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Random sequential adsorption of human adenovirus 2 onto polyvinylidene fluoride surface influenced by extracellular polymeric substances

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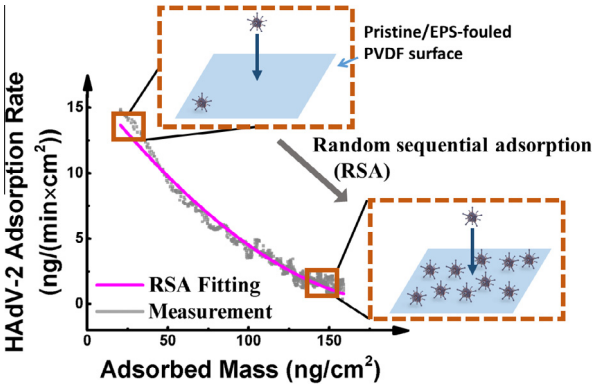
HIGHLIGHTS

- HAdV-2 adsorption to pristine and EPS-fouled PVDF surfaces is irreversible.
- The RSA model sufficiently describes the kinetics of HAdV-2 adsorption onto pristine and EPS-fouled PVDF surfaces.
- Virus–membrane and virus–virus interactions determine HAdV-2 adsorption.

GRAPHICAL ABSTRACT



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ABSTRACT

Virus removal by membrane bioreactors depends on virus–membrane and virus–foulant interactions. The adsorption of human adenovirus 2 (HAdV-2) on polyvinylidene fluoride (PVDF) membrane and a major membrane foulant, extracellular polymeric substances (EPS), were measured in a quartz crystal microbalance. In 3–100 mM $CaCl_2$ solutions, irreversible adsorption of HAdV-2 was observed on both pristine and EPS-fouled PVDF surfaces. The HAdV-2 adsorption kinetics was successfully fitted with the random sequential adsorption (RSA) model. The applicability of the RSA model for HAdV-2 adsorption is confirmed by comparing the two fitting parameters, adsorption rate constant k_a and area occupied by each adsorbed HAdV-2 particle a, with experimentally measured parameters. A linear correlation between the fitting parameter k_a and the measured attachment efficiency was found, suggesting that the RSA model correctly describes the interaction forces dominating the HAdV-2 adsorption. By comparing the fitting parameter d_{ads} with the hydrodynamic diameter of HAdV-2, we conclude that virus–virus and virus–surface interactions determine the area occupied by each adsorbed HAdV-2 particle, and thus influence the adsorption capacity. These results provide insights into virus retention and will benefit improving virus removal in membrane filtration.

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1. Introduction

In the context of increasing water demand in many countries including the United States, municipal wastewater reuse has been proposed as an effective approach to increase the water supply [1]. Though non-potable reuse of municipal wastewater has been in practice, safety issues, especially microbial safety, are the major concern of water consumers [2]. Among pathogens in wastewater, special attention has been paid to viruses because of their low-dose infectivity [3], long survival time in the environment [4], and the lack of systematic monitoring [5].

Compared to conventional processes, membrane bioreactors (MBR) have the potential to achieve higher virus removal and to ensure public safety in wastewater reuse [6–8]. Investigation of virus removal by MBR found that pristine membranes alone achieved relatively low virus removal, while membrane foulants greatly increased the virus removal efficiency [9–11]. However, virus removal by a fouled membrane is energy-intensive and unstable [10]. The necessity of developing anti-fouling membranes with a high virus removal efficiency has been highlighted [12]. One of the obstacles to developing these membranes is the lack of knowledge on virus behavior at the water–membrane interface. Previous research of virus adsorption on or elution from membranes focused on the mechanism of virus–membrane interaction forces [13–16]. For oppositely charged virus and membranes, the attractive electrostatic force dominates virus adsorption. In the condition that virus and membranes are both negatively charged, electrostatic interaction, hydrophobic interaction, and salt bridges jointly determine the virus adsorption onto membranes.

Knowledge of interaction forces is significant but not sufficient to predict virus behavior on membrane surfaces, especially in the aspect of adsorption kinetics and capacity. The kinetics of virus adsorption onto the membrane influences the virus removal both directly and indirectly. The direct influence is that there are less adsorption sites available as the filtration goes on, resulting in a decrease of virus removal over the filtration time. The indirect influence is that the viruses adsorbed to the membrane will decrease the effective membrane pore size and even completely block the pores, leading to an increase of the virus removal. With these two mechanisms, virus adsorption influences the dynamics of virus removal both in the short-term and long-term membrane filtration [17–19]. Therefore, a quantitative understanding of virus adsorption kinetics onto membranes is required to predict the virus removal efficiency by membrane filtration.

The random sequential adsorption (RSA) model has been shown to be applicable in explaining the adsorption of colloids and proteins [20–26]. According to the RSA model, an incoming particle adsorbs onto the surface at a random position if there is no overlap with previously adsorbed particles. The adsorption site on the surface is assumed to be continuous, unlike the assumption of discrete adsorption sites in the Langmuir model. Considering that the size of viruses is larger than 20 nm, and that the distance between adsorption sites on membrane surfaces is much smaller, the RSA model is closer to the nature of virus adsorption than the Langmuir model. A better prediction of colloid adsorption with RSA than Langmuir has been validated, especially in the range of high surface coverage [22,26]. The RSA model is applied in this work to investigate the virus adsorption kinetics and capacity onto membrane surfaces.

The specific objective of this work is to quantitatively investigate the virus adsorption onto the polyvinylidene difluoride (PVDF) membrane with the adsorbed mass measured in real time using a quartz crystal microbalance with dissipation (QCM-D). Human adenovirus 2 (HAdV-2) is used as a model virus because human adenovirus has been suggested to be an indicator of human viruses due to its high detection frequency in wastewater, and also because of its virulence causing respiratory and diarrhea diseases [27–29]. PVDF is one of the most commonly used materials for micro- and ultrafiltration membranes in the MBR market because of its excellent chemical, thermal, and mechanical properties [30,31]. Since membrane foulants in MBR influence membrane surface properties, the effect of a major MBR foulant, extracellular polymeric substances (EPS) [32–34], on HAdV-2 adsorption is also discussed in this study.

2. Methods and materials

2.1. HAdV-2 propagation

The HAdV-2 (ATCC, VR-846) used in this study was propagated in the A549 human lung carcinoma cells (Diagnostic Hybrids). The A549 cells were propagated at 37 °C in 5% CO_2 with Ham's F12K growth media supplemented with 10% fetal bovine serum (FBS), 100 U/ml of penicillin, 100 μg/ml of streptomycin, and 0.25 μg/ml of amphotericin B [35]. Right after a full confluence on the flask, the A549 cells were inoculated with HAdV-2. The media for HAdV-2 propagation was supplemented with 2% FBS, with other components the same as the A549 cell propagation media. After the cytopathic effect of the cells was observed, the flask was repeatedly frozen at −80 °C and thawed at 4 °C for 3 cycles. The cell debris was removed by centrifuging the suspension at 230×*g* for 10 min, and then filtering the supernatant with a 0.45 μm pore size membrane (Corning CLS431155). The filtrate was transferred to an Amicon stirred cell (Millipore), and the HAdV-2 was retained in the stirred cell with a 100 kDa ultrafiltration membrane (Koch HFM-180), while impurities smaller than 100 kDa were washed away by a 1 mM $NaHCO_3$ solution. The finished HAdV-2 stock concentration was quantified with the quantitative real-time PCR (qPCR) method, as described in our previous study [19].

2.2. EPS extraction from a full scale MBR

The full scale MBR activated sludge sample was collected from Traverse City Wastewater Treatment Plant (Michigan). EPS was extracted from the activated sludge with formaldehyde and NaOH [36]. Specifically, the biomass was precipitated by centrifuging 20 mL of the activated sludge at 5000*g* for 30 min, and the supernatant was discarded. After rinsing the biomass with 0.85% NaCl solution to remove the supernatant residues, the biomass was resuspended into a 10 mL 0.85% NaCl solution. 120 μL of 36% formaldehyde was added to the suspension, and the mixture was shaken gently at 4 °C for one hour. Afterward, 8 mL of 1 M NaOH was added and the sample was shaken gently at 4 °C for an additional three hours. By centrifuging at 20,000*g* for 30 min at 4 °C, extracted EPS was separated from the biomass and was in the supernatant. Solids in the supernatant were filtered with a 0.2 μm membrane. NaOH and formaldehyde in the filtrate were removed with a 3500 MWCO dialysis membrane (Thermo Scientific). The dialysis was complete when the conductivity of the buffer water in equilibrium was below 15 μS/cm. Dialyzed EPS went through lyophilization and was stored at −20 °C.

2.3. Hydrodynamic diameter and electrophoretic mobility of HAdV-2 and EPS

The hydrodynamic diameter and electrophoretic mobility (EPM) of HAdV-2 were examined with a Zetasizer ZS90 (Malvern, UK) at the wavelength of 633 nm and the scattering angle of 90°.