Investigation on water adsorption on 3-crosslinked circular polyacrylamide membrane using ab initio, molecular dynamics and monte carlo calculations for dewatering microalgae

A R Villagracia1,6*, M David1,6, N Arboleda Jr1,6, H L Ong2, R Doong5, A Culaba3, J Chang4 and W Chen4

1 Physics Department, De La Salle University, Manila, Philippines 0922
2 School of Materials Engineering, Universiti Malaysia Perlis, Arau, Perlis, Malaysia
3 Mechanical Engineering Department, De La Salle University, Manila, Philippines
4 National Cheng Kung University, Taiwan
5 National Tsing Hua University, Taiwan
6 Advanced Nanomaterials Investigation by Molecular Simulations, DLSU, Manila

E-mail: arcvillagracia@gmail.com

Abstract. Microalgae has been identified as a source of biomass and biofuel which can be cultivated easily in large amounts given a small land area requirement. However, minimizing microalgae’s moisture content to 10% has been a bottleneck due to its energy intensive requirement and/or poor-quality outcome. A solution for this is the low-energy efficient forward osmosis system which needs a water superabsorbent polyacrylamide (PAM) hydrogels to maintain the salt concentration on the draw solution. Water sorption on 3-crosslinked circular polyacrylamide membrane was investigated using ab initio principles, molecular dynamics and monte carlo calculations. The PAM structure was geometrically optimized using density functional theory, and then equilibrated at room temperature and 1 atm pressure for 1 ns using molecular dynamics simulation. Monte Carlo simulations at room temperature with 2,500,000 steps and geometry optimization per step were performed to identify the adsorption sites for 25, 50, 75, 100, 125, and 150 water molecules by calculating their adsorption energies under the Dreiding Forcefield Model. A mathematical model was fitted to identify the relationship of adsorption energies with the number of water molecules that can be absorbed. Results showed this material can potentially adsorbed 1082 kg - 2345 kg of water per cubic meter of material when translated from calculated amount of water molecules that was adsorbed per unit cell volume. This study serves as a foundation for exploration of the new material circular polyacrylamide membrane that can facilitate microalgae drying to produce biomass and biofuel.

1. Introduction
Microalgae is identified as superfood, and it is considered as the most sustainable and renewable energy and food source which is environment friendly to climate change [1]. With the high-density production and easy cultivation, it is concluded that it can supply the long term demand for fuels [2]. Microalgae as the fourth-generation biofuel source can absorb and convert carbon dioxide directly to fuel [3].
A major challenge preventing the global utilization of microalgae is the costly production from microalgae to its viable products requiring an energy-intensive method dewatering and drying [4]. Several studies have been performed to investigate different methods in dewatering and drying of microalgae [5]. Some of these methods are solar drying, freeze drying, vacuum drying, rotary drying, and spray drying [6-8]. However, the cost in dewatering and drying is still high, and further studies are still needed to fine a reasonable method of dewatering and drying that would yield good quality of biomass.

In a nanoscale context, dewatering and drying are simply separation of water molecules from the substance. Thus, the objective is to enhance the separation at a lower cost without damaging the essential components of microalgae [9]. Several studies investigated this process of separation of water from microalgae using computational methods [12-15]. This would be very similar to studies on membrane filtration for water with an objective to separate water from other elements or chemicals [16-19]. Itliong et al. (2018) proposed forward osmosis process which will need a good water absorbent to maintain the salt concentration in the draw solution [19].

Polyacrylamide membranes are non-toxic material and resistant to microbiological degradation, and it is currently being used for water treatment using reverse osmosis [20]. Asadi et al. (2018) have shown the effectiveness of these hydrogels in wastewater filtration and basic drugs filtration in breast milk [21]. Other studies have used these hydrogel membranes with embedded protein to act as a device for sensing, grow cells, and develop organisms as substrate [22]. A controlled membrane’s pore size and thickness can easily be synthesized based on the previous studies [22]. Linear polyacrylamides [23] dissolves in water, while cross-linked polyacrylamides do not dissolve, but it swells when water is added, and it can easily be removed because it agglomerates with each other forming a big chunk of gel. This is the reason why polyacrylamides are called super-absorbent polymer [24].

In this study, 3-crosslinked polyacrylamide membrane is investigated using first principle calculations molecular dynamics, and monte-carlo simulations to determine its ability to absorb water molecules as a potential material for dewatering microalgae. No prior computational studies have been found on cross-linked membranes for water adsorption. The 3-crosslinked polyacrylamide membrane would yield to the smallest diameter of cylindrical membrane.

2. Methodology
Spin-polarized density functional theory [25] is used in obtain a geometrically structure a repeating acrylic monomer, polyacrylic, and 3-crosslinked polyacrylic membrane in a hexagonal lattice with high symmetry was obtained forming a periodic 3-crosslinked polyacrylic membranes. The final single isolated membrane structure has a length of 8 basic units. A molecular dynamics calculation is performed to determine its structure at 293 K and 1 atm for 1 ns with a time incremental step of 1 femtosecond using canonical ensemble. The canonical Monte-Carlo calculations implemented 2,500,000 steps to obtain the adsorption energies at 293 K. The final structure is used for the canonical monte carlo calculations at 293 K. The structures are shown in Figure 1.
Monte-Carlo calculations were used to identify the adsorption energies for 50, 75, 100, 125, and 150 water molecules all over the PAM. Geometry optimization was performed as well in every attempt to add a water molecule on the system.

2.1 Calculation Details
Quantum Espresso [26] was used to perform the spin-polarized DFT calculations. The exchange-correlation (XC) potential used in this study is the generalized gradient approximation Perdew–Burke–Ernzerhof (PBE) [27] and Rappe–Rabe–Kaxiras–Joannopoulos (RRKJ) for the ultrasoft pseudopotential [28] was used. The kinetic energy cutoff was set to 30 Ry, and a Monkhorst-Pack k-point sampling with $8 \times 8 \times 1$ with a $10^{-10}$ Rydberg convergence criteria for the energy self-consistent calculations, and $10^{-3}$ Ry/Bohr for force convergence criteria were used.

The large-scale atomic/molecular massively parallel simulator (LAMMPS) [29] was used for molecular dynamics simulation and Monte-Carlo calculations [30] with interaction parameters based on the Dreiding forcefield [31].

3. Results and Discussion

Figure 2 shows one of the most favorable configurations which has lowest energy at different amounts of H$_2$O. The lowest adsorption energies and intermolecular energies are found in Figure 3. The maximum number of water molecules that can be adsorbed by the 3-crosslinked can be interpolated from Figure 3a is around 130+ water molecules. The minima in the adsorption energy curve corresponds to 60+ water molecules. This means that this single membrane can easily absorb 54%–117% amount of water relative to the membrane’s mass, and equivalently equal to 1,082 kg – 2,345 kg of water per cubic meter.
The intermolecular energy diagram in Figure 3b shows that addition of water molecules increase the intermolecular energy shifting to the right. This would like explain why only a certain number of molecules can be adsorbed on the surface. More positive intermolecular energy (repulsion) occurred between the water molecules. The inner diameter for the 3-crosslinked PAM is 2.923 Å, and the sides of a triangle representing PAM are 7.890 Å, 7.987 Å, and 7.623 Å as shown in Figure 4a. Figure 4b-4e show hydrogen bonding between the hydrogen (oxygen) atoms of H₂O and oxygen (hydrogen) atoms of PAM. It is expected that bigger number of cross-linked PAM and/or longer membrane can hold larger number of water molecules. This mean that with a cluster of 3-crosslinked PAM would be a good candidate to synthesize for water absorbent in the forward osmosis system of Itliong et al (2018) [19].

4. Conclusions
A 3-crosslinked PAM was optimized using density functional theory, equilibrated at 293 K using molecular dynamics, and ran Monte-Carlo simulations to determine the adsorption energies for 25, 50, 75, 100, 125 and 150 water molecules. Results showed that the most favorable number of water molecules adsorption is around 60+ while the system can adsorb approximately 130+ water molecules. The intermolecular interaction between water molecules explains the decrease in the number of water molecules that can be adsorbed in the PAM. Further investigation are on-going to explore the dependence of water adsorption on the different number of PAM that are cross-linked, radius and length of the membrane. This study is a good foundation in identifying a good material for dewatering microalgae through water adsorption.
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