Carbohydrate Polymers 164 (2017) 162–169

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

A structural basis for the amphiphilic character of alginates – Implications for membrane fouling

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ARTICLE INFO

Article history:
Received 26 October 2016
Received in revised form 9 January 2017
Accepted 19 January 2017
Available online 22 January 2017

Keywords:
Membrane fouling
Alginates
Beta-D-mannuronic acid
Alpha-L-guluronic acid
Molecular dynamics

ABSTRACT

Ostensibly hydrophilic alginates are known to foul hydrophobic membranes, under various conditions. Here, controlled experiments have been conducted at high and low pH on the fouling of a polypropylene membrane by alginate and the results suggest that the observed fouling is due to an intrinsic property of the alginate. Thus quantum chemical calculations on the M and G monomers of alginate reveal that M adopts an equilibrium geometry that is hydrophilic on one face and hydrophobic on the other, i.e. is potentially amphiphilic. Molecular dynamics simulations on short alginate chains of different sequences interacting with a modelled polypropylene surface, show that this characteristic is carried over to the polymer and results in hydrophobic patches along the chain that facilitate attractive interactions with the polypropylene surface. This concept is buttressed by an analysis of the binding characteristics of a previously reported X-ray structure of the mannuronan C-5 epimerase AlgE4 enzyme.

1. Introduction

Membrane-based separation technologies are widely utilised, with broad applications including desalination, water reclamation and desalination – as well as in the food and dairy processing industries (Daufin et al., 2001; Lee, Arnot, & Mattia, 2011; Pouliot, 2008; Wintgens et al., 2005). A major issue for all such applications is the challenge of organic fouling (Lee, Amy, & Croué, 2004). This is particularly difficult for the reclamation and treatment of natural surface waters, where the composition and concentration of natural organic matter (NOM), as well as other solutes such as metal ions, can be constantly fluctuating. Due to the highly complex and variable nature of NOM in bulk water samples, researchers often select model compounds that represent a particular category. For example, bovine serum albumin (BSA) may be employed to represent proteins and sodium alginate may be used to represent the high molecular weight hydrophilic biopolymer fraction. Thus their individual and synergistic effects on membrane behaviour may be scrutinized (Gray, Dow, Orbell, Tran, & Bolto, 2011; Gray et al., 2008; Henderson et al., 2011; Jermann, Pronk, Meylan, & Boller, 2007; Myat et al., 2014).

Sodium alginate is the sodium salt of alginic acid, which is a linear polyuronic acid produced naturally by brown algae and some bacteria (Donati & Paoletti, 2009; Gorin & Spencer, 1966; Goven, Fyfe, & Jarman, 1981). Alginates are unbranched copolymers produced from irregular, but generally not random, blocks of two monomers; namely β-D-mannuronic acid (M) and α-L-guluronic acid (G). In alginate, these two monomers are linked via (1 → 4) glycosidic bonds, to form three distinct types of sequence blocks – homopolymeric blocks of both M and G, as well as the heteropolymeric block of alternating G and M subunits. A schematic diagram of such polymer sequences is depicted in Fig. 1.

In spite of such polysaccharides being regarded as ostensibly hydrophilic in nature, due to the preponderance of hydrogen bonding functional groups such as hydroxyl and carboxylate, recent studies that have examined the effects of sodium alginate on membrane fouling have found that alginates adhere to both hydrophilic (Katsoufidou, Yiantsios, & Karabelas, 2007, 2008; Nghiem & Espendiller, 2014) and hydrophobic (Gray et al., 2011; Guo, Chen, & Hu, 2009; Less, Ang, & Elimelech, 2006) polymeric membrane surfaces, such as polyamide and polypropylene, respec-

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http://dx.doi.org/10.1016/j.carbpol.2017.01.072
0144-8617/

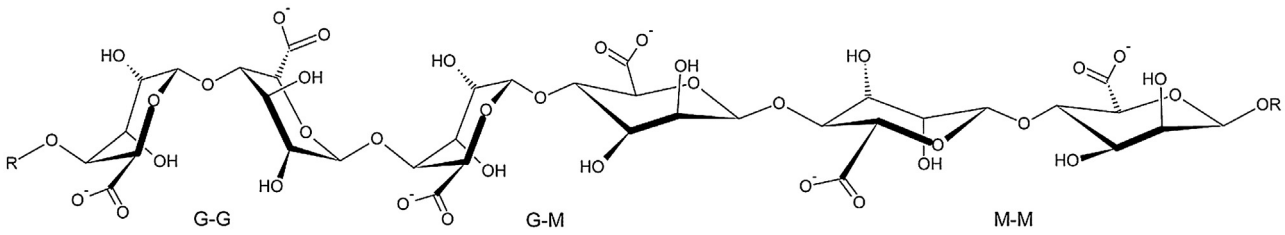

Fig. 1. A representative section of an alginate polymer chain displaying the two different monomers, G and M, and the three possible sequences. The carboxylate groups are deprotonated at a neutral pH.

tively. Thus whilst there is research at the molecular level on how alginate interacts and irreversibly binds to hydrophilic membrane surfaces, including directly via metal ion bridging (Xiang, Liu, Mi, & Leng, 2013) or hydrogen bonding (Xiang, Liu, Mi, & Leng, 2014), there is a paucity of such information as to how the supposedly hydrophilic alginate chains, counterintuitively perhaps, bind in a seemingly thermodynamically unfavourable way to hydrophobic surfaces. To date, there has been no molecular-scale explanation offered for this phenomenon.

The work presented here addresses this problem by identifying the origin of the amphiphilic nature of alginates through quantum chemical characterization of the individual M and G monomers and subsequent molecular dynamics simulations that simulate actual interactions between alginate chains and a model hydrophobic polypropylene surface. These studies have also been benchmarked to complimentary laboratory membrane fouling experiments and compared to a biochemical example of hydrophobic enzymatic active site interacting with its alginate derivative substrate.

2. Experimental method

2.1. Feed solution preparation

Sodium alginate from brown algae was obtained from Sigma-Aldrich, with the molecular weight specified by the manufacturer as being in the range of 12–80 kDa and a composition of 39% G and 61% M. A stock solution containing 1 g/L of sodium alginate in DI water was prepared.

2.2. Membranes

A single hollow fibre (HF) membrane filtration rig was used to examine the fouling rate of an sodium alginate feed solution. A single fibre polypropylene membrane obtained from Memcor with an outside diameter of 0.50 mm, an inside diameter of 0.25 mm and 600 mm in length, was inserted into a transparent polyurethane tubing and then sealed with epoxy resin. This membrane material is hydrophobic polypropylene with a nominal pore size of 0.2 μm as specified by the membrane supplier. The filtration experiments were performed at constant flux and the water was pumped from the outside to the inside of the hollow fibre. The filtrate was weighed on a balance and liquid backwashing of the membrane was achieved via pressurized water and a series of valves. The backwashing regime consisted of a flow reversal for 20 s so that filtered water entered the inside of the hollow fibre and forced out any accumulated foulant to the outside. The outside of the fibre was then flushed by a cross flow of feed water past the membrane for a further 20 s. A data acquisition system was used to control the backwash sequence as well to record the transmembrane pressure (TMP) via a pressure transducer. The ambient air temperature was also recorded during the run. Clean water fluxes were also monitored before each test.

2.3. Membrane filtration

The filtration unit was operated with pumped permeate (controlled flux) and a dead-end configuration. The feed solution was supplied to the outside of the HF membrane module using a positive displacement pump at a set flow rate, and the filtrate (permeate) was collected from the inside of HF membrane. The TMP was recorded continuously and backwashing with clean water was carried out for 5 min after every hourly filtration cycle.

2.4. Quantum chemical calculations

Equilibrium geometries and electrostatic potential energy maps for the alginate monomers G and M and their respective anions were computed at the B3LYP/6–31 + G* level of theory SPARTAN06 (Wavefunction, Inc.).

2.5. Molecular dynamics

All simulations were carried out using a modified CHARMM all22 force field (MacKerell et al., 1998) and the NAMD 2.7 package (Phillips et al., 2005). Topology and parameter files for carbohydrates were appropriately edited to allow for the addition of the carboxylic acid groups to the parameterised carbohydrates. Atomic point charges were recalculated from density functional equilibrium geometry calculations – at the B3LYP/6-31G(d) level of theory on the G and M monomers and applied to the polymer topology. Initially, fully deprotonated hexamers of sequence GGMMGG were constructed using the Visual Molecular Dynamics (VMD) program (Humphrey, Dalke, & Schulten, 1996) and optimised using MD in a TIP3P water box which measured 50 Å × 50 Å × 50 Å, which included six sodium ions to neutralise the charge of the hexamer. These optimisations involved 1000 conjugate gradient minimization steps, followed by 2 ns of molecular dynamics simulation time under NPT conditions in a periodic box. The temperature and pressure was maintained using Langevin dynamics as implemented in NAMD. This optimised hexamer was used as the starting geometry for the polypropylene membrane simulations. The deprotonated decamers were similarly optimised as previously described for the deca-G (Stewart, Gray, Vasiljevic, & Orbell, 2014a), deca-M and penta-GM (Stewart, Gray, Vasiljevic, & Orbell, 2014b) chains.

In order to study how these, now-optimized, hexamer and decamers chains interact with a polypropylene membrane, a model of this surface was also required. Again, atomic point charges were calculated from density functional equilibrium geometry calculations, at the B3LYP/6-31G(d) level of theory. The surface was developed by building linear chains of polypropylene that were 12 monomers long. Fifteen of these chains were then placed approximately 3.5 Å apart relative in two rows, with the top row lining up with the space between the lower chains. This construct was solvated in a TIP3P waterbox 70 Å × 70 Å × 70 Å in size, and subjected to MD simulations in order to form a consolidated polymer mass. This MD simulation consisted of 1000 conjugate gradient mini-