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Computational study of NF membrane removal in rejection of specific NOM compounds

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ABSTRACT

A computational study was conducted to verify natural organic matter removal of two types of nanofiltration (NF) membranes. NF membranes used in this study were fully aromatic polyamide based on trimesoyl chloride and 1,3-benzenediamine (NE90) and semi-aromatic polyamide based on trimesoyl chloride and piperazine with polyvinyl chloride coating (NE70). The solute–membrane interaction was modeled using density functional theory (DFT) to clarify and verify the experiment results of our previous study. The calculations were performed by the calculated highest occupied molecular orbital and lowest unoccupied molecular orbital with frontier orbital gap which reflexed adsorption energy between organic molecules and the membrane surface materials. DFT showed as an effective tool to predict interaction phenomenon between solute and membranes, which is relative to membrane fouling and rejection of particular organic substances. The calculation results showed that carboxylic compound has high-energy gap and tend to adsorb on the membrane surface than the other compounds (phenolic and acetic acid) and it bound higher energy with NE90 than NE70. This is comparable with the experimental results that NE90 is consists of surface material, which is easily to be adsorbed by organic molecule, especially carboxylic type compound.

Keywords: Natural organic matter (NOM); Adsorption; Rejection; Fouling; Polyamide membrane; Density functional theory (DFT)

1. Introduction

Nowadays, nanofiltration (NF) technology could be considered as one of the most useful membrane technologies for advanced water treatment as it requires low-energy consumption while high flux can be achieved. NF membrane properties consist of size selectivity, electrical surface charge, and diffusion mechanisms. NF membrane fouling is a complex phenomenon because the fouling process takes place at a nanoscale and is difficult to understand [1]. Fouling control and membrane productivity are still important subjects, and we require a better understanding of these phenomena and mechanisms. NF membrane foulant can be organic solutes, inorganic

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solutes, colloids, and biological solids [2]. NF has been studied and utilized as an advanced water treatment process with respect to the removal of natural organic matter (NOM) and micropollutants. They are removed through mechanisms, including size exclusion, adsorption, charge repulsion, and hindered transports [2]. NF rejection of organic matter takes place through a complex interaction of steric effect, Donan exclusion, solution properties, and other membrane properties [1]. Fouling phenomenon occurs relative to adsorption mechanism, electrostatic attraction or the repulsion force between foulant and membrane surface, as well as the membrane surface charge [2]. It is hard to describe how NOM was removed by NF process, since NOM is a heterogeneous substance. Also, membrane fouling and rejection characteristics are complex phenomenon. To get insight into the phenomenon, it is crucial to analyze NOM component fractions. However, it is still unclear that what kinds of NOM take important role on adsorption mechanism.

Adsorption is the most basic interaction between membrane surface and organic and inorganic ions in water. In recent years, with the fast development of quantum chemistry, theoretical calculations have been carried out for the prediction, testing, and verification of the adsorption energy. Molecular simulation is increasingly demonstrating its practical value in the investigation of biological systems. Molecular simulation can fundamentally advance ability to gain insights and detailed information on biosystems and material science. Since the application of *ab initio* methods, especially high-level theories, had its limitations, many researches were focused on calculation using density functional theory (DFT) methods. DFT is a quantum mechanical modeling method used for the investigation of electronic structure (principally the ground state) of particular atoms and molecules. In the calculation, the properties of a many-electron system can be determined by using functional, that is, functions of another function, which in this case are the electron density. Hence, the name density functional theory comes from the use of functional of the electron density. According to the fundamental theorems of Hohenberg and Kohn [3] and Kohn and Sham [4], the electron density carries all the information that one might need to determine any property of the electron system [5]. These had led to good achievements; a large number of organic or inorganic compounds were well predicted.

DFT molecular simulation, as an extremely successful approach for the description of structural and electronic properties of bulk materials and complex materials such as biomolecules and interaction system, has been primary choice to evaluate the electronic structure of NOM compounds/NF membrane composite system. DFT methods have been proved to be suitable for the calculation of the energy-minimized structures, electronic distribution, molecular orbitals, electron transfer, and electronic absorption spectra of metal and polymers [6,7]. The solute–membrane interaction was modeled using DFT to clarify and verify the experiment results of our previous study. DFT methods were applied to investigate the adsorption configurations of NOM compound on the NF membrane surface.

2. Materials and methods

2.1. Membrane characteristics

The NF membrane used in this study was thin film composite NF membranes (NE70 and NE90, Woongjin, Korea) with loose and tight surface material, respectively. NE70 is semi-aromatic polyamide and NE90 is fully aromatic polyamide. Table 1 shows the membrane characteristics. Structure of the membrane material is shown in Fig. 1.

2.2. Computational analysis

Computational analysis of atomic and molecular organics adsorption to the surface of the NF membranes were carried out using the density functional theory (DFT) and employing GAMESS. The calculations were carried out in all the cases with the B3LYP/6–31G* level of theory. The specific NOM compounds selected in the calculation were considered based on their functional group. The four compounds were p-Coumaric acid (hydrophobic phenolic molecule), L-leucine (hydrophilic amino acid), acetic acid (nonionic hydrophilic carboxylic molecule), and L-tryptophan (hydrophobic amino acid).

3. Results and discussion

3.1. Electronic structure of NE90, NE70 material chemistry, and NOM compounds

To understand structural and energetic properties of NE90, NE70 material chemistry was drawn and calculated electronic structure in terms of high occupied molecular orbital (HOMO) and low unoccupied molecular orbital (LUMO). HOMO shows active side of membrane surface, which is easy to have interaction with organic or other material in water. LUMO is the opposite of HOMO, which is the nonactive side of the membrane surface. Geometries of the structure of the compounds as fundamental models were analyzed and their structures are present in Figs. 2

Table 1
The characteristic of NF membrane [15]

Membrane	Materials	MWCO (Da)	Zeta potential at pH 7 (mV)	Contact angle (°)	Roughness (nm)
NE70	Sulfonated polyethersulfone based thin-film composite (TFC)	350	−47.2	22.6 ± 1.9	8.69
NE90	Meta-phenylene diamine (MPD) TFC	210–310	−38.7	41.5 ± 3.7	26.9

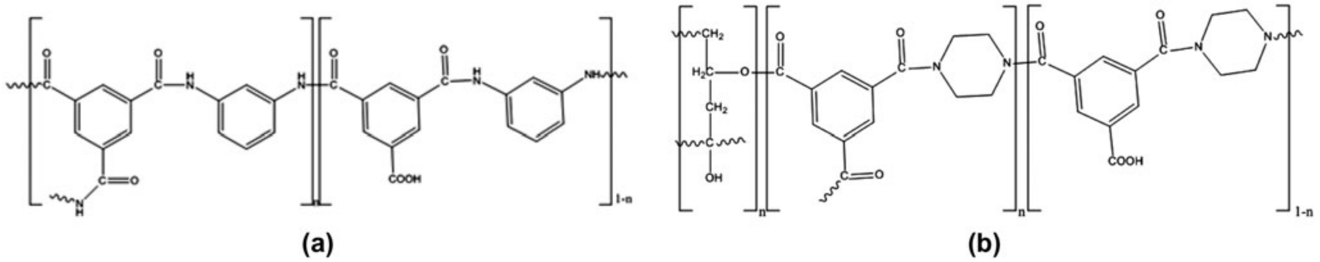


Fig. 1. Structure of fully aromatic polyamide based on trimesoyl chloride and 1,3-benzenediamine (NE90) (a) and semi aromatic polyamide based on trimesoyl chloride and piperazine with polyvinyl chloride (PVA) coating (NE70) (b).

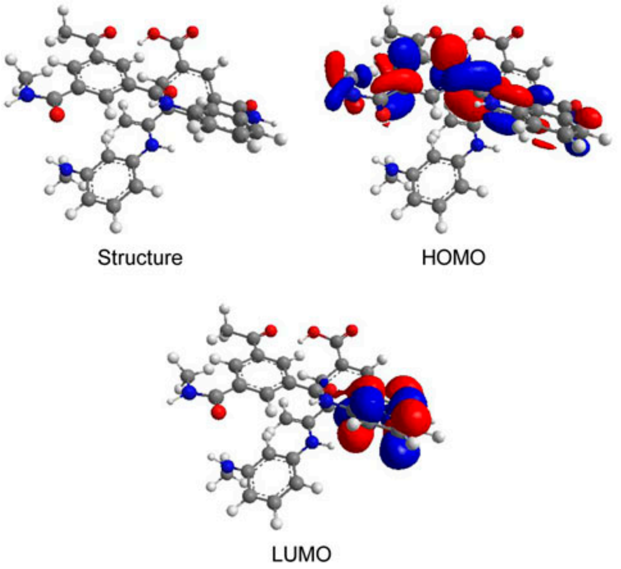


Fig. 2. Fully aromatic polyamide based on trimesoyl chloride and 1,3-benzenediamine (NE90).

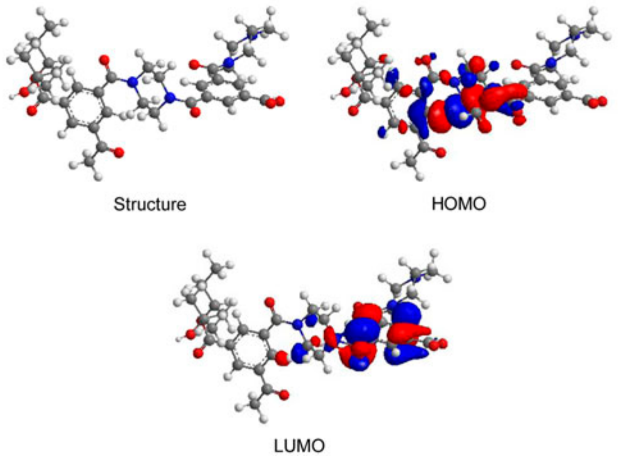
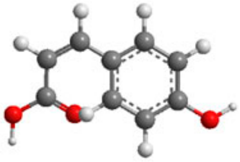
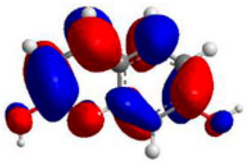
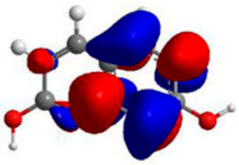
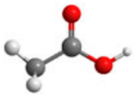
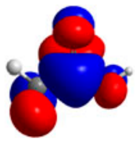
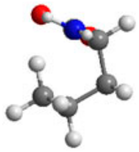
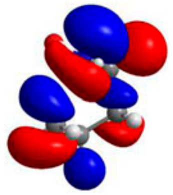
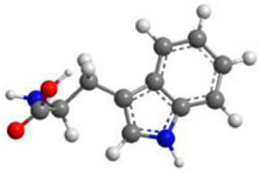
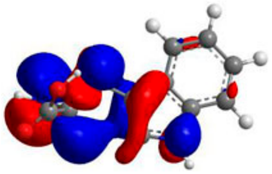
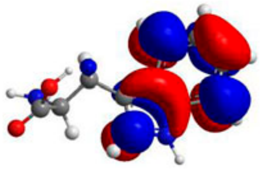


Fig. 3. Semi aromatic polyamide based on trimesoyl chloride and piperazine with PVA coating (NE70).

and 3. From Fig. 2, the most significant atoms were found to be at the ring having carboxylic (COO-R) and amide (NH_2-R) group as their high density of electron (HOMO) contain higher energy than the other molecules. These results are similar with the study of Meeto et al. [8], and they simulate geometry of polymer using same calculation. This can be further described by HOMO and LUMO energy. COO-R and NH_2-R have high electron density, occupying the HOMO. To stabilize energy of the compounds, electron from side to side make it has HOMO-LUMO energy gap between the two sides. HOMO and LUMO energy have been used to calculate electronic properties of organic molecules. Comparing with experiment results [9], HOMO–LUMO energy modeling can be used to predict characteristics for the NOM compounds react on the membrane surface. The basic evidence is that oxidants react at site of high electron density, computed as the energy of HOMO.

HOMO–LUMO ("filled-empty") orbital Interactions involve either proton transfer or unshared pair/empty orbital interactions. When the interacting atomic orbitals are considered, all heterolytic reactions are just examples of interactions between filled atomic or

Table 2
Surrogate NOM compound (p-coumaric acid, acetic acid, L-leucine) electronic structure

Compound	Structure	HOMO structure	LUMO structure
p-Coumaric acid (phenolic: HPOA)			
Acetic acid (carboxylic: HPI)			
L-Leucine (amino acid: HPI)			
L-Triptophan (amino acid: HPON)			

molecular orbitals and empty atomic or molecular orbitals. The interaction of any two atomic or molecular orbitals produces two new orbitals. One of the new orbitals is higher in energy than the original ones (the antibonding orbital), and one is lower (the bonding orbital). The "filled/empty" interaction therefore is stabilizing [10]. To deal with interacting molecular orbitals, the two that interact are generally the HOMO of one molecule, and the LUMO of the other molecule. These orbitals are the pair that lies closest in energy of any pair of orbitals in the two molecules, which allows them to interact most strongly. From the previous results, COO-R and NH_2-R have high electron density, occupying the HOMO. Here are pictures of the two orbitals from AM1 semi-empirical molecular orbital calculations of each compound (Table 2). From these results, to stabilize energy of the compounds, electron from side to side make it has HOMO–LUMO energy gap between the two sides. HOMO and LUMO energy have been used to calculate electronic properties of organic molecules [11–14]. In comparison with our experimental study [9], HOMO–LUMO energy modeling can be used to predict characteristics for the NOM compounds react on the membrane surface. The basic evidence is that oxidants react at site of high electron density, computed as the energy of HOMO.

3.2. Adsorption energy of between the membranes and the NOM compounds

DFT was carried out to examine the adsorption of the NOM compounds by approaching the NOM

Table 3
Properties of the membrane and the NOM compounds structure

Compound	HOMO (eV)	LUMO (eV)	Gap energy (eV)
NE90	−4.688	−3.312	1.376
NE70	−6.489	−4.971	1.518
p-Coumaric acid (C)	−4.454	−1.174	3.280
Acetic acid (A)	−12.937	0.396	13.333
L-Leucine (L)	−8.464	1.435	7.029
L-Triptophan (T)	−10.331	−1.920	8.411

Table 4
Adsorption energy between the membranes and the NOM compounds

Species	VDW	HOMO (eV)	LUMO (eV)	Gap energy (eV)
NE90-p-coumaric acid	30.2085	−9.648	−5.324	4.324
NE90-acetic acid	20.9921	−9.654	−4.789	4.865
NE90-L-leucine	26.6796	−9.651	−4.782	4.869
NE90-L-triptophan	26.6563	−9.648	−4.782	4.866
NE70-p-coumaric acid	59.0374	−5.085	−4.811	0.274
NE70-acetic acid	53.3642	−8.011	−4.753	3.258
NE70-L-leucine	57.4819	−7.667	−4.725	2.942
NE70-L-triptophan	60.8381	−8.757	−4.738	4.019

compounds onto the surface of NE70 and NE90 membrane in their HOMO/LUMO side. From Table 3, the adsorption energy was shown in terms of gap energy. Phenolic (p-Coumaric acid) and hydrophilic amino acid (L-leucine) are weakly bound to the surface of NE70 with lesser adsorption energy than the small nonionic carboxylic molecule (acetic acid) and amino acid (L-tryptophan). The physisorption with small adsorption force will favor suspend in solution rather than adsorb on membrane. On the other hand, the carboxylic and amino acid molecules tend to adsorb on membrane. From our previous study [9], carboxylic compound was major substances in the membrane permeate. This can be expected that although high adsorption force between NE70 and acetic acid (3.258 eV), it is not enough to fix acetic acid on membrane surface under working condition with high pressure (80 kPa).

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From these results, it can be briefly included that carboxylic compound has high-energy gap and tend to adsorb on the membrane surface than the other compounds (phenolic and acetic acid). And it bound higher energy with NE90 than NE70. This is comparable with the experimental results that NE90 is consists of surface material which is easily to be adsorbed by organic molecule, especially carboxylic type compound. Thus, the use of NE90 for organic compound rejection has to be faced with fouling problems. However, from the experimental result, it was also found that the presence of carboxylic compound in NF permeates. This can be described that the adsorbed carboxylic compound on the membrane surface may diffuse through the membranes during the operation.

4. Conclusions

From these results, it can be included that carboxylic compound has high-energy gap and tend to adsorb on the membrane surface than the other compounds (phenolic and acetic acid). And it bound higher energy with NE90 than NE70. This is comparable with the experimental results that is consists of surface material which is easily to be adsorbed by organic molecule, especially carboxylic type compound. Thus, the use of NE90 for organic compound rejection has to be faced with fouling problems. In comparison with the experimental results, it was also found that the presence of carboxylic compound in NF permeates. This can be described that the adsorbed carboxylic compound on the membrane surface may diffuse through the membranes during the operation.

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