

PAPER • OPEN ACCESS

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

To cite this article: A R Villagracia *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **268** 012144

View the [article online](#) for updates and enhancements.

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

A R Villagrancia^{1,6*}, M David^{1,6}, N Arboleda Jr^{1,6}, 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: arcvillagrancia@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]. The



Content from this work may be used under the terms of the [Creative Commons Attribution 3.0 licence](https://creativecommons.org/licenses/by/3.0/). Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

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 find 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 to 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.

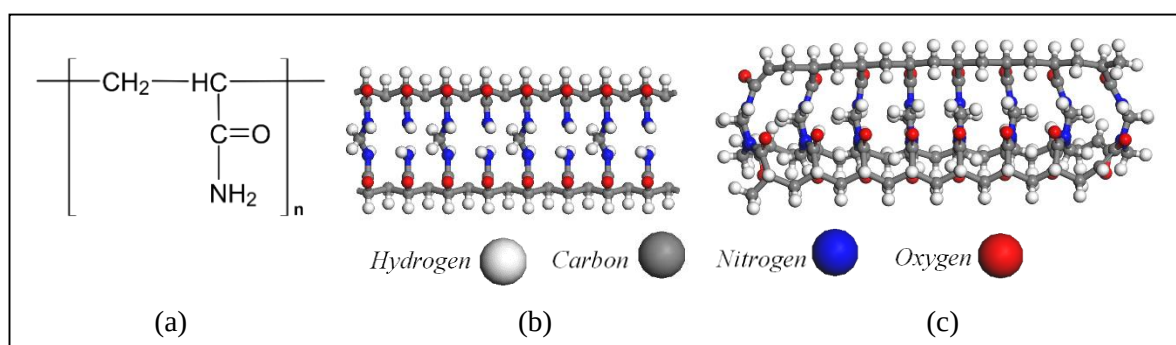


Figure 1 PAM Structure (a) Linear (b) 2-Crosslinked (c) 3-Crosslinked

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

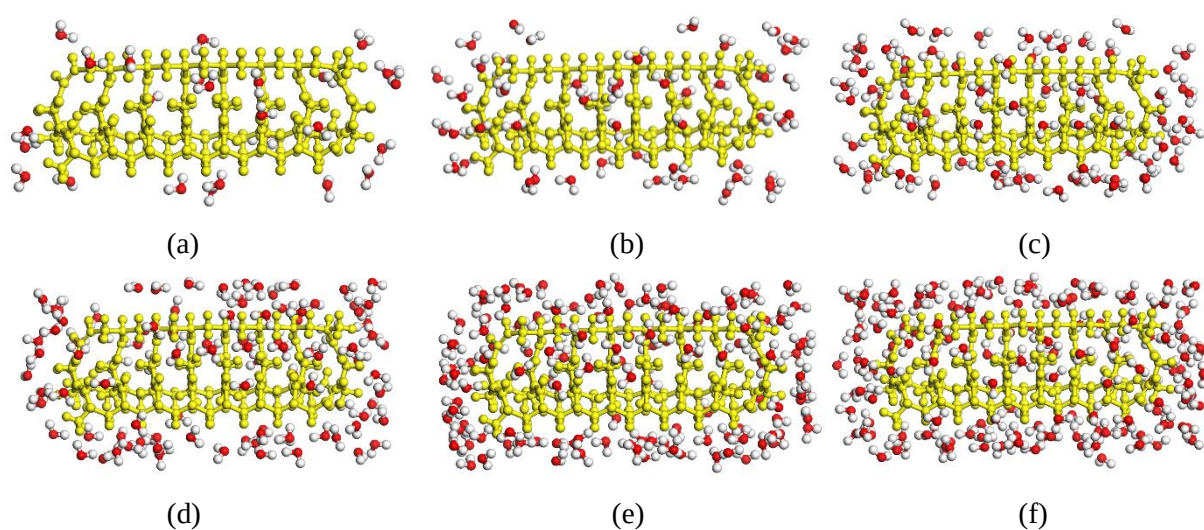


Figure 2 PAM (a) with 25 H₂O (b) with 50 H₂O
(c) with 75 H₂O (d) with 100 H₂O (e) with 125 H₂O (f) with 150 H₂O

Figure 2 shows one of the most favorable configurations which has lowest energy at different amounts of H₂O. 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.

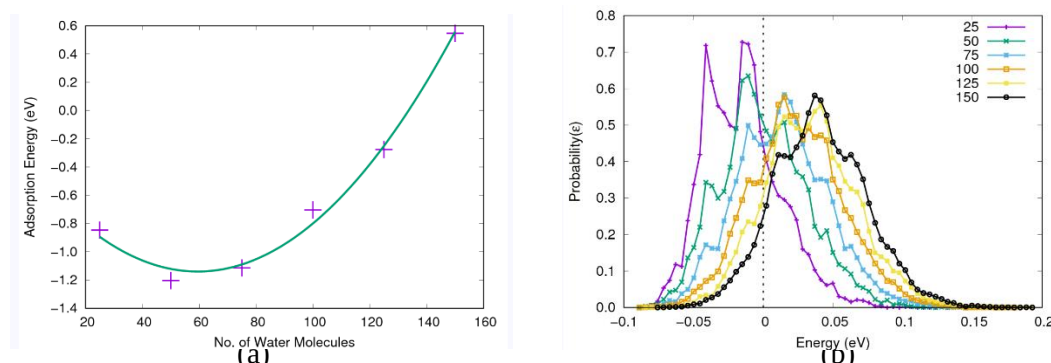


Figure 3 (a) Adsorption energy (b) H₂O Intermolecular Energy on PAM

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].

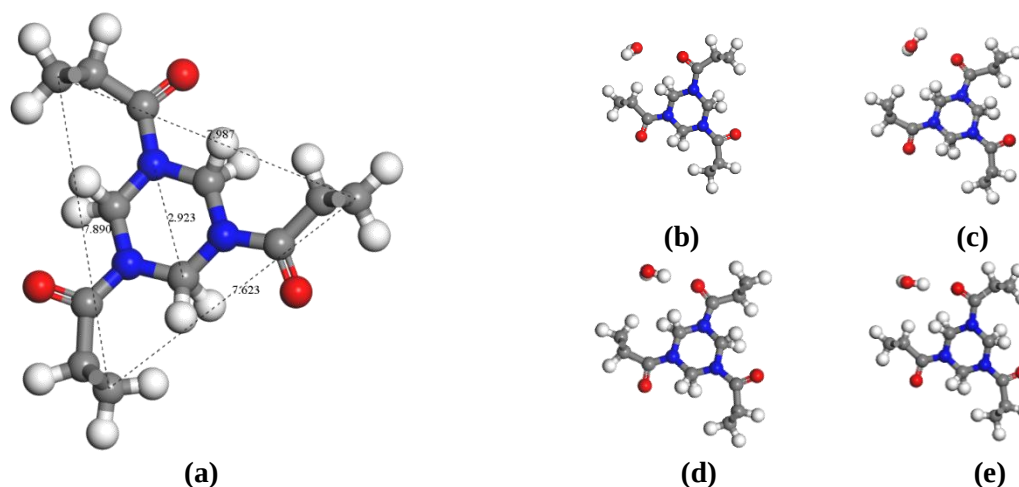


Figure 4 (a) Cross-section view (b)-(e) lowest energy configuration of H₂O on PAM

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.

5. Acknowledgments

The authors would like to thank the Commission on Higher Education-Philippine Research Network, High-Performance Computing Laboratory (HPCL) and Advance Nanomaterials Investigation & Molecular Simulations (ANIMoS) research unit of the Center for Natural Sciences and Environmental Research (CENSER), DLSU for the use of facility. The authors are grateful to the support of DLSU's Office of Vice Chancellor for Research and Innovation, and Physics Department through the Computational Materials Design Research Group (CMDRG).

6. References

- [1] Vigani M, Parisi C, Rodríguez-Cerezo E, Barbosa M J, Sijtsma L, Ploeg M and Enzing C 2015. Food and feed products from micro-algae: Market opportunities and challenges for the EU. *Trends in Food Science & Technology*, **42**(1), 81-92.
- [2] Randrianarison G and Ashraf M A 2017. Microalgae: a potential plant for energy production. *Geology, Ecology, and Landscapes*, **1**(2), 104-120.
- [3] Lü J, Sheahan C and Fu P 2011. Metabolic engineering of algae for fourth generation biofuels production. *Energy & Environmental Science*, **4**(7), 2451-2466.
- [4] Acuña F G, Fernández J M, Magán J J and Molina E 2012. Production cost of a real microalgae production plant and strategies to reduce it. *Biotechnology advances*, **30**(6), 1344-1353.
- [5] Villagrancia A R C, Mayol A, Ubando A T, Biona J, Arboleda N B, David M, Tumlos R, Lee H, Ong H L, Espiritu R and Culaba A 2016. Microwave drying characteristics of microalgae (*Chlorella vulgaris*) for biofuel production. *Clean Technologies and Environmental Policy*, **18**(8), 2441-2451.
- [6] Show K Y, Lee D J, Tay J, Lee T and Chang J 2015. Microalgal drying and cell disruption—recent advances. *Bioresource technology*, **184**, 258-266
- [7] Chen C, Chang J and Lee D J 2015. Dewatering and drying methods for microalgae. *Drying technology*, **33**(4), 443-454.
- [8] Tanzi C D, Vian M and Chemat F 2013. New procedure for extraction of algal lipids from wet biomass: A green clean and scalable process. *Bioresource technology*, **134**, 271-275.
- [9] Uduman N, Qi Y, Danquah M K, Forde G and Hoadley A 2010. Dewatering of microalgal cultures: a major bottleneck to algae-based fuels. *Journal of renewable and sustainable energy*, **2**(1), 012701
- [10] Manrique R, Moreno J L, Villagrancia A R C, Ubando A, Kasai H, Arboleda N, David M and Culaba A 2017 Effects of salinity on the CO₂ permeation across lipid bilayer for microalgae biofixation: a molecular dynamics study. *Journal of Applied Phycology*, **30**(1) 55-61
- [11] Manrique R, Ubando A, Villagrancia A R C, Corpuz J, Padama A, David M, Arboleda N, Culaba A and Kasai H 2014 A molecular dynamics investigation of water migration in a lipid bilayer for microalgae drying *Philippine Science Letters* **7**(1) 171-178
- [12] Enriquez J, Villagrancia A R C, Moreno J L, Arboleda N, David M, Ubando A, Culaba A, and Cuello J 2018 Effect of structural and dynamical properties of lipid bilayer on water permeation studied using coarse-grained molecular dynamics simulation. *In Humanoid, Nanotechnology, Information Technology, Communication and Control, Environment and Management (HNICEM)*, IEEE Xplore Digital library. 1-7
- [13] Enriquez J, Villagrancia A R C, Moreno J L, Arboleda N, David M, Ubando A, Ong H L, Cuello J 2018 Coarse-Grained Molecular Dynamics Investigation on the Effects of Uniform Electric Field on DPPC Lipid Bilayer: with and without Vacuum Space. *In Humanoid, Nanotechnology, Information Technology, Communication and Control, Environment and Management (HNICEM)*, 2015 International Conference on, IEEE Xplore Digital library
- [14] Mayol A, Villagrancia A R C, Ubando A, Biona J, Ong H L, Espiritu R, Lee H, Tumlos R, Arboleda N, and Culaba A 2015. Investigation of the drying characteristics of microalgae using microwave irradiation. *In Humanoid, Nanotechnology, Information Technology,*

- Communication and Control, Environment and Management (HNICEM), 2015 International Conference on*, IEEE Xplore Digital library 1-6
- [15] Ducut M, Villagrancia A R C, Corpuz J, Arboleda N, David N, Manrique R, Ubando A and Culaba A 2014 "Molecular dynamics study on the effects of varying temperature and pressure on phosphatidylcholine lipids for microalgae drying." In *Humanoid, Nanotechnology, Information Technology, Communication and Control, Environment and Management (HNICEM), 2014 International Conference on*, IEEE, Xplore Digital library 1-4
 - [16] Jackson E A and Hillmyer M A 2010. Nanoporous membranes derived from block copolymers: from drug delivery to water filtration. *ACS nano*, **4**(7), 3548-3553.
 - [17] Padaki M, Murali R, Abdullah M, Misdan N, Hilal N and Ismail A 2015 Membrane technology enhancement in oil–water separation. A review. *Desalination*, **357**, 197-207.
 - [18] Alsbaiee A, Smith B J, Xiao L, Ling Y, Helbling D E and Dichtel W R 2016. Rapid removal of organic micropollutants from water by a porous β -cyclodextrin polymer. *Nature*, **529**(7585), 190.
 - [19] Itliong J, Rojas K, Villagrancia A R, Ong H L, David M, Manrique R, Arboleda A, Culaba A, Chang J, Chen W 2018, Density Functional Theory-based modeling and calculations of a polyamide molecular unit for studying forward-osmosis-dewatering of microalgae using molecular dynamics. In *Humanoid, Nanotechnology, Information Technology, Communication and Control, Environment and Management (HNICEM)*, IEEE, Xplore Digital library
 - [20] Zhang X, Lin B, Zhao K, Wei J, Guo J, Cui W, Jiang S, Liu D and Li J 2015. A free-standing calcium alginate/polyacrylamide hydrogel nanofiltration membrane with high anti-fouling performance: Preparation and characterization. *Desalination*, **365**, 234-241.
 - [21] Asadi S, Tabani H and Nojavan S 2018. Application of polyacrylamide gel as a new membrane in electromembrane extraction for the quantification of basic drugs in breast milk and wastewater samples. *Journal of pharmaceutical and biomedical analysis*, **151**, 178-185.
 - [22] Nghe P, Boulineau S, Gude S, Recouvreux P, van Zon J S and Tans S J 2013. Microfabricated polyacrylamide devices for the controlled culture of growing cells and developing organisms. *PloS one*, **8**(9), 75537
 - [23] Lambin P and Fine J M 1979. Molecular weight estimation of proteins by electrophoresis in linear polyacrylamide gradient gels in the absence of denaturing agents. *Analytical biochemistry*, **98**(1), 160-168.
 - [24] Huang Y, Zeng M, Ren J, Wang J, Fan L and Xu Q 2012. Preparation and swelling properties of graphene oxide/poly (acrylic acid-co-acrylamide) super-absorbent hydrogel nanocomposites. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **401**, pp.97-106.
 - [25] Yang W and Ayers P 2003. Density-functional theory. In *Computational Medicinal Chemistry for Drug Discovery* (103-132). CRC Press.
 - [26] Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C, Ceresoli D, Chiarotti G, Cococcioni M, Dabo I and Dal Corso A 2009. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of physics: Condensed matter*, **21**(39), 395502
 - [27] Perdew J P, Burke K and Ernzerhof M 1996. Generalized gradient approximation made simple. *Physical review letters*, **77**(18) 3865.
 - [28] Hamann, D R 2013. Optimized norm-conserving Vanderbilt pseudopotentials. *Physical Review B*, **88**(8), 085117.
 - [29] Plimpton S, Crozier P and Thompson A 2007. LAMMPS-large-scale atomic/molecular massively parallel simulator. *Sandia National Laboratories*, **18**, 43.
 - [30] Metropolis N and Ulam S 1949. The monte carlo method. *Journal of the American statistical association*, **44**(247), 335-341.
 - [31] Mayo S L, Olafson B and Goddard W 1990. DREIDING: a generic force field for molecular simulations. *Journal of Physical chemistry*, **94**(26), 8897-8909.