



Adsorption Modes of Natural Organic Matters on Fabricated Calcite Ooids Surfaces Using Molecular Dynamic Simulations Study



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ONE of the major challenges in seawater reverse osmosis (RO) desalination plants is the feed water quality which causing a significant RO membrane fouling. Natural organic matter (NOM) is mainly consisting of humic substances (HSs) which derived from natural degradation of some organic substances within the ecological systems and from human activities and vastly meet fouling species in natural water resources. The significant reduction (63.4%) of total organic compounds (TOC) on surface of calcite ooid grains after 3 hrs. has been studied. According to the molecular dynamic simulations (MDS), the interaction between different main molecular building blocks forming HSs and CaCO_3 crystal of fabricated calcite ooids surfaces was accomplished to interpret the action of its adsorption modes.

Keywords: Seawater treatment, Calcite ooids, Desalination plants, Molecular dynamic simulation, Humic substances, Natural organic matter, TOC.

Introduction

To meet the challenges of rapid population, economic growth and natural water shortages, the desalination processes are considered to be one of the most effective solutions [1,2]. Adaptable to all capacities, reverse osmosis is the most widespread desalination process and well-suited when local energy source is not available [3]. Recently, the fabricated calcite ooid grains [4] as new pretreatment filtration media of seawater desalination plants instead of conventional media were used to removing and restraining turbidity, suspending solids, iron and total organic carbons to maintaining RO membrane of seawater desalination plants from fouling [5].

The natural water resources contain natural organic matters which extracted from natural degradation of some organic substances within the ecological systems and from human activities

[6,7]. NOM is mainly consists of humic substances (about 50-80%) that vary in their composition, structure, molecular weight, number and position of functional groups depending on their origin and age [8,9]. During water treatment processes, several problems arise due to the presence of NOM that facilitate the transport of organic and inorganic pollutants through water treatment steps. The presence of humic substances as humic complexes, increase the demand of coagulant and enhance biological growth in distribution systems [10,11].

The chemical structure and nature of HSs are still not fully understood, they are classified into three main categories according to their solubility in water, including fulvic acids, humic acids and humins with no sharp division exists among them, since the differences stem is the variations in acidity and hydrophobicity [12].

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Received 8/9/2019; Accepted 13/10/2019

DOI: 10.21608/ejchem.2019.16547.2016

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The main objective of this paper is removing the natural organic matters particularly humic substances using the molecular dynamic simulation to simulate the main molecular building blocks forming HSs on calcite (CaCO_3) of fabricated calcite ooids surfaces. Therefore, the molecular and 3D structures of SiO_2 and CaCO_3 crystals with their electron cloud are studied.

Adsorption method

Generally, it has been presumed that humic substances comprise a considerable fraction of dissolved natural organic matter in the sea, making about 50-80 % that mainly consists of partially decomposed plant materials. Hydrophilic acids and simple organic compounds may be present besides HSs [13]. The molecular dynamic simulation was carried out using Forcite module in materials studio 6.0 software. MDS was performed to simulate the main molecular building blocks forming HSs including; quinone, catechol, phenol and D-glucose on the calcite (CaCO_3) with (100) cleavage [14]. MDS is performed in a 5×5 supercell using the COMPASS forcefield and Smart algorithm. The CaCO_3 (100) crystal is constrained so its atoms wouldn't be disturbed throughout the simulation process. The temperature was fixed at 298 K, with NVE (microcanonical) ensemble and also the effect of solvent was taken into consideration (200 H_2O molecules in each run).

Experimental of total organic carbon

The total organic carbon was measured using a TOC analyzer (Jena Analytik, multi N/C 2100S) to evaluate the adsorption desorption efficiency of the organic's removal during the adsorption process.

Results and Discussion

Total organic carbon removal

The ability of ooids grains to reducing TOC from seawater [5], can be explained by the differences in mineral surface properties between quartz and calcite. There are some differences in the electron densities between quartz (SiO_2), which is the major constituent of sand and calcite (CaCO_3) is the major constituent of fabricated calcite ooids. Therefore, Figure 1 illustrates the TOC removal from seawater by the fabricated calcite ooids and reveals a significant reduction (63.4%) in the organic content after 3 hrs. from the initial concentration of TOC content (3.15mg/l) to reach the maximum reduction (65.2%) after 4 hrs.

Figure 2 shows the molecular and 3D structures of SiO_2 and CaCO_3 crystals with their electron cloud. Therefore, the CaCO_3 solids increasing the positive surface charge from Mg incorporation into the crystal lattice. That is potentially creating more favorable conditions and yielding a greater affinity for adsorbing negatively charges of organic molecules [15].

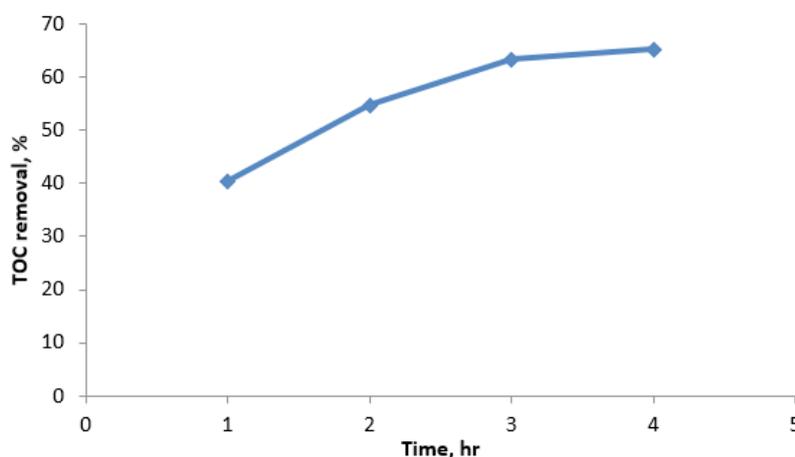


Fig. 1. Variations of TOC removal percentage onto the surface of calcite ooid during the adsorption experiment at different times.

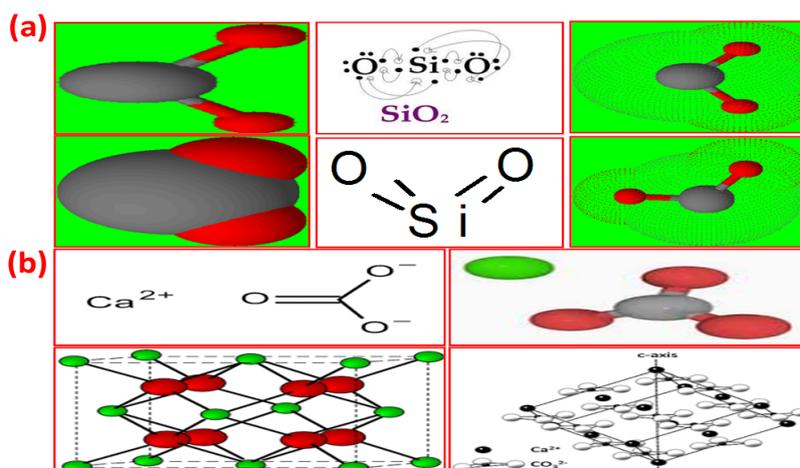


Fig. 2. Molecular and optimized structures of (a) SiO₂ and (b) Calcite (CaCO₃) crystals.

Adsorption modes of HSs with calcite surface using MDS study

Chemical and 3D optimized structures

The chemical and 3D optimized structures of the main molecular building blocks forming humic substances have been identified as hydrocarbons, quinone, phenol, catechol, and

sugar groups, Figure 3 [14]. In water purification technologies, removal of NOM is an extremely important challenging research particularly HSs, while in our present work, the calcite ooids have a great synergistic effect of humic substances removal from seawater.

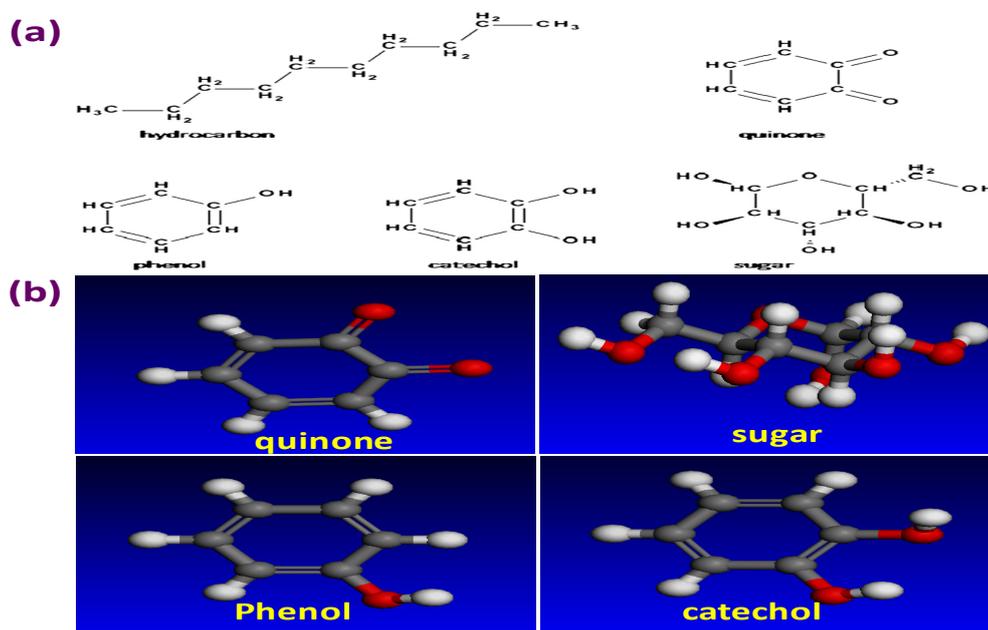


Fig. 3. The chemical (a) and 3D optimized structures (b) of the main molecular building blocks forming humic substances [14].

According to the molecular dynamic simulation, the interaction between different main molecular building blocks forming HSs and CaCO₃ crystal (calcite surface) was accomplished to

interpret the action of its adsorption mode. Owing to the chemical structure and composition of HSs, it remains controversial, not fully understood and the simple organic molecules mentioned above in

Figure 3 are often used to stand for complicated natural organic matters and particularly applied to simulate HSs. Generally, we consider that the structures of HSs consist of polyelectrolyte organic compounds involving large and small amounts of condensed aromatic rings with many numbers of $-OH$, $-C=O$, and $-COOH$ functional groups which bonded to the aliphatic or aromatic carbons in the macromolecules and make them contain both hydrophobic and hydrophilic moieties. The presence of carboxylic and phenolic

groups results in predominantly carrying negative charges in aqueous solutions [16-18].

On the other hand, the calcite has a rhombohedral crystal structure and its exposed surface was obtained by cutting calcite crystals along the (100) crystallographic face using in MDS as shown in Figure 4. This cleavage plane is stabilized by hydration and it has a relatively large surface and attachment energies even though there are some surfaces have relaxed considerably.

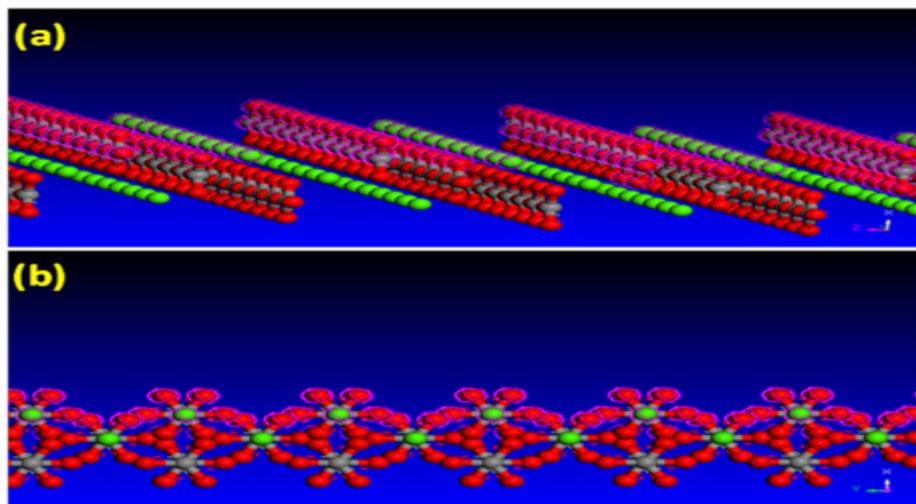


Fig. 4. Calcite ooids, $CaCO_3$ (100) crystal surface in; (a) X-Z dimension and (b) X-Y dimension.

Possible modes of interaction between humic substances and calcite ooids

From the crystallographic point of view, calcite consists of positively charged calcium (Ca^{2+}), ionically bonded with negatively charged carbonate (CO_3^{2-}). In the bulk structure, each calcium atom is coordinated by six oxygen atoms and each oxygen atom is bound covalently to one carbon atom and coordinated with two calcium atoms [19,20].

There is a general consensus that there are main three contributions responsible for the

adsorption process between the investigated organic molecules, Figure 5 and the calcite surface namely; (i) Electrostatic interactions between the electronegativity of oxygen atom of the molecule and the surface of calcium atom (ii) Hydrogen bonding between the hydrogen atom of molecule and the oxygen atom of carbonate group and finally (iii) Dispersion interactions between all atoms of molecule and surface. Therefore, the adsorption geometries of the main molecular building blocks forming HSs (quinone, D-glucose, phenol and catechol) on calcite (100) surface are shown in Figure 5.

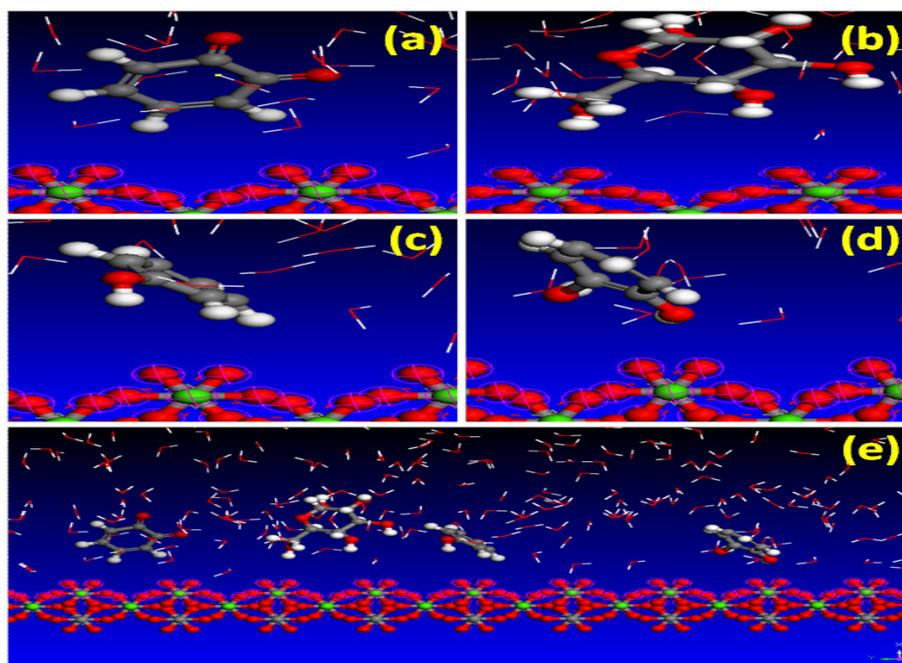


Fig. 5. Possible modes of interaction between the main molecular building blocks forming humic substances with calcite ooids, CaCO_3 (100) crystal surface; (a) quinone; (b) D-glucose; (c) phenol ; (d) catechol and (e) all of them.

It is clearly shown from Figure 5 that the investigated molecules placed on the calcite surface promote the possible interactions between the functional groups and the surface atoms. Consequently, the oxygen containing polar molecules may be tended to form a hydrogen bond with surface in addition to an electrostatic interaction. The surface groups affect the adsorption geometry in two categories: (a) by alteration of the electronic structure of functional groups that changes the strength of electrostatic interactions and hydrogen bonding and (b) by modulation of strength of dispersion interaction between adsorbed molecule and surface. The stable adsorption geometry of phenol and catechol is shown in Figure 5(c,d), respectively, and it strongly influenced by side groups interactions and subsequently they cannot exhibit the effect of hydrogen atoms or phenyl groups on the adsorption behavior of hydroxyl functional groups that create a strong dispersion interaction between phenyl ring as a result of surface which appears in a flat adsorption geometry and this affects the interaction between the hydroxyl group and the surface [21].

Admittedly, due to the heterogeneous character of humic substances, it is difficult to

identify the predominant adsorption mechanism since they can occur simultaneously. Therefore, the polydispersity and polyelectrolytic characters of HSs play a major role in its adsorption onto mineral surfaces [22-24].

Conclusions

The natural organic matters which mainly consist of humic substances, hydrophilic acids and simple organic compounds are dissolved in seawater. The molecular dynamic simulations were performed to simulate the main molecular building blocks forming HSs including quinone, catechol, phenol and D-glucose on calcite (CaCO_3) of fabricated calcite ooids surfaces and accomplished to interpret the action of its adsorption mode. The molecular dynamic simulations were carried out using Forcite module in materials studio 6.0 software.

The molecular and 3D structures of SiO_2 (main constituent of sand) and CaCO_3 crystals (main constituent of ooids) with their electron cloud and the main contributions responsible for the adsorption process between the investigated organic molecules and the calcite surface were studied. Finally calcite ooids have a great effect

for removal of natural organic matters from seawater.

Compliance with ethical statement

All authors of this paper have no conflict of interest with one or organization.

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