Molecular modeling of interactions between heavy crude oil and the soil organic matter coated quartz surface

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HIGHLIGHTS

- SOM addition increased the mobility of SARA (asphaltene, resin, aromatic, saturate).
- SOM–quartz complex was a more effective medium for SARA adsorption than pure quartz.
- SOM tend to self-associate and also promote asphaltenes aggregation.
- The host oil phase was most preferable for SARA partitioning followed by SOM.
- Quartz surface contributed to <15% of the overall adsorption of SARA.

GRAPHICAL ABSTRACT
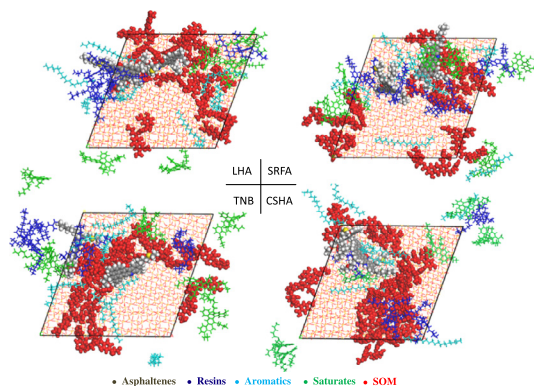
ABSTRACT

Molecular dynamic (MD) simulation was applied to evaluate the mobility, diffusivity and partitioning of SARA (saturates, aromatics, resins, asphaltenes) fractions of heavy crude oil on soil organic matter (SOM) coated quartz surface. Four types of SOM were investigated including Leonardite humic acid, Temple-Northeastern-Birmingham humic acid, Chelsea soil humic acid and Suwannee river fulvic acid. The SOM aggregation at oil–quartz interface decreased the adsorption of SARA on the quartz surface by 13–83%. Although the SOM tended to promote asphaltenes aggregation, the overall mobility of SARA was significantly greater on SOM–quartz complex than on pure quartz. Particularly, the diffusion coefficient of asphaltenes and resins increased by up to one-order of magnitude after SOM addition. The SOM increased the overall oil adsorption capacity but also mobilized SARA by driving them from the viscous oil phase and rigid quartz to the elastic SOM. This highlighted the potential of SOM addition for increasing the bioavailability of heavy crude oil without necessarily increasing the environmental risks. The MD simulation was demonstrated to be helpful for interpreting the role of SOM and the host oil phase for the adsorption and partitioning of SARA molecules, which is the key for developing more realistic remediation appraisal for heavy crude oil in soils.

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1. Introduction

During the last few decades, the rapid development of the petroleum industry resulted in a large number of oil contaminated sites, which constituted a menace to the population's health and the ecosystem. A number of technologies have been developed for the remediation of such soils, but most of them are only effective for specific sites (Wu, 2012). The lack of a universal technology that can be the solution for all contamination is attributed to the complicated nature of soil and oil chemistry (Gan et al., 2009). Research is required to gain insights into

the intricate interactions between oil and soil especially at molecular scale.

Crude oil is a complex mixture of thousands of compounds. Hydrocarbon group type analysis of SARA (saturates, aromatics, resins and asphaltenes) fractions of heavy crude oil is widely used for the choice of remediation technologies and evaluation of the associated hazards (Kamiński et al., 2003). However, a significant body of research on soil remediation only focused on the light fractions such as aromatics and saturates with fewer than 40 carbon numbers (Li et al., 2012a). This may be attributed to the difficulty in the instrumental analysis of heavy fractions of crude oil. For example, resins and asphaltenes cannot be quantified using traditional methods such as Fourier transform infrared spectroscopy (FTIR), gas chromatography–flame ionization detection (GC–FID) or gas chromatography–mass spectrometry (GC–MS). The state-of-the-art in analytical technology indicates that thin-layer chromatography with FID is the quickest method for SARA analysis (Bisht et al., 2013). However, it remains a semi-quantitative approach and does not always produce highly reproducible measurements (Ugochukwu et al., 2013).

Most recently, we demonstrated that the molecular simulation method could be used to assist instrumental analysis, especially when the SARA fractions coexisted in the heavy crude oil (Wu et al., 2013a). Although only a small number of molecules were used in modelling, the calculated mobility, diffusion coefficient and concentration profiles of SARA on quartz surface agreed well with experimental data (Norinaga et al., 2001; Andrews et al., 2006; He et al., 2013). The molecular simulation suggested that isolation of light fractions from the host oil phase may lead to deviant results by ignoring their interactions with other oil fractions. For example, resins coated on the surface of asphaltenes tend to stabilize asphaltene, while saturates were able to promote asphaltene aggregation by dissolving the surface resins or altering the force between asphaltenes and solvents. Large scale asphaltene aggregation would in turn increase the mass transfer resistance, which hinders the release of light fractions of oil from soils and thereby decreases the effectiveness of clean-up. The molecular simulation also highlighted the needs to incorporate soil organic matter (SOM) with the mineral surface for better interpretation of the oil behavior (Wu et al., 2013a).

Understanding the sorption and partitioning of oil contaminants on a SOM–mineral complex is essential for soil pollution assessments. Firstly, SOM and mineral are two of the most important mediums for the persistence of hydrophobic organic contaminants (HOC) in soils. In natural soils, humic substances including humic acid, fulvic acid and humin constitute 50–80% of the SOM (Shaker et al., 2012). A number of studies have used quartz and alumina to simulate soil mineral and used minerals coated with humic substances to model soil matrices (Joo et al., 2008; Radian and Mishael, 2012; Bell and LeBoeuf, 2013; Heggy et al., 2013; Zhang et al., 2013). It was found that the adsorption of HOC on a SOM–mineral complex was consistent with that on bulk soils (Peterson et al., 1988). Secondly, there is increasing interest in employing natural organic matter amendment as a strategy for treating oil contaminated soils (Wu et al., 2013b), because the humic substances in the organic amendments would immobilize HOC by increasing adsorption. Organic matter amendment may also enhance the solubility and mobility of hydrocarbons by forming a SOM–pollutant complex or competing for adsorption sites on the mineral surfaces (Radian and Mishael, 2012). Since the majority of literature reports the sorption of aromatics and saturates on soils as aforementioned, the influence of SOM on the behavior of SARA mixture needs to be clarified before the addition of humic substances addition is widely used as an alternative for the remediation of oil-contaminated soil. Knowledge on the sorption and partitioning of heavy crude oil in the different compartments in the soil is essential for predicting long-term risks and supporting remediation decisions. Although several studies reported the partitioning of polycyclic aromatic hydrocarbons (PAHs) and alkanes in the soil–oil matrix (Wang et al., 2001; Pollard et al., 2008; Coulon et al., 2010), sound data on SARA remains sparse.

Therefore, the specific objectives of this study were to apply MD simulation to (i) quantify the mobility and diffusivity of SARA on a SOM coated quartz surface, and (ii) evaluate the influence of SOM on SARA partitioning in the model sand-oil matrix. Quartz was selected because it is one of the most important constituents of sandy soil. Three humic acids and one fulvic acid were selected as representative SOM in this study. Humin was not investigated due to the lack of an experimentally validated molecular model so far.

2. Methodology

2.1. Model construction

Molecular simulation was performed using the Material Studio software package. The bonded and non-bonded potentials of atoms were calculated using the condensed-phase optimized molecular potential for atomistic simulation studies (COMPASS) force field (Sun, 1998). This force field was directly used in this study, because it has been validated for predicting adsorptive properties for a broad range of substances including humic acids, fulvic acids, asphaltenes, diesel and quartz surface (Zhang and LeBoeuf, 2009; Zhang et al., 2009; Greenfield, 2011; Ling et al., 2012; Wu et al., 2013a).

The adsorption system was modeled using the method described by Wu et al. (2013a) with some modifications. Briefly, a crystal layered structure consisting of four layers was constructed from bottom to top as follows: (i) quartz surface, which was a 3D periodic cell converted from a 7×7 supercell (5.1 nm $\times$ 5.1 nm $\times$ 1.1 nm) built from quartz (1 1 1) ($\alpha = \beta = 90°$, $\gamma = 120°$); (ii) SOM layer, which consisted of 10 SOM molecules. As shown in Fig. 1, four of the most widely found SOM in natural soils and sediments were selected including Leonardite humic acid (LHA, $C_{31}H_{26}O_{12}$, MW: 590) (Niederer and Goss, 2007), Temple-Northeastern-Birmingham humic acid (TNB, $C_{36}H_{40}N_2O_{16}$, MW: 757) (Sein et al., 1999), Chelsea soil humic acid (CSHA, $C_{44}H_{43}NO_{23}S$, MW: 986) (Nuerla, 2012), and Suwannee river fulvic acid (SRFA, $C_{33}H_{36}O_{19}$, MW: 737) (Nuerla, 2012). The molecular number of 10 was designed in order to form a single molecular layer of SOM that could just cover the quartz surface (Figs. SM1–4 in Supplementary Materials (SM)); (iii) oil layer, which contained 2 asphaltenes ($C_{54}H_{65}NO_2S$, MW: 792) (Murgich et al., 1996), 4 resins ($C_{50}H_{80}S$, MW:713) (Murgich et al., 1996), 6 aromatics ($C_{46}H_{50}S$, MW: 635) (Verstraete et al., 2010) and 7 saturates ($C_{20}H_{42}$, MW: 282). The setup of the molecular number of SARA was inspired by the mass ratio of 15:30:35:20 in the heavy crude oil in real oil sands (Li et al., 2012b); and (iv) vacuum layer of 30 Å to elimate direct interactions between oil molecules and the top of the slab. All the molecular models of SARA and SOM were directly used in this study, because they had been previously validated by chemical characterization methods such as average molecular weight, FTIR, elemental analysis and nuclear magnetic resonance.

2.2. Molecular dynamic simulation

The structure of the molecules was optimized by energy minimization using smart minimizer approach (Frenkel and Smit, 2002). The model adsorption systems were subjected to 200 picoseconds (ps) MD simulation at constant volume and temperature (NVT ensemble) with the time step of 1 femtoseconds (fs). Berendsen thermostat (Berendsen et al., 1984) was used to control the