



Characterization of membrane–foulant interactions with novel combination of Raman spectroscopy, surface plasmon resonance and molecular dynamics simulation

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ABSTRACT

Adsorptive fouling, by phenolic compounds, is a serious issue regarding the development and use of membrane based filtration technologies for water purification and wastewater treatment. We have developed a novel, combined, protocol of Raman spectroscopy and surface plasmon resonance (SPR) experiments, along with molecular dynamics (MD) simulation, to study the interaction of vanillin, a model phenolic compound, with the polyethersulfone (PES) surface of a membrane. The adsorption of vanillin to the PES surface was found to be highly pH dependent; the source of this was determined, by MD simulation, to be the stronger interaction with the protonated form of vanillin, predominant at low pH. Vanillin interacts with the PES surface, both through entropy driven, hydrophobic, interactions and, for the case of the protonated form, H-bonding of the hydroxyl group with the sulphur oxygens of the PES molecules. In addition to general insight into the fouling process that can be used to develop new methods to inhibit adsorptive fouling, our results also elucidate the specific interaction of the PES membrane with vanillin that can be used in the development of anti-fouling coatings, based on the structure of vanillin.

1. Introduction

Fouling, the adhesion of foreign materials to a surface in a fluid medium, has emerged as a serious problem regarding the development and application of membrane based filtration technologies [1–7]. Due to fouling, membrane performance can be severely impeded through both (1) a reduction of the pore size, changing the filtration behavior [1] and (2) altering the surface properties of the membrane, e.g. hydrophobicity and surface charge [2].

Membranes generally have a selective surface, *skin layer*, composed of relatively rigid polymers; polyethersulfone (PES) or polyvinylidene fluoride (PVDF) are common choices, possibly with trace quantities of additives, to adjust the properties of the surface [8], e.g. permanently hydrophilic polyethersulfone (PESH). These materials, capable of forming ion–dipole interactions or H-bonding with water [9], are also, however, generally relatively hydrophobic [10]. As a result of their specific properties, surfaces composed of these polymers are very susceptible to fouling.

Adsorptive fouling is challenging to control. This process is governed by weak intermolecular forces, *i.e.* non-bonded interactions, between the foulant molecules and the polymers that form the skin layer of the membrane [11,12]. Clearly, the concentration of foulant molecules in the fluid medium and the nature of their direct interaction with the surface, both play a role; several properties of the fluid environment, in which the membrane is immersed, however, also govern the extent to which adsorptive fouling occurs. These include, hydrodynamics, *i.e.* flow conditions, pH and the presence of other molecules that either accelerate or inhibit the fouling process [13]. A detailed mechanistic understanding of these factors is critical to the development of methods to improve membrane performance through the control of this phenomenon.

A specific class of molecules that both PES and PVDF skin layers are vulnerable to adsorptive fouling from, are phenolic and ligneous compounds [14–16]; they are commonly present in the fluid environments in which these membranes operate. Phenolic compounds, like humic acid, [17] are abundant in surface water, thus an important source of

Abbreviations: DFT, density functional theory; K_D , dissociation constant; MD, molecular dynamics; SPR, surface plasmon resonance; TIR, total internal reflectance; PES, polyethersulfone; PESH, permanently hydrophilic polyethersulphone; ATR, attenuated total reflectance; PVDF, polyvinylidene fluoride; PCA, principal component analysis

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fouling in relation to the use of membrane based technologies for drinking water purification [17]; lignin related compounds are common in many wastewater streams, [18] e.g., effluent from pulp bleaching [19,20], where filtration using membranes has been proposed [21]. Overall, separation and removal of these specific compounds is of significant industrial importance [11,22]. For example, Koivula et al. [15] found the filtration of birch hydrolysate, using a commercial ultrafiltration membrane, to be severely impeded due to the occurrence of acute and rapid fouling; the resultant flux at 5.5 bar and 60 °C was reduced to only $2 \text{ L m}^{-2} \text{ h}^{-1}$. Birch hydrolysate is known to contain phenolic ligneous compounds; the filtration efficiency was found to be significantly enhanced when these were removed: the ligneous compounds were shown to play the key role in the fouling that was observed. Other groups have also found evidence of adsorptive fouling of ultrafiltration membranes by phenolic compounds [22,23].

In possession of both polar and non-polar structural units, phenolic compounds are amphipathic; the hallmark of their structure is the possession of both hydrophobic phenyl rings and hydrophilic OH-groups; these can act as H-bond donors at low pH, in their protonated state and, at higher pH, become ionized (deprotonated), thus more hydrophilic. The mechanism through which they adsorb to the polymer film is thus a combination of both electrostatic, e.g. H-bonding and entropy driven, i.e. hydrophobic, effects [9,24]. Normally, these forms of interaction counteract one another, however, in this case they both work together to increase binding; this is the source of their potency as agents of adsorptive fouling. Susanto et al. [22] studied these interactions in detail and proposed that adsorption is an extremely complex process, involving many different interaction mechanisms, including H-bonding, hydrophobic interactions, π - π stacking of benzene rings and water ordering at the membrane surface. The methodology used by this group did not, however, enable definitive confirmation of what they proposed.

In this study, a novel combination of two experimental methodologies: Raman spectroscopy and surface plasmon resonance (SPR), with computational molecular dynamics modelling (MD) has been applied to obtain further insight into the mechanisms that govern the adsorptive fouling of PES based filtration membranes by phenolic compounds; the goal is to provide insight that could lead to the development of new methods to inhibit this phenomenon. Specifically, the effect of pH and the mechanisms involved in this process have been studied. Vanillin was selected as a model phenolic compound that, additionally, has itself been proposed as an antifouling agent [25–28]. Vanillin, a degradation product of wood lignin, is a weak acid with a hydroxyl group that is protonated at acidic pH and unprotonated at basic pH.

Using Raman spectroscopy in real time, the interaction of vanillin with a commercial ultrafiltration membrane was investigated: the UH004 P (Microdyn-Nadir GmbH) membrane, with a skin layer composed of PESH. The interaction of vanillin with a pure PES surface was also examined, using SPR, not involving a cross-filtration system as in Raman spectroscopy experiments. PESH only differs from PES in the addition of a small quantity of hydrophilic polymer, to control pore structure and increase the hydrophobicity of the surface. Thus, a PES surface can be seen as an appropriate model of the PESH surface of a commercial ultrafiltration membrane. The structure of both PES and vanillin are shown in Fig. 1.

The protonation state of the vanillin molecule, thus pH, clearly plays a role in the nature of the interactions between vanillin and the PES surface. Unprotonated vanillin is more hydrophilic than the protonated form, thus it would be expected to have a decreased tendency to adhere to the PES film. Specific interactions between different functional groups of vanillin and PES are also expected to play a role. It can plausibly be postulated that protonated vanillin molecules possess the capacity to form H-bonds with either the ether or sulphur oxygens of PES. This mechanism could further enhance the strength of the interaction between PES and vanillin in a fashion typical for phenolic compounds. As mentioned above, both electrostatic and entropic effects

would be involved in its interaction with the membrane surface. The specific research questions addressed by this study are shown in schematic form in Fig. 1.

Raman spectroscopy is a minimally invasive spectroscopic technique that has been widely used for off-line identification and characterization of chemical structures and to determine, quantitatively, the amount of analyte in a sample; it has also been used in a wide range of applications relating to process and synthesis monitoring [29]. It is possible to identify a wide range of organic compounds and functional groups from their absorption spectra; the intensity of each spectra can be used to determine the quantity of each compound adsorbed to a given surface [30]. In previous published work [31], we have shown that vanillin adsorbs to PESH membranes and the quantity adsorbed can be monitored in real time using Raman spectroscopy.

Analogous to the intensity of a Raman spectra, the strength of the response signal from an SPR experiment can be directly correlated to the extent of a deposited layer on a surface [32–34]. However, it should be noted that the SPR protocol cannot be used to directly study the surface of a commercial ultrafiltration membrane, as the technique requires spin coating the polymer that comprises the model surface directly onto a sensor chip. Thus, SPR serves only as a protocol to study adsorption and desorption of compounds to the spin coated model surface and the properties of the bulk solution above the interface. Further details regarding the SPR protocol are found in the [Supplementary Material \(SM\)](#), see Fig. S1. Both Raman spectroscopy and SPR are *label free*; they do not involve the insertion of any probe molecule into the system. As such, they are, while extremely sensitive to even the smallest changes in surface concentration, able to investigate a surface without the corrupting effect of the introduction of a new molecule.

Molecular dynamics simulation (MD) can provide a three dimensional picture of the system being studied; a section of the PES surface, $\sim 15 \times 15 \text{ nm}$ in size, can be observed over a timescale of hundreds of nanoseconds. As the result is only a model, the stand alone value is, admittedly, limited, however, when combined with the aforementioned experimental analysis, a window onto the system is opened that adds mechanistic insight to the experimental results; it can be seen, as described in a review written by Lee et al. [35], as a “computational microscope” focussed on the system being studied. In this study, a synergistic combination of all three of these methodologies, Raman spectroscopy, SPR and MD simulation, has been used to study this system.

2. Materials and methods

2.1. Vanillin: the model compound

Vanillin is a moderately lipophilic molecule with an octanol–water partition coefficient of 1.37 (logP), thus has greater affinity for hydrophobic, rather than hydrophilic, environments. This logP value, however, describes the partitioning of the unionized, protonated, form of the molecule; vanillin is in possession of a hydroxyl group with a pKa of 7.4, thus it is a weak acid: the percentages of protonated vanillin will be 100%, 50% and 0.25% at pH values of 2, 7.4 and 10, respectively; both the Raman spectroscopy and SPR experiments were carried out at these three pH values.

2.2. Raman monitoring of the adsorption of vanillin on the surface of the UH004 P PESH membrane

2.2.1. Materials

The UH004 P membrane (Microdyn-Nadir GmbH) that has a skin layer composed of PESH and a molecular weight cut-off of 4 kDa was used in adsorption studies. Vanillin (4-hydroxy-3-methoxybenzaldehyde, 99%) was purchased from Acros Organics. pH was adjusted using sodium hydroxide (Merck, $\geq 99.0\%$) and hydrochloric

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