficient of the polymers for the adsorbents under study ranged from 0.60 to 1.26, which is even higher than those of some commercial lignins (0.33–0.94), which had been adjudged to be good adsorbents for aromatic pollutants reported in literature (Wang & Xing, 2007). The values were relatively steady as

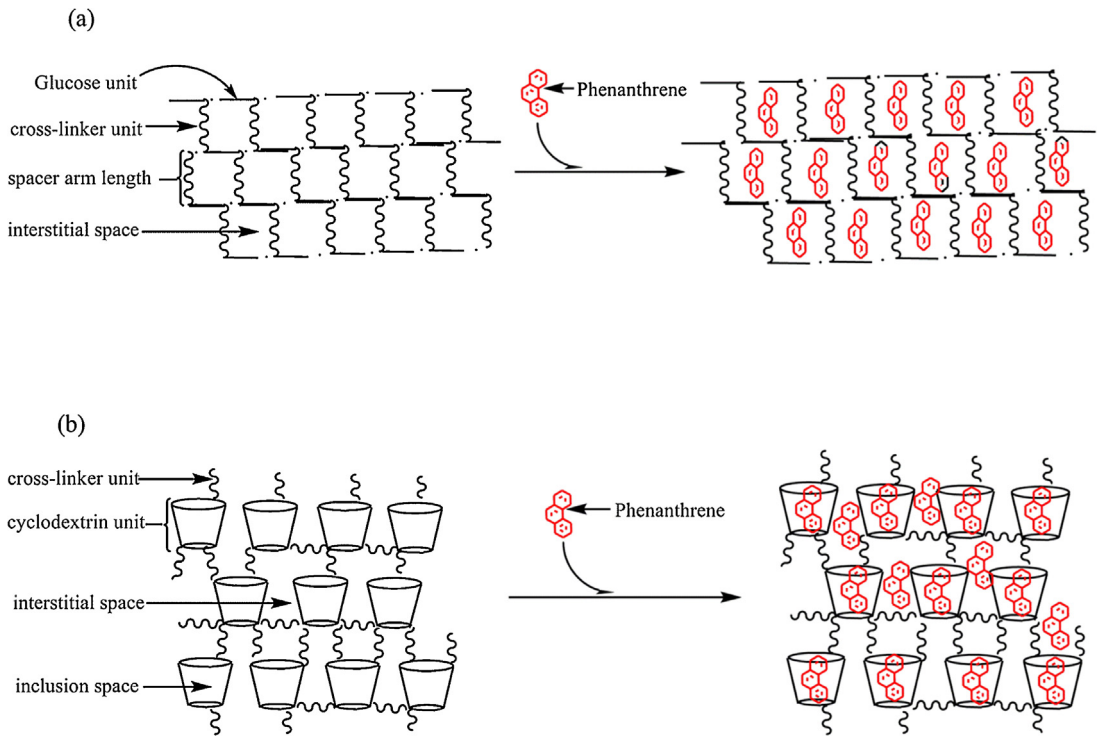

Fig. 3. Adsorption schemes of (a) cross-linked starch adsorbent and (b) β-cyclodextrin polymer adsorbent for phenanthrene.

the degree of cross linking increased for all the adsorbents, except for those of MDI CS and MDIBCD families where there was noticeable decrease.

The C/H atomic ratio (Table 2), which indicates aromaticity, for all the polymers showed no significant change except for those of MDICS and MDIBCD adsorbents, where a progressive increase was observed as the degree of cross linking was increased. This observation is in consonance with a successful introduction of aromatic group into the chemical structure of the starch and β-cyclodextrin polymers as was equally confirmed with IR absorption bands of these adsorbents.

3.3. Batch adsorption studies

3.3.1. Adsorption study using cross-linked starch polymer adsorbents

Fig. 4(a–d) showed the plots of adsorption performance against the arbitrary degree of cross-linking process. From the

Table 2
Elemental analysis showing N, C, H and O contents of the adsorbents.

Adsorbent	N%	C%	H%	O%	C/H ratio	N/C ratio	(O + N)/C ratio
Cross-linked starch adsorbents							
EPI CS 1		40.69	5.77	53.54	7.05		1.32
EPI CS 2		40.98	5.83	53.19	7.03		1.30
EPI CS 3		41.24	5.93	52.83	6.95		1.28
EPI CS 4		41.97	6.22	51.81	6.75		1.23
HDI CS 1	1.57	43.62	6.90	47.91	6.32	0.04	1.13
HDI CS 2	3.62	44.19	6.73	45.47	6.57	0.08	1.11
HDI CS 3	5.63	44.10	7.03	43.24	6.28	0.13	1.11
HDI CS 4	7.88	46.18	7.36	38.58	6.28	0.17	1.01
MDI CS 1	1.64	41.35	6.37	50.64	6.49	0.04	1.26
MDI CS 2	3.55	47.09	6.09	43.27	7.73	0.08	0.99
MDI CS 3	5.86	53.55	5.74	34.85	9.33	0.11	0.76
MDI CS 4	7.65	59.01	5.74	27.60	10.29	0.13	0.60
β-Cyclodextrin polymer adsorbents							
EPI β-CD 1		41.02	5.74	53.24	7.15		1.30
EPI β-CD 2		41.56	5.86	52.58	7.09		1.27
EPI β-CD 3		42.08	5.97	51.95	7.05		1.23
EPI β-CD 4		42.67	6.08	51.25	7.02		1.20
HDI β-CD 1	9.63	54.89	7.63	27.85	7.19	0.18	0.68
HDI β-CD 2	4.30	43.10	6.58	46.01	6.55	0.10	1.17
HDI β-CD 3	6.01	45.01	6.83	42.15	6.59	0.13	1.07
HDI β-CD 4	9.76	48.46	7.45	34.33	6.51	0.20	0.91
MDI β-CD 1	6.32	56.30	5.77	31.61	9.76	0.11	0.67
MDI β-CD 2	5.46	50.89	6.01	37.64	8.47	0.11	0.85
MDI β-CD 3	6.52	55.68	5.75	32.05	9.68	0.12	0.69
MDI β-CD 4	7.58	59.91	5.67	26.84	10.57	0.13	0.57

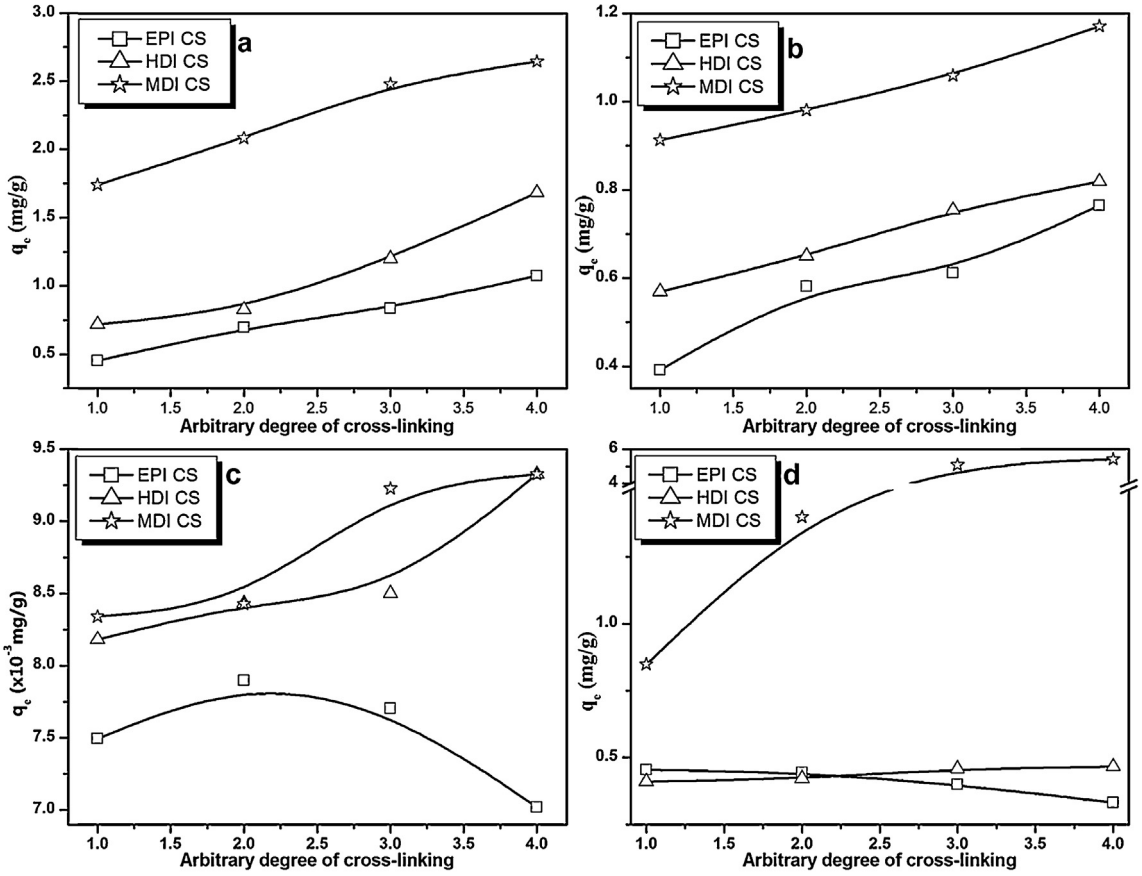

Fig. 4. Effect of nature of cross-linking agent and the degree of cross-linking on the adsorption performance of cross-linked starch adsorbents for (a) acenaphthylene, (b) phenanthrene, (c) benzo[a]anthracene (BaA), and (d) diethyl phthalate (DEP).

experimental results, it is observed that the trend of adsorption performance was MDICS > HDICS > EPICS. This was in tandem with the trend predicted by the DFT study. MDICS family of adsorbents had the highest adsorption capacity for all the studied PAHs of acenaphthylene, phenanthrene, and benzo[a]anthracene. This is attributed to high adsorbent–adsorbate interaction as predicted by DFT parameters. Another contributing factor for this observed performance was the π–π interaction which emanated from the fact that the target pollutants were aromatic compounds, and the MDICS set of polymers possesses aromatic properties as revealed by both their IR spectra and data from elemental analysis. The HDICS family of adsorbents followed as shown by their adsorption capacity for acenaphthylene, phenanthrene, and benzo[a]anthracene, while the EPI CS equally showed the least performance for all the studied PAHs. In addition to having the lowest values for most of DFT molecular interaction descriptors, the chemical structure of EPICS family was expected to have played a significant role in the adsorption process. Wilson, Mohamed, and Berhaut (2011) in explaining the adsorption performance of cross-linked β-cyclodextrin showed that the size of the interfacial spaces was directly dependent on the spacer arm length of the cross-link unit (Fig. 1). Larger interfacial spaces translate to increased access to the binding sites and smaller spaces limit access due to steric hindrance. The adsorption performance of cross-linked adsorbents for a given molecule is therefore, expected to have a positive correlation with spacer arm length of the cross-link unit. Considering the chemical structure of the cross-linked adsorbents, it is obvious that EPICS has the shortest spacer arm length, and thus the smallest interfacial space.

DFT approach predicted positive correlation for degree of cross-linking and adsorption performance. The observed experimental adsorption of starch adsorbents for all the studied PAHs followed this prediction except the adsorption of EPICS adsorbents which did not strictly follow the trend. This observed deviation can be explained on the basis of steric effect which depends on two contributory factors viz.: the spacer arm length of the cross-link unit and the molecular size of the adsorbates. Theoretically, the reduction in size of interfacial space is expected to be comparatively higher in EPICS than HDICS and MDICS, due to the fact that it has the shortest spacer arm length. Therefore, the effect of steric hindrance in the adsorption performance of the adsorbents, with a progressive increase in the degree of cross-linking, is expected to be stronger in EPICS family of adsorbents than others. The strength of this concept manifested in the experimental values and plots of the adsorption performance of the EPICS adsorbents. For acenaphthylene (Fig. 4a), the effect of steric hindrance with a progressive increment in degree of cross-linking was not noticeable due to its small molecular size, however, for phenanthrene (Fig. 4b), a relatively larger molecule, the effect of steric hindrance became noticeable at a very high degree of cross-linking. BaA (Fig. 4c), which is the largest molecule among the studied PAHs (see QSAR volume of adsorbates in Table 1), displayed the strongest effect of steric hindrance. Therefore, it can be said that for a given size of interfacial space, the effect of steric hindrance in adsorption increases with increment in molecular size. This observation is in tandem with what has been reported by Chao, AiMin, DaBo, FuQiang, and QuanXing (2008).

The result of the effect of nature and degree of cross-linking process on the adsorption of DEP on cross-linked starch adsorbent is shown in Fig. 4d. The observed trend was only in agreement with the DFT prediction for the nature of the cross-linking process, while

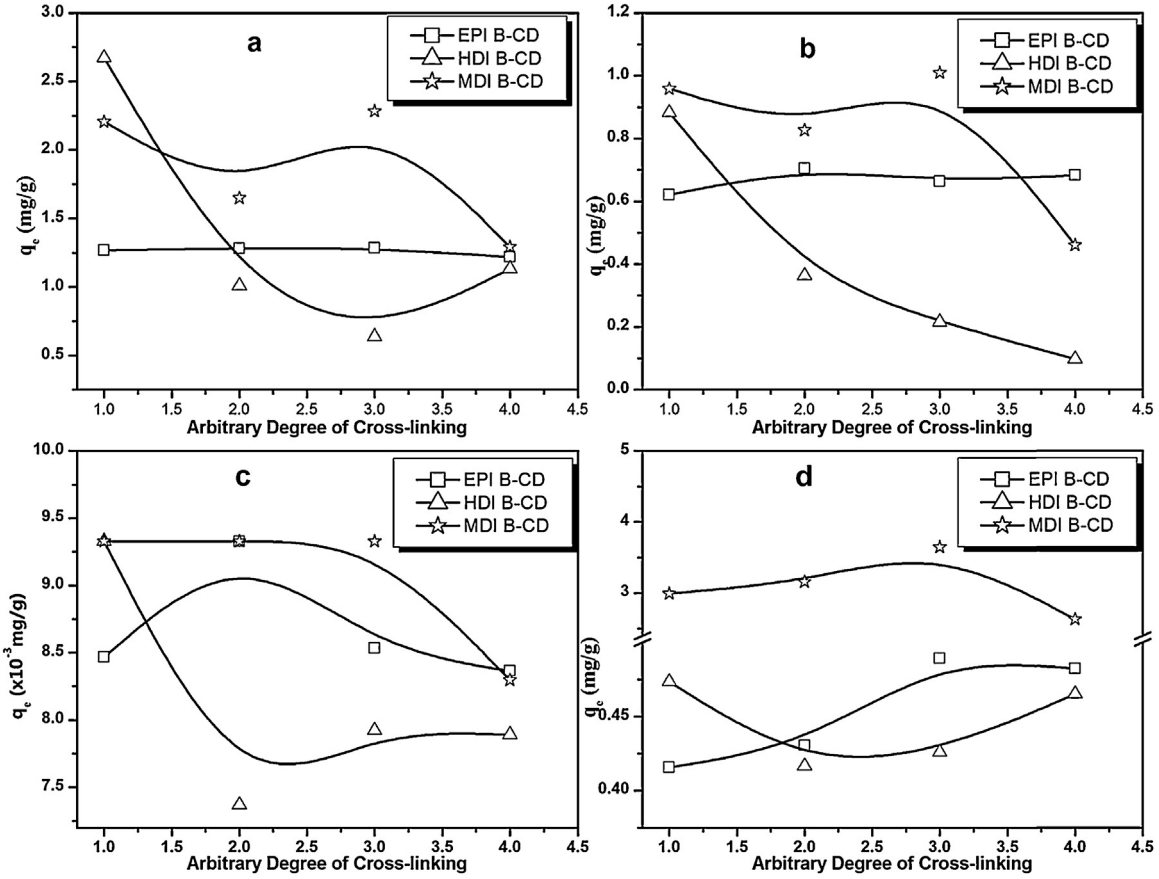

Fig. 5. Effect of nature of cross-linking agent and the degree of cross-linking on the adsorption performance of β-cyclodextrin adsorbents for (a) acenaphthylene, (b) phenanthrene, (c) benzo[a]anthracene (BaA), and (d) diethyl phthalate (DEP).

the observed trend for the degree of cross-linking was very much different. Considering the molecular structure of diethyl phthalate and the value of molecular dipole moment (Table 1), it is expected that the adsorption interaction is controlled by two major contributing interactions of π–π and dipole–dipole interactions. For MDICS family of adsorbents, these two contributing interactions are in operation. However, due to the absence of aromatic group in EPICS and HDICS adsorbents, the π–π interaction is eliminated, and the dipole–dipole interaction dominates.

For the effect of degree of cross-linking on the DEP adsorption on cross-linked adsorbents, only MDICS set of adsorbents followed the trend predicted by the DFT quantum mechanical studies. This can be attributed to decrease in polarity index, (O + N)/C (Table 2), and the subsequent dominance of the π–π interaction over the dipole-dipole interactions with increase in the degree of cross-linking. For EPICS and HDICS, elemental analysis has shown that the polarity index, and subsequently dipole–dipole interaction decrease with increase in degree of cross-linking process. It is likely that this expected decrease in dipole-dipole interaction of these set of adsorbents manifested in the observed trend for the effect of degree of cross-linking on the adsorption performance.

3.3.2. *Adsorption study using β-cyclodextrin polymer adsorbents*

Fig. 5 showed the effects of nature and degree of cross-linking process on the adsorption capacity of β-cyclodextrin adsorbents for acenaphthylene, phenanthrene, BaA and DEP.

The adsorption trend displayed by the β-cyclodextrin adsorbents for the effect of the nature of cross-linking process was in agreement with the DFT prediction, only at low degree of cross-linking process. This apparent deviation from the theoretical predictions is attributed to the type of the molecular interaction that is dominant in the adsorption process in each of the studied cases. Landy, Mallard, Ponchel, Monflier, and Fourmentin (2012) has explained that the adsorption mechanism of cyclodextrin polymer adsorbents involved physical adsorption (dipole–dipole, van der Waal and π–π interactions) in the polymer network, hydrogen bonding, and formation of an inclusion complex on the cyclodextrin molecules through host–guest interaction (Fig. 1b). It is therefore obvious that the nature of cross-linking agent has great influence in determining the dominant adsorption interactions.

Considering the low dipole moment of PAHs, it is evident that only π–π interaction dominated the physical part of the adsorption process. Since MDIBCD has aromatic properties, both π–π interaction and host–guest interaction make significant contribution to the overall adsorption interaction of MDIBCD for PAHs. EPIBCD and HDIBCD adsorbents are non-aromatic, and therefore cannot have π–π interaction. Hence, host–guest interaction dominates the entire PAHs adsorption process by EPIBCD and HDIBCD adsorbents. However, DFT study only considered adsorption in the interstitial spaces of the cyclodextrin polymer adsorbents. Hence, the deviation of the experimental adsorption from the DFT prediction for effect of nature of cross-linking process is attributed to non-consideration of host–guest interaction of cyclodextrin adsorbents in the DFT theoretical studies.

The effect of the degree of cross-linking on the adsorption performance showed entirely different trend from the DFT predicted trend. Due to the size of interfacial spaces and steric hindrance, the increment in degree of cross-linking leads to reduction in the contribution of host–guest interaction to the entire adsorption mechanism. Since host–guest interaction is the dominant

Table 3
Summary of linear correlation of mean adsorption capacity, $\bar{q}_e$ and DFT quantum chemical descriptors.

Adsorbates	Cross-linked starch adsorbents		Cyclodextrin adsorbents	
	Linear equation	R^2	Linear equation	R^2
Energy gap				
Acenaphthylene	$\bar{q}_e = -0.6283x + 5.6311$	0.9626	$\bar{q}_e = -0.2618x + 3.2694$	0.9843
Phenanthrene	$\bar{q}_e = -0.1874x + 2.0425$	0.9551	$\bar{q}_e = -0.1332x + 1.527$	0.5530
Benzo[a]anthracene	$\bar{q}_e = -0.0004x + 0.0109$	0.4272	$\bar{q}_e = -0.0003x + 0.0108$	0.6405
Diethyl phthalate	$\bar{q}_e = -1.3265x + 10.39$	0.9996	$\bar{q}_e = -1.2729x + 9.9654$	0.9990
Chemical hardness				
Acenaphthylene	$\bar{q}_e = -1.2628x + 5.6538$	0.9626	$\bar{q}_e = -0.5261x + 3.2788$	0.9843
Phenanthrene	$\bar{q}_e = -0.3766x + 2.0493$	0.9552	$\bar{q}_e = -0.2677x + 1.5317$	0.5529
Benzo[a]anthracene	$\bar{q}_e = -0.0008x + 0.0109$	0.4264	$\bar{q}_e = -0.0006x + 0.0108$	0.6447
Diethyl phthalate	$\bar{q}_e = -2.558x + 10.011$	0.9990	$\bar{q}_e = -2.558x + 10.011$	0.9990
Chemical softness				
Acenaphthylene	$\bar{q}_e = -12.641x - 2.4474$	0.9594	$\bar{q}_e = -5.2697x - 0.0974$	0.9822
Phenanthrene	$\bar{q}_e = 3.7693x - 0.3666$	0.9517	$\bar{q}_e = 2.7040x - 0.193$	0.5611
Benzo[a]anthracene	$\bar{q}_e = 0.0075x + 0.0060$	0.4192	$\bar{q}_e = 0.0064x + 6.6967$	0.6483
Diethyl phthalate	$\bar{q}_e = 26.733x - 6.7299$	0.9999	$\bar{q}_e = 25.655x - 6.4141$	0.9994
Dipole moment				
Acenaphthylene	$\bar{q}_e = 1.705x + 2.1067$	0.7873	$\bar{q}_e = 0.1094x + 0.891$	0.4375
Phenanthrene	$\bar{q}_e = 1.705x + 2.1067$	0.7873	$\bar{q}_e = 0.0151x + 0.7073$	0.0182
Benzo[a]anthracene	$\bar{q}_e = 0.0004x + 0.0063$	0.9867	$\bar{q}_e = -0.0001x + 0.0087$	0.0021
Diethyl phthalate	$\bar{q}_e = 0.454x - 1.1594$	0.2981	$\bar{q}_e = 0.4272x - 1.0216$	0.2865

adsorption mechanism for EPIBCD and HDIBCD, the adsorption performance is expected to decrease with increment in the degree of cross-linking. For MDIBCD adsorbents, the π–π interaction increased with increment in degree of cross-linking process, despite the decrease in host–guest interaction. The relatively steady adsorption performance observed for MDIBCD, with increment in degree of cross-linking process, is attributed to inverse relationship of these contributing interactions. However, at relatively high degree of cross-linking, the effect of steric hindrance led to the observed decrement.

The adsorption of DEP exhibited a somewhat different trend. For MDIBCD set of adsorbents, with a progressive increase in degree of cross-linking, there was an initial increment of adsorption performance to a certain maximum, after which subsequent increments resulted to decrease in adsorption. For EPIBCD and HDIBCD adsorbents, increment in degree of cross-linking did not result to reduced adsorption performance. These observations though not expected, can be explained on the basis of stability of host–guest inclusion complex of DEP. The stability of cyclodextrin host–guest inclusion complex has a negative correlation with the polarity of the guest molecule (Lichtenthaler & Immel, 1996). Considering the value of dipole moment of DEP (Table 1), it is obvious that the host–guest complex of DEP will be far less stable than those of PAHs. Therefore the adsorption contribution from physical adsorption will be the dominant adsorption mechanism. Since physical adsorption depends solely on the adsorption binding sites of the interstitial spaces, the adsorption performance increases with increase in the degree of cross-linking, until the certain maximum value where the effect of steric hindrance becomes dominant.

3.4. Relationship between computational prediction and experimental adsorption

The mean adsorption capacity (Table S2 of supporting material) for the various families of adsorbents showed linear relationship with the DFT quantum chemical descriptors of ΔE, η, S, and dipole moment (see Figs. S2 and S3 of the supporting material). The result of the correlation studies for this relationship as shown in Table 3 indicated that ΔE, η and S gave better correlation coefficient ($R^2 = 0.8072 \pm 0.2259$) than dipole moment ($R^2 = 0.1861 \pm 0.2124$). The poor correlation of dipole moment is attributed to the fact that hydrophobic interaction is the dominant interaction in the adsorption process. In a similar study, Shirvani et al. (2010) had observed poor correlation of dipole moment with adsorption of non polar organics, and explained that dipole moment only correlates well with adsorption performance when electrostatic contribution plays a dominant role in the interaction process. The linear equation of the relationship, $\bar{q}_e = mx + c$ (where $\bar{q}_e$ is the mean adsorption capacity for a given adsorbent family, x is the DFT quantum chemical descriptor which translates to the nature of cross-linking process/agent) can be applied for estimating the mean adsorption capacity and subsequently the suitability of a given cross-linking agent for the synthesis of starch/cyclodextrin adsorbents for a given pollutant (adsorbate). The slope (m) and the intercept (c) are constants that were found to be a function of the nature and the concentration of the adsorbates.

On the predicted effect of degree of cross-linking, linear correlation analysis for the plots of Figs. 4 and 5 indicated that the experimental adsorption trend for effect of degree of cross-linking process conformed better to theoretical predictions in starch adsorbents ($R^2 = 0.8787 \pm 0.1877$) than the cyclodextrin adsorbents ($R^2 = 0.3983 \pm 0.2766$). The linear relationship was defined by the equation; $q_e = mx + c$, (where q_e is adsorption capacity for individual adsorbents, and x is the arbitrary degree of cross-linking). The slope m, and the intercept c, were found to be highly dependent on the nature of the adsorbent (precursor and cross-linking agent) and adsorbate properties (nature and concentration) (see Table S4 of the supporting material for details of individual correlation of the plots). This situation primarily implied that the effect of degree of cross-linking process on adsorption capacity q_e was more pronounced with increment in the initial adsorbate concentration.

In summary, adsorption capacity of cross-linked starch and cyclodextrin polymer adsorbents is a function of the three intrinsic factors (nature of precursor, cross-linking process/agent, and adsorbates) and two external/experimental factors (degree of cross-linking and adsorbate concentration). DFT computational approach incorporated all the intrinsic factors in deriving the quantum chemical descriptors. Hence, quantum chemical descriptors are reliable tools for predicting the adsorption interaction of cross-linked starch and cyclodextrin polymer adsorbents.

4. Conclusions

The experimental adsorption performance for both starch and β-cyclodextrin polymer adsorbents correlated well with the computational predictions on the basis of nature and degree of cross-linking process/agent. However, β-cyclodextrin adsorbents showed deviations from computational predictions on the effect of degree of cross-linking process. Hence, this study has shown that DFT quantum chemical descriptors can reliably be used to predict the adsorption performance of cross-linked adsorbents for a given adsorbate (pollutant). The import of this feat is that computational approach can reliably be used for testing the suitability of using certain compounds as cross-linking agents for starch and cyclodextrin without necessarily going through the rigors of synthesis of the adsorbents and the subsequent batch adsorption studies. This approach saves resources, time and labor.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.08.065.

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