A mechanistic study on Decontamination of Methyl Orange Dyes from Aqueous Phase by Mesoporous Pulp Waste and Polyaniline

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ABSTRACT

The dispersion-corrected density functional theory (DFT-D3) is used to investigate the mechanism of mesoporous pulp waste (MPW) and polyaniline (PANI) adsorptive removal methyl orange (MO) dye from their aqueous solutions. The results are absolutely reliable because of the sufficiently accurate method although such big systems are studied. It is demonstrated that hydrogen bond and Van Der Waals interactions play a significant role in MO adsorption by MPW and PANI. For MO adsorption by MPW, hydrogen bond and Van Der Waals interactions are both weakened in S_1 state. In contrast, hydrogen bond and Van Der Waals interactions between PANI and MO are both enhanced in S_1 state. The thermodynamic parameters such as enthalpy and free energy change reveal that the MO adsorption by MPW and PANI are spontaneous and exothermic. The adsorption of MO on MPW is less favorable in S_1 state and the adsorption of MO on PANI is more favorable in S_1 state. Therefore, the photoexcitation should be controlled during the MO adsorption by MPW and applied for MO adsorption by PANI.

1. Introduction

Dyes and coloring materials which are lethal for the aquatic life are used in many industry productions such as household goods, plastic leather, textile, rubber, food and other productions (Mondal, 2008; Nandi et al., 2009). These dyes are difficult to biodegrade due to their photo-stability and compound structures. And they could create toxic and hazardous intermediates after being oxidized in water. Hence, in recent years, removal of dyes from wastewater has become a real challenge to global scientists.

The many conventional chemical, physical, and biological treatment methods such as ozonation(Lackey et al., 2006), electrochemical methods(Zhu et al., 2005), precipitation (Rehman et al., 2006), solar-assisted photocatalytic degradation (Rehman et al., 2008) and nano-filteration (Jody et al., 2013) have been performed to decontaminate the dyes from wastewater. However, limitations have been found in most of these methods. Then, the adsorption method was regarded as the most economic and most efficient method to decontaminate the dyes from wastewater and appears to offer the best prospects over others(Crittenden et al., 1997; Wang et al., 2005). The adsorption technology could work under room temperature without generating any hazardous byproducts (Gupta and Ali, 2008; Gupta et al., 2011; Gupta et al., 2009). Although the activated carbon is regarded as an effective adsorbent, the cost is considerably high. Therefore, the

interest in finding cheaper materials as potential adsorbents has been stimulated. Various low cost adsorbents such as pumice stone (Kitis et al., 2007), pumice powder(Akbal, 2005), apricot waste (Demirbas et al., 2008), soy meal hull (Mahmoodi and Arami, 2008) and silkworm pupa(Noroozi et al., 2007) have been used successfully to remove various water-soluble toxic dyes from wastewater. The hydrogen bond which is widely employed in chemistry, physics, and biology (Li et al., 2015; Ma et al., 2015; Miao and Shi, 2011; Song and Ma, 2013; Yang et al., 2015; Wang et al., 2015; Yu et al., 2011; Zhang and Zhao, 2012; Zhao and Han, 2008; Zhao and Han, 2012; Zhao et al., 2015; Yu et al., 2013; Zhao and Han, 2007; Zhao et al., 2007) plays a significant role in physical adsorption.

As a well-known anionic dye, MO has been widely used in printing, research laboratories and textile. Acute exposure to MO could cause tissue necrosis, jaundice and cyanosis(Rui et al., 2013). Recently, Ahmaruzzaman et al. address the development of mesoporous pulp waste (MPW) and its application in sequestering of MO from wastewater in the experiment. They found that the MPW is a promising adsorbent for MO dye from aqueous phase because of its micro-mesoporous and high surface area in nature(Ahmaruzzaman and Reza, 2014). Their investigation not only solves the problem of waste disposal caused by waste pulp but also decontaminates the MO dyes from wastewater economically and efficiently. Kumar et al. investigate MO dye adsorption by polyaniline (PANI), which is the most inten-

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sively studied adsorption in industrial applications because of its low cost, good environmental stability and easy synthesis(Janaki et al., 2012; Park et al., 2015). They found that the PANI is essentially monodispersed and highly efficient for the adsorption of MO(Mahto et al., 2015). However, the adsorption mechanisms and the properties of MO adsorption upon photoexcitation have not been exactly investigated for MPW and PANI. It is necessary to unveil the mechanism of MO adsorption in order to further understand the adsorption process and provide guidance for the practical application.

In this work, the geometry structures of six MPW-MO compounds and MO-PANI compound are optimized in both the ground and excited states. These models may shed light on the mechanism of MO adsorption by MPW and PANI. The electrostatic potential (ESP) on van der Waals (vdW) surface has been investigated to study and predict intermolecular interaction between MO and adsorbent (MPW and PANI). The reduced electron density gradient (RDG) analysis has been performed to further explore the intermolecular interaction in the real space. The electron density difference maps have been investigated to obtain detail information of the charge redistribution upon photoexcitation. In addition, thermodynamic analysis of MO adsorption is also performed.

2. Computational methods

In this work, the MO, PANI, MPW, MO-MPW compound and MO-PANI compound are investigated theoretically using DFT-D3(Grimme et al., 2011). The DFT-D3 approach can almost reach the accuracy of highly correlated wavefunction methods for non-covalent interactions at the cost of modest computational (Tasinato and Grimme, 2015). The TD-DFT-D3 method has been confirmed to be reliable tool to gain insight into the hydrogen bonding interaction that occurs in the excited state of hydrogen-bonded systems. All geometric optimization are performed in the ground state using the DFT-D3 and in the electronic excited state using the TD-DFT-D3 respectively. The excited configurations are optimized base on the stable configuration of ground state. All the local minima geometries in excited state are confirmed by the absence of an imaginary mode in vibration analyses and calculations. The absence of imaginary frequencies confirms that the stability of optimized geometries. All molecular geometrics are optimized by M06-2X-D3(Goerigk and Grimme, 2011) density functional method in combination with 6-311++G(d,p)(Krishnan et al., 1980) basis set with both polarization and diffuse functions. As an ideal choice for main group elements, the M06-2X can faithfully represent hydrogen bonds(Burns et al., 2011). The equilibrium polarizable continuum model (PCM) is used to explain the solvent effects. MO is optimized by putting a negative charge on one oxygen atom in the SO_3^- group and PANI is optimized by specifying the positive charge on the alternating nitrogen atoms. All calculations in the present work are carried out using the Gaussian 09 program package(Frisch et al., 2009). Plots of RDG versus sign(λ_2)ρ are performed by Multiwfn 3.2.1(Lu and Chen, 2012), which is a multifunctional wavefunction analysis program can be freely downloaded. All isosurface maps are performed by VMD 1.9.1 program(Humphrey et al., 1996) based on the outputs of Multiwfn. Thermodynamical parameters for all configurations are obtained by harmonic frequency calculation at M06-2X-D3/6-311++G(d,p) based on the geometry optimized at the same level.

3. Results and Discussion

In order to investigate the mechanism of decontamination of MO dye from aqueous phase by MPW and PANI, the ESP of MPW, MO and PANI are calculated by using M06-2X-D3/6-311++G(d,p) level as shown in Fig. 1. ESP on vdW surface has been prevalently used to study and predict intermolecular interaction(Murray and Peter, 2011). The site which possesses bigger negative ESP has stronger ability to attract electrophiles and is thus more possible to form hydrogen bond.

The red color represents the positive diffusion region and the blue color represents the negative diffusion region. As shown in Fig. 1b, it is clear that the electro negativity of SO_3^- group of MO molecular is particularly strong. The global minimum of ESP on the surface (-127.52 kcal/mol) corresponds to the oxygen atom in SO_3^- group. All the hydrogen atoms of hydroxyl in MPW possess positive diffusion region. There are six global minima on the surface of ESP (39.74, 44.21, 44.44, 46.53, 47.89 and 44.48 kcal/mol) which illustrates that six compounds could be formed between MPW and MO. The remarkable red regions are entirely localized on the hydrogen atom of amino group and imino group. The significant local maximum on the surface of ESP for PANI is 42.60 (kcal/mol). Thus, the intermolecular interaction behavior will exist between the SO_3^- group of MO and imino group of PANI.

According to the analysis of ESP, the MO has been placed near the six surface local maxima of ESP for MPW (see Fig. 1a) and one surface local maxima of ESP for PANI. The optimized six MPW-MO compounds and PANI-MO compound are shown in Fig. 2, which demonstrates that the intermolecular hydrogen bonds can be formed in different compounds. However, upon photoexcitation, the intermolecular hydrogen bonds change in opposite ways. For compound I (Fig. 2a), the dihydrogen bond is formed between the SO_3^- group of MO and two hydroxyls (hydroxyl 1 and hydroxyl 2) of MPW. It is obvious that the dihydrogen bond is weakened from 1.77 Å and 1.71 Å to 1.88 Å and 1.83 Å upon photoexcitation, respectively. For compound II (Fig. 2b), two intermolecular hydrogen bonds are formed between two oxygen atoms of SO_3^- group of MO and two hydroxyls (hydroxyl 2 and hydroxyl 3) of MPW. And both two hydrogen bonds are weakened upon photoexcitation (from 1.79 Å and 1.83 Å to 1.85 Å and 1.87 Å, respectively). Fig. 2c and its geometrical parameters show that the hydrogen bond between the oxygen atom of SO_3^- group of MO and hydroxyl 3 (see Fig. 1a) of MPW is weakened in the S_1 state. For compound IV, the two intermolecular hydrogen bonds are lengthened from 1.81 A° and 1.72 A° in S_0 state to 1.87 A° and 1.76 A° in S_1 state. For compound V, the hydrogen bonds are formed between the oxygen atoms and hydroxyls (hydroxyl 4 and hydroxyl 6) of MPW although the SO_3^- group of MO is placed near the hydroxyl 5 position. And both the two hydrogen bonds are weakened in S_1 state. Similarly, two hydrogen bonds are also formed between the oxygen atoms and hydroxyls (hydroxyl 4 and hydroxyl 6) of MPW and then weakened in S_1 state. For compounds VII, the geometrical parameters show that the hydrogen bond is sharply enhanced from 1.96 A° in S_0 state to 1.57 A° in S_1 state. In a word, the hydrogen bonds in six MPW-MO compounds are weakened, while the intermolecular hydrogen bond of PANI-MO is significantly strengthened in the excited state.

The interaction energies of all compounds in both S_0 and S_1 states are summarized in Table 1. The interaction energies between the PANI and MO as well as the MPW and MO are calculated by using the following equation:

$$\Delta E_{interaction}(PANI - MO) = E_{(PANI-MO)} - E_{PANI} - E_{MO} + E_{BSSE} \tag{1}$$

$$\Delta E_{interaction}(MPW - MO) = E_{(MPW-MO)} - E_{MPW} - E_{MO} + E_{BSSE} \tag{2}$$

where $\Delta E_{interaction}$(PANI-MO) represents the interaction energy between the PANI and MO, $\Delta E_{interaction}$(MPW-MO) represents the interaction energy between the MPW and MO, E(PANI) represents the energy of PANI, E(MO) represents the energy of MO, E(PANI-MO) represents the energy of the PANI-MO compound, E(MPW-MO) represents the energy of the MPW-MO compound, and E_{BSSE} represents the energy calculated with the basis set superposition error method. As shown in Table 1, the corrected interaction energies calculated for MPW-MO compounds 1-6 are −32.94, −29.04, −28.49, -31.51, −29.66 and -31.78 kJ/mol in S_0 state, respectively. After being excited to S_1 state, the corrected interaction energy for the six compounds change to −25.75, −25.83, -26.59, -24.10, -24.93 and -25.95 kJ/mol, respectively. It can be seen that the interaction energy between MPW and MO for six compounds are all reduced, which