

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.

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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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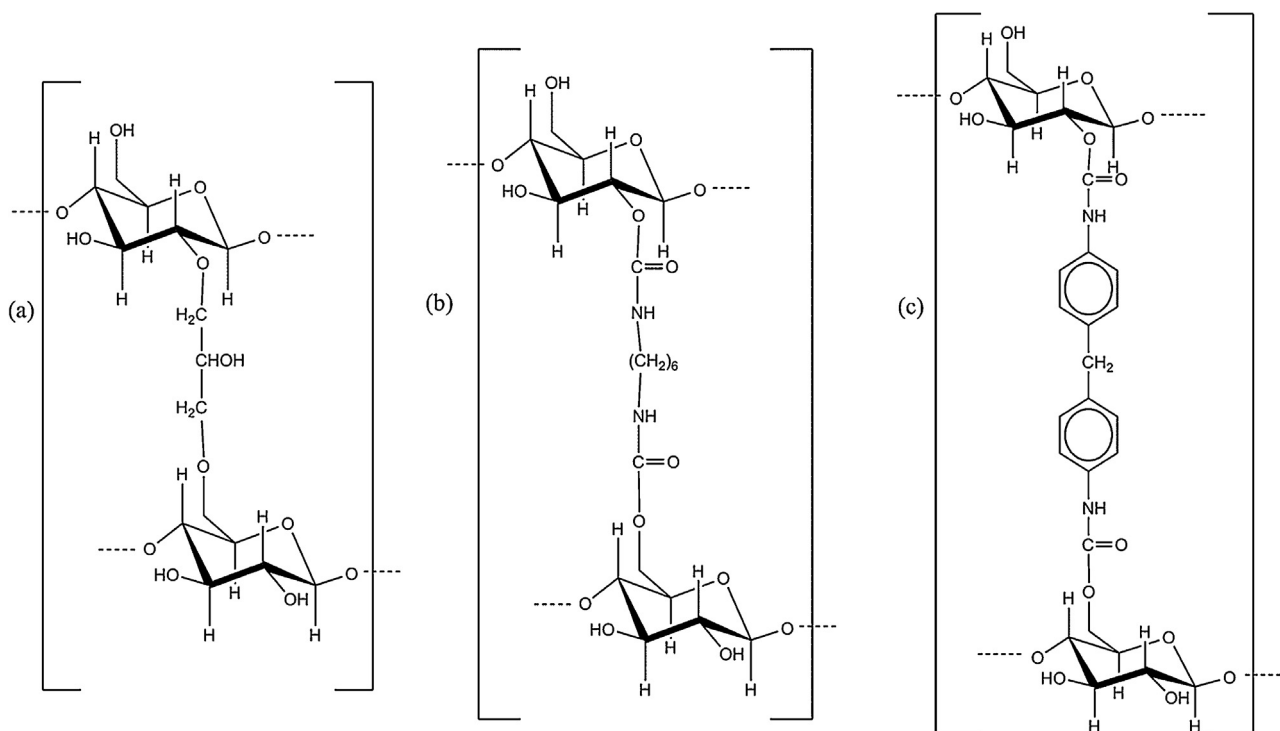


Fig. 1. Monomer structures of (a) EPI, (b) HDI, and (c) MDI cross-linked adsorbents.

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

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