Application of laser-induced breakdown-detection as a sensitive detector for UF membrane surrogate challenge tests

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ABSTRACT

Characteristics of ultrafiltration membranes with respect to the removal of nanoscale particles can be determined by surrogate challenge tests (SCTs). Key elements of a successful SCT are the selection of a suitable surrogate and a reliable quantification method. A major challenge when using nanoparticles as surrogates is their quantification in the filtrate, since commonly used particle detection methods are often lacking in sensitivity. The applicability of laser-induced breakdown-detection (LIBD) as a monitoring tool for SCTs has therefore been evaluated. The SCTs were carried out using polystyrene (PS) and silicate particles spiked into ultrapure water and into bank filtrate. Nanoparticles were detectable down to 10 nm and, depending on the material, down to a few ng/L. The nominal pore-size of the ultrafiltration membrane could be confirmed during the tests, demonstrating the suitability of LIBD as a highly sensitive monitoring technique for SCTs.

Key words | laser-induced breakdown-detection, nanoparticles, surrogate challenge tests, ultrafiltration

INTRODUCTION

Low pressure membrane filtration processes including microfiltration and ultrafiltration (UF) have come into widespread use in the water sector over the last decade, and a variety of different UF systems now exist. UF systems can differ by e.g. membrane pore-size distributions, membrane material or operation modes (AWWA Staff 2005). Knowledge of nanoparticle (NP) retention characteristics and operational behavior of a UF system is important when selecting which particular UF system and operational design to use, and also for quality and integrity control. This is particularly important when safe, hygienic water is required, or when the removal of engineered NPs is of concern. Several methods exist to characterize the ability of UF systems to retain NPs. Pressure-based characterization methods (e.g. bubble-point test), which are well-established methods that are conducted directly at the membrane modules, can be used to detect micrometer-sized pores or breaches where NPs might pass through. However, for characterizing pores in the nm-range unpractical high pressures would be necessary (Guo et al. 2010). Furthermore, they cannot be applied online and are unable to yield any information on the particle content of the filtrate. Indirect methods determine the UF system characteristics by analyzing the filtrate stream. However, the detection and quantification of NPs in the filtrate is a special challenge for analytical methods, and commonly used indirect online methods (turbidity measurement, particle counting) exhibit a lack of sensitivity toward NPs.

Surrogate challenge tests (SCTs) offer an alternative means of characterizing the NP retention of a UF system. Surrogates (representing substances to be removed) such as microorganisms (Kreißel et al. 2015) or NPs (Gitis et al. 2012), are spiked into the feed stream of a UF system and the unretained fraction is quantified in the filtrate. For a SCT to be effective, it requires the right combination of a suitable surrogate and an appropriate quantification method of sufficient sensitivity (Guo et al. 2010). Different approaches
exist for the quantification, depending on which surrogate is used; they may involve, for example, counting plaque-forming units (PFUs) for SCTs using microorganisms (Kreißel et al. 2012), or turbidity monitoring (Van Hoof et al. 2001). Anodic stripping voltammetry has been used, in a sensitive SCT with gold NPs as the surrogate (Gitis et al. 2006). Typical drawbacks of SCTs are the limited sensitivity in terms of detectable particle size or concentration by the applied detection method (e.g. turbidity monitoring), time-consuming analysis methods (e.g. PFU counting), or high cost of expenses for surrogates.

The overall objective of the present study was to establish a SCT method for the characterization of NP retention of UF systems that might overcome such drawbacks. This should be achieved by utilizing the capabilities of laser-induced breakdown-detection (LIBD) as an analytical detection device for SCTs with NPs.

LIBD is a highly sensitive method for the detection, size characterization and quantification of particles in the nanometer to sub-micrometer size range. It is a rapid, easy to use measurement system that has been shown to be reliable for detecting NPs in UF filtrates (Lipp et al. 2009), and is hence considered to be a promising method for monitoring SCTs (Guo et al. 2010). LIBD was first developed by Japanese researchers (Kitamori et al. 1988) and subsequently improved for application in environmental matrices (Scherbaum et al. 1996; Walther et al. 2002; Walther et al. 2006). The measurement principle used in LIBD is based on the generation of dielectric breakdowns of solid matter in the high-electrical field of a focused-pulsed laser beam, and the subsequent detection of these breakdowns (Walther et al. 2002). Generating a breakdown requires a minimum power density \( P_{A,\text{min}} \) (breakdown threshold) of the incident laser beam (Bettis 1992). \( P_{A,\text{min}} \) varies with the size of solid particles, increasing as the particle size decreases. Particle breakdowns can be induced, depending on the laser pulse energy and the characteristics of the particles within the focal volume of the laser beam, allowing these particles then to be detected, size characterized and quantified. Detection limits as low as \( 10^6 \) particles/mL for 20 nm particles (Walther 2005) are achievable, equivalent to a few ng/L (depending on the shape and density of the particles). Since LIBD is a non-specific method, its application for particle monitoring is not restricted to any particular NP type.

In previous work, it has been proved that NPs can be quantified in UF filtrate by means of LIBD (Lipp et al. 2009) and that LIBD is a method that can be utilized to detect breaches in UF membranes (Troester et al. 2014). Based on these outcomes, the application of LIBD as an analytical detection device for reliable, fast and sensitive SCTs was evaluated in the present study. The aim of these SCTs was to characterize NP retention (i.e. particle size-dependent cut-offs in the nm-range) of UF systems. The method was evaluated with a laboratory-scale membrane system. Both synthetic and environmental waters were used for the evaluation.

**MATERIALS AND METHODS**

**Suspensions and particles**

National Institute of Standards and Technology-certified polystyrene (PS) particles in the 20–500 nm size range (nanosphere 3000 series, Duke Scientific, USA) were used for size and concentration calibration of the LIBD instrumentation. Similar PS particles with sizes of 20 and 30 nm, and 10 nm silicate (SiO2) particles (Micromod, Germany) were used for the SCTs. The particle sizes for the SCTs were chosen based on the applied membrane, i.e. particles were used that exhibited diameters similar to the nominal membrane pore size (20 nm, see section below) and diameters that were smaller (10 nm) or larger (30 nm) than the membrane’s nominal pore size. The dispersed NP standards were diluted with ultrapure water (UPW) (specific resistivity 18.2 M\( \Omega \) cm at 25 °C; Sartorius Arium 611UF, Germany) and treated by ultrasonication (2 × 160 W; Sonorex, RK100SH, Bandelin, Germany) in order to obtain standard suspensions with the required concentrations. All suspensions were prepared in cleaned perfluoralkoxy alkane flasks.

**Membrane system**

SCTs were performed on a laboratory-scale membrane filtration test device, which simulated the operating conditions of full-scale processes in dead-end mode, including backwash programs. Transmembrane pressure (TMP) and flux were controlled through a control system that adjusted the pump speed. Flow rates of up to 0.5 L/h were achieved for
membrane modules with membrane areas of 24 cm². The applied polyethersulfone membrane was operated in in/out mode; it had a membrane area of 24 cm² and a pore size stated by the manufacturer to be 20 nm. The membrane had not been used for other filtration processes prior to the SCTs.

**LIBD**

The LIBD system was self-assembled based on the design of Walther et al. (2002). A pulsed Nd:YAG laser (Ultra, Quantel, France) was used that delivered a beam with a diameter of 1.17 mm with pulses (7 ns) up to 6.6 mJ at a wavelength of 532 nm in TEM00 mode and a pulse repetition rate of 20 Hz. Breakdowns were detected acoustically. For size and concentration calibration, seven different sizes of suspended PS particles in the range between 20 and 500 nm were used at different concentrations. Energy curves (S-curves), which plot the dependency of the number of breakdowns on the laser pulse energy ($E$), were recorded for each particle size. The number of breakdowns that occurred was measured as the breakdown probability (BDP), as defined in Equation (1), in which $n_{BD}$ = number of pulses at $E_i$ leading to at least one breakdown, and $n_{tot}$ = total number of laser pulses at $E_i$ ($n_{tot}$ = 1,000).

$$\text{BDP} = \frac{n_{BD}}{n_{tot}}.$$  

Discrete particle size distributions (PSDs) were obtained by analyzing the S-curves (Walther et al. 2006), using the breakdown thresholds and the concentration dependency of the S-curve slope, as obtained by the calibration.

**Surrogate challenge tests**

SCTs were carried out using UPW and bank filtrate (BF) (river water after being naturally filtered by passage through the river banks) as matrices in order to determine the applicability of LIBD as a SCT-monitoring device. BF was taken from a pilot plant in which BF is further treated by UF. The pH of the BF was 7.9 and the conductivity was 37 mS m⁻¹; its turbidity was measured to be 0.25 FNU and the UV absorption at 254 nm was 2.4 m⁻¹. PS particles with diameters of 20 and 30 nm, and SiO₂ particles with diameters of 10 nm, were used for those SCTs using UPW. The SCTs using BF were conducted using 20 nm PS particles. For the SCTs, the matrices were spiked with appropriate volumes of the standard suspensions. The membrane was chemically cleaned prior to each SCT and the fluxes and corresponding TMPs checked. Samples of 0.5 L were used for the SCTs. The filtrate was collected in a beaker for particle content quantification and size characterization by LIBD. Log removal values (LRVs) (Equation (2)) were determined based on nominal (i.e. spiked) concentrations in the feed and on concentrations in the filtrate as determined by LIBD.

$$\text{LRV} = \log \left( \frac{C_{\text{Feed}}}{C_{\text{Filtrate}}} \right).$$  

**RESULTS AND DISCUSSION**

**Detection and quantification of NP surrogates by LIBD**

The LIBD instrumentation and calibration used enabled PSDs in aqueous suspensions to be determined for particle sizes between 20 and 500 nm. The lower size end of the calibration was limited by the availability of size-certified PS standards. The size-dependent breakdown thresholds ranged between 0.12 mJ (for 500 nm particles) and 0.78 mJ (for 20 nm particles). The minimum quantifiable concentrations ranged between $7.3 \times 10^4$ particles/mL ($5 \mu g/L$ for spherical PS particles) for 500 nm particles, and $3.4 \times 10^6$ particles/mL ($15 \mu g/L$ for spherical PS particles) for 20 nm particles. The concentration ranges covered approximately two orders of magnitude for each particle class.

With this high sensitivity to NPs, LIBD is superior to other particle detection methods such as dynamic light scattering, turbidity measurement or particle counting (Walther 2005). Hence, application of LIBD enables monitoring solid NPs in SCTs with enhanced sensitivity.

Since LIBD is not specific to any particular type of solid material, it allows a variety of different solid NPs to be used for SCTs. The particulate matter can therefore be chosen on the basis of e.g. its stability, size, availability or cost. However, the breakdown process depends not only on particle size but also on a particle’s shape and material characteristics (e.g.
ionization potentials, absorption coefficients etc.) (Scherbaum et al. 1996). Unless the same material is measured that is used for calibration, the measured sizes and concentrations have to be regarded as equivalent to those of the calibration material. As mentioned previously, both PS and SiO₂ particles were used for the SCTs in this study: SiO₂ particles \(d_p = 10 \text{ nm}\) were used because no 10 nm PS particles were available. Although PS calibration can reasonably be used for a wide range of different materials, some substances exhibit significantly different breakdown thresholds for similar sized particles, and other BDP dependency on the laser pulse energy. For detecting Al₂O₃ particles, for example, a two orders of magnitude higher number concentration is required as compared with PS particles (Scherbaum et al. 1996). Inducing breakdowns on SiO₂ particles requires a higher laser pulse energy than inducing breakdowns on PS particles (Wagner 2005) and the breakdown behavior of SiO₂ particles also differs significantly from that of PS particles (Figure 1). Therefore, the LIBD system was concentration calibrated with 10 nm SiO₂ particles. This calibration was used when applying SiO₂ NPs for SCTs.

Application of LIBD in surrogate challenge tests

Throughout the SCTs the flux was maintained at 100 L/m²/h. The corresponding TMPs ranged between 140 and 150 mbar \((t = 0)\). The TMP remained constant for SCTs with PS particles in UPW, whereas a slight TMP increase (10%) was observed when SCTs were performed with BF.

For the SCTs with UPW, concentrations of 1 mg/L were used for PS particles \(d_p = 20 \text{ nm and } d_p = 50 \text{ nm}\), and of 125 mg/L for SiO₂ particles \(d_p = 10 \text{ nm}\). The LRVs were determined by using LIBD to be 0.30 (for \(d_p = 10 \text{ nm}\)), 3.5 (for \(d_p = 20 \text{ nm}\)) and 4.2 (for \(d_p = 50 \text{ nm}\)). A cut-off curve was derived from these SCTs, describing the NP retention characteristics of the membrane (Figure 2). The 20 nm pore size stated by the membrane supplier could thus be determined and confirmed, demonstrating the reliability of LIBD for monitoring SCTs.

Prior to the SCTs, S-curves were measured for the BF and for the UF filtrate of the BF in order to determine the PSDs of the natural particles before and after UF. Natural particles larger than 500 nm were detected in the BF, which were outside the LIBD calibration size range. Since this affected the shape of the S-curve, the BF was filtered using a 0.2 μm filter prior to quantification. The concentration of natural 20 nm particles in the 0.2 μm filtrate was determined to be \(1.4 \times 10^8 \text{ particles/mL}\). No particles from the 20 nm size class were present in the UF filtrate, resulting in an LRV > 1.6 for the natural particles. Natural particles can, in theory, be used to determine the retention of NPs by a UF system when using LIBD as a monitor. However, this is only possible in applications where the PSDs in both the feed and the filtrate fall within the LIBD measurement range.

Since the stability of NPs in aqueous matrices is influenced by their physico-chemical parameters, as well as by hydrochemical conditions (e.g. ionic strength, pH) (Klaine et al. 2008), it is important to determine the stability of the

![Figure 1](https://iwaponline.com/ws/article-pdf/15/2/377/415445/ws015020377.pdf)

**Figure 1** | BDPs of PS and SiO₂ particles at fixed laser pulse energies (1.2 mJ for PS particles and 1.5 mJ for SiO₂ particles).

![Figure 2](https://iwaponline.com/ws/article-pdf/15/2/377/415445/ws015020377.pdf)

**Figure 2** | Membrane cut-off characteristics, as determined by SCTs with LIBD measurements.
NPs used as surrogates in the test matrix. The BF was therefore diluted 1:1 with UPW and spiked with 20 nm PS particles at a concentration of 2 μg/L. Dilution with UPW was necessary to reduce possible masking effects and to dilute natural particles with diameters larger than 500 nm, which were detected (and influenced the S-curve shape) but were out of the calibration size range. The stability of the particles was determined by measuring the concentration of 20 nm particles 20 minutes after spiking and then again 144 minutes after spiking, the latter exceeding the SCT duration. Although the dilution step changed the hydrochemical conditions, the determined stability was assumed to represent the behavior in the undiluted matrix. The results are presented in Figure 3 (the S-curve of a 20 nm PS suspension is also shown, for comparison) and Table 1.

The flattening of the S-curve of the spiked diluted BF for laser pulse energies greater than 0.78 mJ after 144 minutes was due to the loss of 20 nm particles. A reduction in the 20 nm particle concentration of 0.15 log units was observed after 20 minutes and of 0.73 log units after 144 minutes. This effect was most likely caused by the attachment of a proportion of the spiked particles to surfaces of other particulate constituents, or to the surface of the vessel. However, a large proportion remained stable in the aqueous phase. The stability of particles during a SCT is not related to the use of LIBD for monitoring, but the use of LIBD allows the stability to be monitored, which is crucial for reliable data interpretation. The stability of the particles in the UF filtrate from the BF was evaluated by spiking the UF filtrate with 20 nm PS particles (c(PS) = 2 μg/L) and monitoring the concentration levels over a period of 2 hours. No changes were detected in the particle content, indicating that the spiked PS particles remained stable in the UF filtrate from the BF.

The results of the SCTs when the BF was spiked with 20 nm PS particles at concentrations of 10 μg/L and 1 mg/L are shown in Table 2. A slight increase could be observed in the BDP of the UF filtrate when the feed sample was spiked

![Figure 3](image-url)  
*S-curves for the stability test (left) and for the SCT using BF as an environmental matrix (right).*

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Results of the stability test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time/minutes</td>
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</tr>
<tr>
<td>Concentration/(10^8 particles/mL)</td>
<td>5.2^a</td>
</tr>
<tr>
<td>Log decrease</td>
<td>0</td>
</tr>
</tbody>
</table>

^aNominal concentration.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Results of the SCT using BF as an environmental matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed matrix</td>
<td>Concentration of 20 nm particles (particles/mL)</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Feed</th>
<th>UF filtrate</th>
<th>LRV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bank filtrate</td>
<td>1.4 × 10^8^a</td>
<td>&lt;3.4 × 10^6</td>
</tr>
<tr>
<td>Spiked BF, c(PS, 20 nm) = 10 μg/L</td>
<td>2.3 × 10^6^b</td>
<td>&lt;3.4 × 10^6</td>
</tr>
<tr>
<td>Spiked BF, c(PS, 20 nm) = 1 mg/L</td>
<td>2.3 × 10^11^b</td>
<td>3.8 × 10^7</td>
</tr>
</tbody>
</table>

^a0.2 μm filtrate.  
^bBackground particles neglected.
with 10 μg/L, but the increase was less than the limit of quantification for 20 nm particles. Hence, the LRV was determined to be >2.8. When the feed sample was spiked with 1 mg/L of 20 nm PS particles, the LRV was determined to be 3.8. LRVs determined in the BF closely matched the LRV of 3.5 derived from the SCTs with UPW (Figure 2). The higher LRV for 20 nm PS particles when using UF, as compared with the SCT with UPW, can be explained by the 20 nm PS particles not being completely stable in BF. A fraction might have been removed by adsorption to vessel surfaces, by the formation of larger aggregates or attachment to natural particles present in the BF, which were removed efficiently by UF. Furthermore, the formation of a fouling layer, as indicated by the slight increase in TMP throughout the SCT, might have enhanced NP retention.

The results with BF indicate that LIBD is also applicable as a SCT detection device in environmental matrices. It can therefore potentially be applied directly in full-scale treatment processes. This might be of high relevance in both cases, after installation of an UF system when it is checked and characterized for its specifications and during operation for quality control. Furthermore, the influence of different parameters, such as membrane fouling or changing raw water quality, on NP retention could be determined. However, depending on the naturally occurring particles in the raw water and the filtrate, a high amount of NPs for the SCTs might need to be spiked. In order to ensure that the spiked NPs applied for the SCTs can be measured by the non-specific method of LIBD, the concentration of spiked NPs must be sufficiently high so that no masking effects occur by the natural particulate background. For proving the applicability of SCTs with NPs and LIBD in full-scale UF processes, further evaluation of this proposed method in such full-scale processes is required.

The removal efficiency of microorganisms (MS2 and phiX174 bacteriophages with sizes of 25 nm and 27 nm, respectively) in UF processes with similar UF membranes as in this study (same manufacturer and same module specification) was investigated in another study of the authors’ group (Kreißel et al. 2022). Depending on the filtration conditions (i.e. water matrix and flux value), removal values ranged from 2.5 to 6 LRVs for MS2 and from 2.5 to 4.5 for phiX174. Comparing these LRVs and the cut-off curve derived from the SCTs with NPs and LIBD (Figure 2) indicates that the removal of microorganisms in UF processes can be estimated through such SCTs.

CONCLUSIONS

LIBD has been shown to be applicable as a highly sensitive monitoring system for NP surrogate challenge tests. Surrogate challenge tests can be performed with either artificial matrices (e.g. ultrapure water) or natural matrices (e.g. BF). With its high sensitivity to particles in the lower nm range, LIBD is able to overcome drawbacks that are encountered when other detection methods (e.g. turbidity monitoring) are used for surrogate challenge tests. Different solid particles can be applied for surrogate challenge tests with LIBD as a monitoring system since LIBD is a non-specific particle detection method. This enables surrogates to be selected on the basis of different criteria. Since LIBD provides information on both particle size and particle concentration, the stability of the surrogates can be evaluated and the PSD in the filtrate can be analyzed, which is crucial for reliable data interpretation. The results also indicate that the removal of microorganisms can be estimated through the use of NPs and LIBD in SCTs, but further research is required to confirm the comparability.

REFERENCES


Development of a new testing system. In The AWWA Membrane Technology Conference, San Antonio, TX.

Kolloidchemie in Aquatischen Systemen. Doctoral Thesis, Department of Chemistry and Pharmacy, University of Regensburg, Germany.


Probing particle size distributions in natural surface waters from 15 nm to 2 µm by a combination of LIBD and single-particle counting. J. Colloid Interface Sci. 301 (2), 532–537.

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