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Laser-Induced Breakdown-Detection for reliable online monitoring of membrane integrity

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ABSTRACT

The applicability of Laser-Induced Breakdown-Detection (LIBD) as an online membrane integrity monitoring system during ultrafiltration processes has been evaluated by linking a laboratory-scale membrane filtration test system to acoustic LIBD instrumentation. The results demonstrate that LIBD is a sensitive and reliable indirect online system suitable for testing and monitoring membrane integrity in ultrafiltration processes. Particles present in the filtrate can be detected continuously online using a fixed laser pulse energy (continuous mode). The LIBD monitoring system proved to be sensitive to nanoscale particles leaching through breaches in a membrane. In continuous mode 20 nm particles could be detected at concentrations as low as a few ng/L. This is superior in terms of both minimum detectable particle size and minimum concentrations to the turbidity measurement and particle counting methods that are commonly used for continuous online monitoring. Depending on the feed water characteristics and the membrane used, the LIBD system can be adjusted to specific processes by varying the measurement settings. Particle size distributions in the feed and filtrate can also be determined through non-continuous online LIBD measurements by varying the laser pulse energies (non-continuous mode), thus allowing the particle retention characteristics of the membrane to be analyzed.

1. Introduction

Membrane filtration processes have come into widespread use in the water sector over the last decade. The number of low pressure membrane systems, including microfiltration (MF) and ultrafiltration (UF) systems, installed in drinking water plants has increased, as has their capacity [1,2]. MF and UF systems have been established because of the advantages that they offer over conventional clarification processes, such as a product water quality that is largely independent of the raw water characteristics, and the ability to remove microorganisms such as bacteria. UF membranes also present a physical barrier to viruses [3–5]. The retention of particles (including microorganisms) can, however, be compromised by membrane defects or by failure of the membrane system. Defects in membrane fibers or sheets can, for example, be caused by oversized pores, chemical corrosion, mechanical stress from operational processes such as backwashing, or the presence of sharp objects in the feed water. Faulty membrane glue lines, O-rings, or connectors can also result in incomplete separation [6]. It is therefore of great importance to be able to monitor the integrity of the membrane system in order to ensure the reliability of the filtration process, especially if it is being applied for the removal of microorganisms.

There are currently a variety of membrane integrity monitoring techniques in use. Comprehensive overviews of these techniques can be found in published literatures [7–11]. The various techniques can be divided into two broad groups. The first group comprises the direct methods, in which the tests are applied directly to the membrane module. These direct methods include, for example, the bubble point test [12], the pressure decay test [13], and the acoustic sensor test [14]. The second group of techniques comprises the indirect methods that are applied to determine various water quality parameters in the filtrate solution, and include turbidity monitoring [15], particle counting [16–18], particle monitoring, nanoscale probe challenge tests [19], and microbial challenge tests [13]. Each of these methods has its own advantages and disadvantages.

Direct methods such as the pressure decay test or the bubble point test are reliable and sensitive, and are well established in industrial applications. They are, however, generally non-continuous (continuous monitoring is considered to provide at least one reading every 15 min [20]) and have to be conducted

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offline, resulting in plant downtime. Another disadvantage is that they provide no information concerning the filtrate quality.

Indirect methods such as turbidity monitoring, particle monitoring, and particle counting are commonly used as routine online measurement systems for continuous monitoring of membrane integrity [17]. These methods monitor the membrane integrity by comparing the current signal obtained from measuring the particular parameter of the filtrate against a previously established baseline. The use of these continuous online measurement system means that the continued operation of the membrane system following membrane integrity failure can be avoided. However, turbidity monitoring, particle monitoring, and particle counting can offer only a low detection sensitivity for MF and UF processes and are unable to detect nanometric sized breaches in a membrane system [7], which means that the retention of small particles with low μm or nm dimensions (including viruses) can not be reliably controlled.

Laser-Induced Breakdown-Detection (LIBD) is a highly sensitive method for detecting particles in the nanometer and submicrometer size range and can be operated online. This method may therefore offer a promising alternative for monitoring the integrity of UF membranes, and is in theory capable of meeting requirements for a sensitive, reliable, and continuous method that can detect membrane defects, even in the nm-range. LIBD was originally developed by Japanese researchers [21,22] and has been further improved for the detection, size characterization, and quantification of nanoscale particles in environmental matrices [23–26].

Among NP analysis methods that can be conducted online and continuously, LIBD is currently the most sensitive analytical method available for detecting particles below 100 nm. Concentrations of 20 nm particles as low as 10^6 particles/mL can be detected [27,28], which is equivalent to just a few ng/L (depending on the density of the particles).

This paper proposes the use of acoustic LIBD as an alternative method for indirect monitoring of membrane integrity and reports on testing carried out to ascertain the applicability of this method for continuous online control of membrane integrity. The sensitivity of this method has been evaluated for the reliable detection of nanoscale particles in the filtrate of UF processes, and of membrane breaches, by monitoring changes in the particle content of the filtrate. LIBD has also been used to determine the nanoscale particle retention characteristics of both an intact and a compromised UF membrane.

2. Experimental

2.1. Particles and suspensions

National Institute of Standards and Technology (NIST) certified polystyrene (PS) reference particles with sizes ranging between 20 nm and 500 nm (nanosphere 3000 series from Duke Scientific Corporation, USA) were used for size and concentration calibration of the LIBD instrumentation. The particle standards, obtained as aqueous suspensions, were diluted with ultrapure water (UPW) (specific resistivity at 25 °C: 18.2 MΩ cm; Sartorius Arium 611 UF, Germany) and treated by ultrasonication (2 × 160 W; Sonorex, RK 100 SH, Bandelin, Germany) in order to obtain the standard suspensions with the requiered concentrations. All suspensions were prepared in volumetric PFA flasks and bottles. Prior to use, all PFA material was cleaned with water and nitric acid, and then rinsed with UPW. The standard suspensions were stored in the dark at room temperature.

A suspension of UPW containing 40 nm PS particles (PS40 suspension) and another containing 200 nm PS particles (PS200 suspension), both at concentrations of 100 μg/L, were used in all the experiments to evaluate the use of LIBD for online integrity-monitoring of membrane filtration processes. Local tap water as received (in Karlsruhe, Germany) was used as natural feed water for the experiments.

2.2. LIBD instrumentation

The measurement principle of LIBD is based on the generation of dielectric breakdowns of solid matter followed by the formation of a hot and dense plasma in aqueous suspensions in the high electrical field of a focused pulsed laser beam [29] and the subsequent detection of these breakdowns. The breakdowns can be detected acoustically [21,23,30], optically [24], or by comparing the laser pulse energy before and after passing through the sample [31].

The generation of such a breakdown requires a minimum critical power density $P_{A,crit}$ of the incident laser beam (the breakdown threshold). $P_{A,crit}$ is strongly dependent on the state of aggregation; it is highest for gases, lower for liquids, and lowest for solid materials [32]. In addition to this dependency on the state of aggregation, $P_{A,crit}$ is also dependent on the size of the solid particles. The smaller the particles, the higher the $P_{A,crit}$ value.

$$P_{A,crit}(s) < P_{A,crit}(l) \ll P_{A,crit}(g) \quad (1)$$

The dependency shown in Eq. (1) is utilized for the detection and quantification of particles suspended in liquid matrices. A pulsed laser beam is focused into a measurement cell and its energy adjusted in such a way that it does not exceed the breakdown threshold of the liquid. Breakdowns of the suspended particles can be induced, depending on the laser pulse energy (i.e. the resulting power density) and the characteristics of those particles present within the focal volume of the laser beam. Particles with a high water content, such as biogenic particles (e.g. bacteria), can only be detected at higher laser pulse energies (as compared to dense solid particles) and at elevated concentrations (mg/L-range) [33]. With optical detection, a mean diameter for the particles can be derived from the spatial distribution of the breakdown events along the axis of the laser beam. When detecting the breakdowns acoustically, a particle size distribution can be obtained by recording the number of breakdown events that occur, depending on the laser pulse energy.

LIBD systems are not yet commercially available. The LIBD instrumentation used for the experiments was based on the design by Walther and co-workers [25], and is shown schematically in Fig. 1. A pulsed Nd:YAG laser (Ultra, Quantel, France) that delivers a laser beam with a diameter of 1.17 mm, with pulses at 7 ns (full width at half maximum) of up to 6.6 mJ at a wavelength of 532 nm in TEM00 mode, was used as the light source. The repetition rate of the laser pulses was 20 Hz. Following its emission, part of the beam was guided into a CCD camera in order to analyze the spatial beam characteristics before it passed through the energy control and the focusing optics. The energy of the laser beam could be controlled by two λ/4-sheets with the second one mounted in a holder that could be rotated, and a Glan–Thompson polarizer. The power passing through the Glan–Thompson polarizer could be adjusted by varying the angle of the second λ/4-sheet. After passing through the energy control, part of the beam (5%) was split off and guided into a pyroelectric detector (818E, Newport, USA) to monitor the current energy of the laser pulse. The beam was focused into a 450 μL flow-through cell (Hellma, Germany) via a two lens system (plano concave, $f=-50$ mm and plano convex, $f=50$ mm). After the flow-through cell the beam was collimated by a symmetrical lens setup. Part of the beam was then guided into a photodiode connected to a digital oscilloscope in order to characterize the temporal pulse