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When used in municipal water treatment, ceramic membranes offer robust resistance to damage, but experience fouling. Silver nanoparticles offer attractive antimicrobial properties, but there is still much to be understood regarding their adhesion to ceramic surfaces. This research provides laboratory data and a statistical model to better understand and predict silver nanoparticle removal under different water conditions.

The Effects of Water Chemistry on the Detachment and Dissolution of Differently Stabilized Silver Nanoparticles from Ceramic Membranes

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Abstract

Silver nanoparticles (Ag NPs) are an attractive addition to membranes used for drinking water treatment due to their antimicrobial properties. This research examined the role of stabilizing agents, used during the synthesis of Ag NPs, on their detachment/dissolution from ceramic membranes exposed to different types of drinking water sources typical in the United States. Ag NPs that had been stabilized by citrate, polyvinylpyrrolidone (PVP), or branched polyethylenimine (BPEI) were deposited on the surface of porous aluminum oxide membranes, which are commonly used for municipal water treatment. Results demonstrated that Ag NP stabilizer influenced release from the membranes. For Ag NPs electrostatically stabilized (citrate), hard water was found to remove the Ag NPs for longer periods of time and at higher quantities than in water without hardness. The reverse was found for sterically stabilized Ag NPs (BPEI and PVP). Additions of natural organic matter (NOM) were added to waters filtered by membranes coated in citrate Ag NPs and were found to prolong the release of the citrate Ag NPs in the hard water test condition. Variations in total Ag released from ceramic membranes were explained by differential impacts on the NP and membrane's electrical double layers when switching from Ag NP deposition to filtration water chemistry conditions (zeta potential measurements are provided in this paper). Despite these differences, our findings show that, in waters that do not contain NOM, Ag release quickly falls below silver drinking water standards (0.1 mg/L) and greater than 50% remained on the membranes. This study demonstrates that the type of Ag NP stabilizing agent and water chemistry should be considered when these membranes are utilized for municipal water treatment.

Keywords silver nanoparticles, stabilizing agent, ceramic membranes, multilevel model, water treatment, filtration, water chemistry

1. Introduction

The objective of this paper is to gain a deeper understanding of how silver nanoparticles (Ag NPs) stabilized by different capping agents detach/dissolve from the surface of ceramic membranes used for water treatment. Ceramic membranes are used extensively for municipal drinking water treatment throughout Japan and have been more recently introduced as a treatment technology in the United States. Ceramics are more resistant to high temperatures, pressures, and cleaning solutions than polymeric based membranes [1]. Nanocomposite membranes are seen by some researchers as a solution to challenging treatment objectives required for wastewater recycling or to achieve lower energy demands from pressure driven systems [2-5]. The incorporation of Ag NPs is particularly attractive due to their antimicrobial properties. Researchers have determined that Ag NPs not only provide disinfection, but also reduce fouling through reduction of biofilms on the surface of membranes [6-12]. However, it is also well known that NPs' physical-chemical properties are substantially altered by the stabilizing agent utilized during synthesis to control size and prevent aggregation [13-17]. A better understanding of the interplay between stabilizer and water quality is required. This understanding will allow design of more robust antimicrobial systems that control the retention or release of Ag.

The use of Ag NPs in previous research suggests that certain water types have a significant impact on the release of Ag NPs from ceramic water filters and others do not. Historically, point-of-use ceramic water filters manufactured in developing countries have been the most actively used technology integrating Ag NPs for antimicrobial purposes. Some manufacturers use silver nitrate painted on filters, but most use casein stabilized Ag NPs. As such, for ceramic water filters casein stabilized Ag NPs have been studied the most extensively of all types of Ag NPs [18]. A quartz crystal microbalance study monitored the release of casein stabilized Ag NPs from nonporous silicon wafers [19]. They found that valence, turbidity, and pH had very little effect on the release of the casein Ag NPs from the surface of the silicon wafer. On the other hand, high release rates were observed in the presence of high concentrations of organic compounds (10% tryptic soy broth) and in the presence of sodium hypochlorite (8.0 mg/L as Cl_2) which removed 85% of Ag from the surface of the silica wafer within 3 hours. Others found that, under three different water conditions (a no hardness, hard, and water with organic matter), release of casein Ag NPs was minimal (5 to 10%) and bacterial inactivation performance of point-of-use ceramic water filters was unaffected [20]. When water chemistry conditions were compared between [19] and [20], the findings were consistent. A more recent and comprehensive study, by a subset of authors from [20], found influent water conditions of pH 5, I = 50 mM $NaNO_3$, or influent conditions containing divalent cations resulted in release of Ag from the filters at levels that were 5-10 times the World Health Organization's drinking water standard (0.1 mg/L) [21]. The same study found that less saline, less acidic, or softer conditions were acceptable after an initial flushing period. These authors observed increased eluent Ag concentrations when influent water quality was switched from low to high ionic strength conditions. This result indicated that the dominant Ag release mechanism was cation exchange as opposed to compression of the electrical double layers of the NPs. Different results between [19] and [21] could be related to the use of different substrates (silicon wafers without porosity vs. clay-based filters) and their dominant release mechanisms (cation exchange vs. electrical double layer). These findings are important to our work because they demonstrate that clay-based point-of-use ceramic water filters and alumina-based membranes may have different release mechanisms.

Several studies have examined the role of Ag NP stabilizer. Our previous work in Ghana found that release differences were not statistically significant for citrate, polyvinylpyrrolidone (PVP), or branched polyethylenimine (BPEI) Ag NPs on point-of-use ceramic filters, but that different types of Ag NPs may have different effectiveness at disinfection of bacteria [22]. Another study using casein, maltose (with PVP), and rosemary extract Ag NPs found that more Ag remained on point-of-use filters using rosemary then maltose and casein coated Ag NPs. The study also found that Ag impregnation of filters improved removal of *Escherichia coli* and lead [23]. Finally, two studies focused on alumina-based ceramic water filters decorated with different types of Ag NPs and linking agents. Both studies demonstrated improved removal of *E. coli* from water with the addition of Ag [24, 25].

These studies demonstrate that Ag NPs effectively impart antimicrobial properties when added to both clay and alumina-based ceramic water filters. They also indicate that the water chemistry impacts the release of Ag from filters. However, the interplay between different Ag

NP stabilizers and ceramic substrate is not fully understood. Ag NPs' surface functionalization has been primarily researched and put into practice for point-of-use clay based ceramic filters. Ceramic membranes composed of pure alumina have not benefited from as much research and development despite their growing use. This study is the first of its kind to systematically investigate the differences in Ag NPs release from the membrane materials used in centralized municipal water treatment in developed countries.

2. Materials and Methods

2.1. Ag NP Synthesis and Analysis

Ag NPs stabilized with citrate, polyvinylpyrrolidone (PVP), and branched polyethylenimine (BPEI) were prepared and characterized according to procedures outlined in previous work [26]. Size distributions, aggregation curves, and images are also available in the same publication. On average, the particles were 10-15 nm in diameter, as measured by transmission electron microscopy image processing. Their aggregation, as measured by a Nanosight particle analyzer, was found to be negligible under conditions used to prepare the filters for this study. Citrate and PVP represent the two most frequently used stabilizing molecules for Ag NP synthesis and BPEI imparts a positive surface charge to the Ag NP unlike the other two stabilizers [27]. Throughout this work, total suspension phase Ag (ionic + NP) was measured using an Agilent ICP-OES at a wavelength of 328 nm. The instrument detection limit was 1 µg/L. Total Ag deposited on membranes was measured by digesting the membrane in 1 mL of concentrated trace metal grade HNO_3, followed by adding 10 mL of ultrapure water and subsequently diluted within the range of the standard curve. Solution phase Ag was digested using 6% concentrated trace metal grade HNO_3. One sample per filtration time was measured in triplicate by ICP-OES, with average % RSD values below 5% considered to be data of sufficient quality to be used in the statistical analysis. Each membrane-water-Ag NP combination was repeated in triplicate. Membrane integrity was visually assessed at the end of each experiment and only non-cracked membranes' results were used in the statistical analysis. All standards were prepared using a NIST traceable standard (Inorganic Ventures, Christiansburg Virginia) and standard curves achieved R^2 values >0.99. Zeta potential measurements were performed in quadruplicate on a Malvern Zetasizer using 5 mg/L Ag NP solutions.

2.2. Membrane Preparation

Porous aluminum oxide (Al_2O_3) ceramic disks (Whatman Anodisc, 13 mm flat disks with 0.1 µm diameter pores according to manufacturer specifications and verified using scanning electron microscopy shown in Figure 1) were used as representative membranes. Porous Al_2O_3 substrates were selected because ceramic membranes used in municipal water treatment plants are typically fabricated from Al_2O_3. They also minimize the cation exchange mechanisms observed in clay based ceramic filters, but still provided a porous substrate unlike a silicon wafer used in previous research. The disks were prepared for filtration tests by soaking them in 100 mg/L Ag NP suspensions at I=10 mM as KNO_3 for 3 hours at pH values that promoted deposition (pH 5 for Citrate and PVP Ag NPs, and pH 7 for BPEI Ag NPs). Adsorption curves for these conditions are available in [26]. The point of zero charge of the membranes was at a pH value of approximately 5.5 at which point the zeta potential value for Citrate Ag NPs was equal to approximately -25 mV, PVP Ag NPs -9.7 mV, and BPEI Ag NPs 32.5 mV [26]. The membranes were held upright under fully submerged conditions by custom made glass holders that prevented cracking of the membranes and promoted deposition of Ag NPs on both sides of the membrane (Figure 2A). Membranes were soaked in amber glass jars, to avoid UV transformations of the Ag NPs. Nitrogen gas was maintained in the headspace of the jars to assist in pH control which was monitored and adjusted using KOH or HNO_3 to maintain initial conditions throughout the duration of the soaking (Figure 2B). After soaking, the disks were allowed to dry overnight. Membranes were carefully inserted into 13 mm polypropylene Swinnex filter holders (EDM Millipore). Use of flat silicone gaskets on either side of the disks and zip ties on all tubing connections was essential for preventing leakage during filtration or cracking the membrane upon tightening the holders.

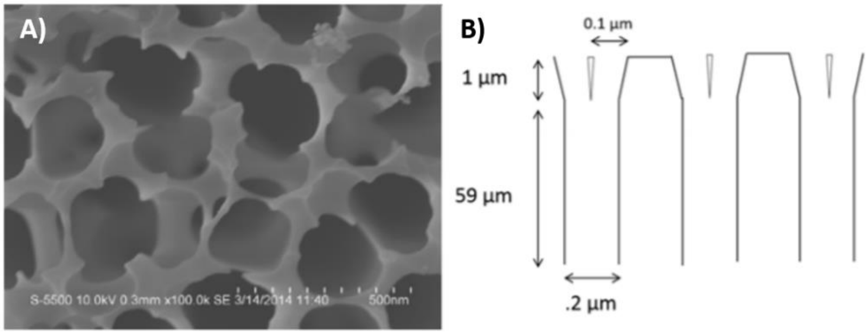

Figure 1. A) Planar view and B) side view of Al_2O_3 membranes (Anodisc). Planar view obtained on a Hitachi S5500 Scanning Electron Microscope.

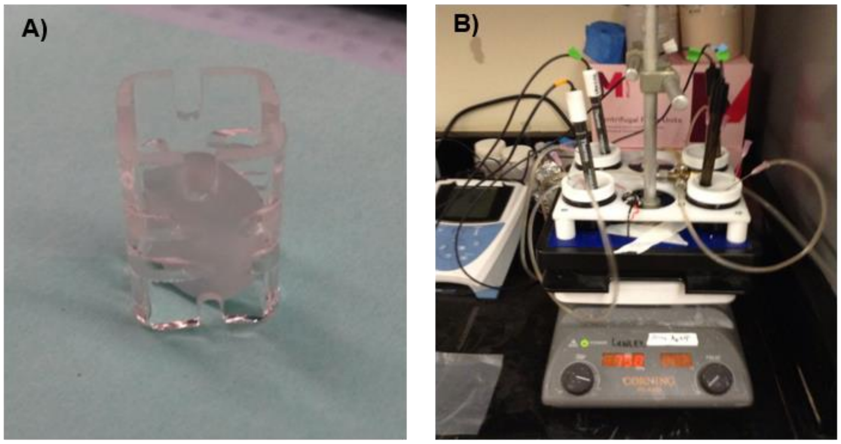

Figure 2. Membrane preparation setup for deposition of Ag NPs. A) Al_2O_3 membranes (Anodisc) in glass membrane holder and B) Attachment experimental setup.

2.3. Filtration

Two base test waters were used in these experiments. The “Hard Water” represents a relatively hard water, as found in many places in the central United States, with a hardness (added as magnesium nitrate salt) of approximately 200 mg/L as $CaCO_3$ (i.e., 4 meq/L), alkalinity of approximately 200 mg/L as $CaCO_3$ (added as $NaHCO_3$), and a pH of 8.3 (adjusted using KOH when necessary). The “No Hardness Water” represents water similar to water supplies found in the northeast United States. This water had no hardness but an ionic strength of 10 mM (added as $NaNO_3$), an alkalinity of approximately 50 mg/L as $CaCO_3$ (added as $NaHCO_3$), and a pH of 6.5 (adjusted using concentrated HNO_3). NOM was also added to these base water recipes during experiments with membranes covered with citrate Ag NPs. For this portion of the work, both waters were spiked with 5 mg/L Humic Acid (equivalent to 2.6 mg/L as DOC) to represent typical NOM in water systems. Suwannee River Humic Acid from the International Humic Substances Society was used. Table 1 summarizes the filtration experiments that were performed. During filtration, the water was stored in covered beakers and a multichannel peristaltic pump was used to flow water through multiple membranes at a flow rate of 0.5 mL/min. Experimental water conditions were repeated on three different membranes. For each membrane, samples were collected until Ag stopped, or nearly stopped, detaching/dissolving from the membranes (as defined by the instrument detection limit of 1 µg/L).

Table 1: Summary of Filtration Experimental Factors

Membrane Material	**Ag NPs Capping**	**Test Waters**	
		Base Recipe	**Additions**
Al_2O_3	Citrate BPEI PVP	*Hard Water* (Hardness = 200 mg/L $CaCO_3$ as $Mg(NO_3)_2{\cdot}6H_2O$; Alk = 200 mg/L $CaCO_3$ as $NaHCO_3$; pH = 8.3)	NOM* (5 mg/L Humic Acid) *Only tested for Citrate-Ag NPs
		No Hardness Water (I = 10 mM as $NaNO_3$; Alk = 50 mg/L $CaCO_3$ as $NaHCO_3$; pH = 6.5)	

2.4. Statistical Analysis using Multilevel Modeling

To assess significant differences in release of Ag, according to stabilizing agent and water type, a multilevel model was built and run using the *lme4* package in the open source software R Version 1.2.1335 (see Supporting Information for code) [28]. A multilevel model is required because repeated measurements violate the assumption of independence of data points used in analysis of variance (ANOVA) and the sample set is small and unbalanced. The *lme4* package provides functions for fitting and analyzing mixed models. To construct a parsimonious yet robust model, random slope and intercept were used for the development of the conditional model. Significance testing on the multilevel model was completed used the R package *lmerTest*, which provides p-values and summary tables in conjunction with the *lme4* package [29]. Model fit was compared using Akaike Information Criteria (AIC) with maximum likelihood estimator (i.e., restricted maximum likelihood (REML) = false in code) [30]. A lower AIC value corresponds to better model fit. Model results for each condition (i.e., water type and silver type) were generated using the fixed effects from the *lme4* package output to calculate model slope and intercept values, and the *effects* package was used to graph model results with 95% confidence intervals. The assumptions of linearity, normality, and independence were evaluated using graphical examination of QQ plots and scatter plots of the raw data and modeled residuals (Figure SI-1). All three assumptions were found to be upheld; therefore the use of a multilevel model was considered appropriate for this data set.

In brief, multilevel modeling is an iterative process that includes fitting an unconditional model (no explanatory variables) first, and then developing a conditional model [31]. The unconditional model is run to establish baseline statistics used for evaluating improvement (reduction in unexplained variation) by the inclusion of one or more explanatory variables in the conditional model. The unconditional model used in this work was:

$$LnAg_{ij} = \gamma_{00} + \gamma_{10}\,LnVolume_{ij} + (u_{oj} + u_{1j}LnVolume_{ij}) + r_{ij} \qquad (1)$$

Where “LnAg” is the natural log of the total eluted Ag (ionic + nano) in µg/L and “LnVolume” is the natural log of water filtered in mL. The subscript “i” refers to a specific sample of filtered water and the subscript “j” refers to a specific membrane (i.e., FilterID). The symbols “γ” are parameters that were estimated using restricted maximum likelihood (i.e., REML = true). The symbol “r” represents the overall unexplained variation of these parameter estimates and “u” represents the random effects of the slopes and intercept coefficients for individual membranes.

For development of the final conditional model, the model was run multiple times to individually evaluate the amount of variation explained through inclusion of the following factor combinations: 1) water type, 2) Ag type, 3) water type and Ag type (without interactions), and 4) water type and Ag type (with interactions). NOM was not included as a water type in the analysis because not all types of Ag NPs were tested with water that included NOM. A separate analysis of the significance of NOM with only citrate Ag NPs covered membranes was performed. Table SI-1 in the Supporting Information summarizes how variation was accounted for as specific variables were included in the model. It also notes, in the “Significant Fixed Effects” column, which variables, as a group, were considered significant for explaining how Ag released from the membranes (a p-value < 0.05 was used for the significance criteria). The conditional model that provided the most reduction in variance of the slopes and intercepts (36%) included both Ag type and water type and a term to account for different interactions between the water and type of Ag NP. The final reduced form of the model used in this work was:

$$\begin{aligned} LnAg_{ij} = (&\gamma_{00}+\gamma_{01}\,SilverType_j + \gamma_{02}WaterType_j + \gamma_{03}SilverType_jWaterType_j \\ &+ \gamma_{10}\,LnVolume_{ij} + \gamma_{11}\,SilverType_jLnVolume_{ij} \\ &+ \gamma_{12}WaterType_jLnVolume_{ij}) + (u_{oj} + u_{1j}LnVolume_{ij}) + r_{ij} \qquad (2) \end{aligned}$$

Where “Silver Type” refers to the three different types of Ag NPs, “WaterType” is the identifier for the water conditions described in the filtration methods section. This model was used for significance testing of how Ag type, water type, and their interactions influence the detachment/dissolution of Ag from the membranes and it provided equations that can be used to predict Ag release for particular types of Ag when a particular water is being filtered.

3. Results and Discussion

3.1. Ag Release Analytical Results

The measured concentration of Ag released from the membranes, as a function of volume of water filtered, is displayed in Figure 3 in the graphs labeled “Analytical Results.” A total of 33 membranes and 187 observations were used in the statistical analysis. The error bars represent the standard deviation for Ag concentration for volumes where multiple membranes were run under the same water condition. The volumes that do not include standard deviations are because membranes cracked in a manner that compromised filtration and were excluded from analysis, resulting in only one measurement in several instances. The initial water sample was collected at either 5 mL or 10 mL. Note, the modeled intercept values represent a theoretical "back" estimate to instantaneous release from the membrane, not a measured concentration. Ideally, the initial sample would have been collected after 1 mL of filtration because the intercept data would have represented the average Ag concentration measured in the first set of samples (ln 1 equals zero). However, this could not be implemented due to sample volume constraints for the ICP-OES.

The volumes of water filtered represent approximately 14 hours of operation, or a "first-flush" condition, for a municipal treatment membrane unit with 25 m^2 of surface area operated at 170 L/m^2-hr. Initially, some membranes released Ag at concentrations higher than the World Health Standard of 0.1 mg/L, but the released Ag quickly declined to within regulatory limits [32]. Citrate Ag NPs demonstrated a trend of increased release under hard water conditions compared to water that did not contain hardness. The reverse was true for PVP and BPEI Ag NPs. The sustained release (slope) of BPEI Ag NPs appeared to be steeper than for Citrate and PVP Ag NPs. However, considering variation in the experimental results, it is difficult to discern significant differences in Ag released by water and Ag type from the analytical results alone. The statistical modeling portion of this work quantivatively accounts for this variation, and therefore, modeling results were used to draw conclusions.

Different types of Ag NPs deposit more or less favorably on the Anodiscs, with Citrate Ag NPs depositing roughly 20 times more mass of Ag on Anodiscs than BPEI Ag NPs and twice as much as PVP Ag NPs [26]. These differences were found to be controlled by the steric and surface charge differences of the particles [26]. For this reason, the amount of Ag left on the membrane was measured using ICP-OES at the end of the filtration run to ensure none of the membranes lost all the initially deposited Ag (Figure 4). Estimates of the initial Ag on the membranes were assessed by integration of the Ag release curve with addition of the final amount of Ag on the membrane determined by digesting the membrane and measuring the Ag concentration using ICP-OES. These results demonstrate that a high fraction of Ag was retained on the membranes, i.e., the Ag was not completely released during initial flushing of membranes and is potentially still available for biological fouling control.

3.2. Ag Release Modeling Results

The modeling results are displayed in Figure 3 in the graphs B), D), and F). The resulting coefficient estimates, standard error, and hypothesis tests for the unconditional model are presented in Table SI-2 of the supporting information. The p values of less than 0.05 in the fixed effects portion of the table indicate that Ag is coming off the membrane, and the estimates tell us that the average "initial" amount is 213 μg/L and average rate of loss is 3.01 μg/L, ignoring Ag or water type groupings. The results also indicate that, prior to the addition of explanatory variables, unexplained variation (random effects) is present. This variation is largest for the "initial" release of Ag between membranes (variance of 1.85), but is also present for the rate of loss of the Ag (0.07) and for the unexplained variation attributed to the repeated measures of a particular membrane (0.76).

Table SI-3 in the supporting information contains the parameter estimates and significance test results for all the different water-Ag NP combinations tested using the final conditional multilevel model. The parameters' fixed estimates were used to generate equations in

Figure 5 where one can solve for ln values of Ag released for each type of Ag NP-water combination (volume is in terms of mL).

Figure 6 demonstrates different interactions with hard and not hard water when controlling for interactions between Ag NP type and water type. Sustained Ag release was similar for all NPs in the water without hardness, but for the citrate stabilized Ag NPs the hard water removed the Ag from the membranes for a longer period than the others (BPEI p-value = 0.01, PVP p-value = 0.02) whereas PVP and BPEI's Ag elution was similar (p-value = 0.96). Water type did not influence the initial release of Ag for citrate Ag NPs (p-value = 0.66), PVP Ag (p-value = .09), or BPEI Ag (p-value = 0.09); however, citrate and PVP Ag NPs had significantly different initial release values in hard water (p-value = 0.002). These results are consistent with citrate Ag NP granular media filtration research that has demonstrated a the dominant role of the electrical double layer and slower release rates with divalent salts [33].

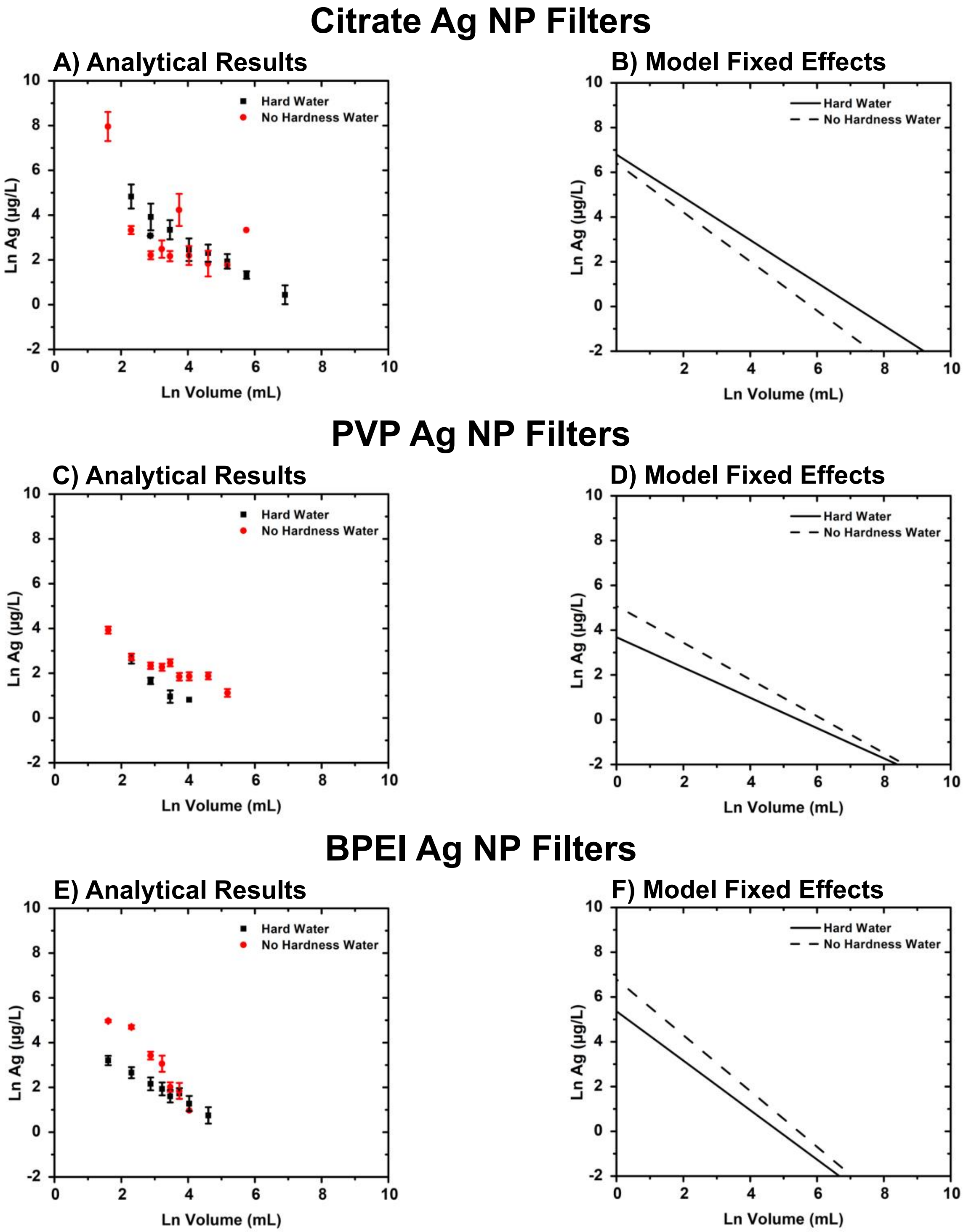

Figure 3. Ag Release Results. Graphs A, C, and E are average effluent data from membranes with different types of Ag NPs deposited on their surface. Error bars represent standard error when effluent Ag was measured from multiple membranes prepared and challenged in the same manner. Graphs B, D, and F are release results generated from the fixed effects of the multilevel statistical model built from the analytical Ag effluent data.

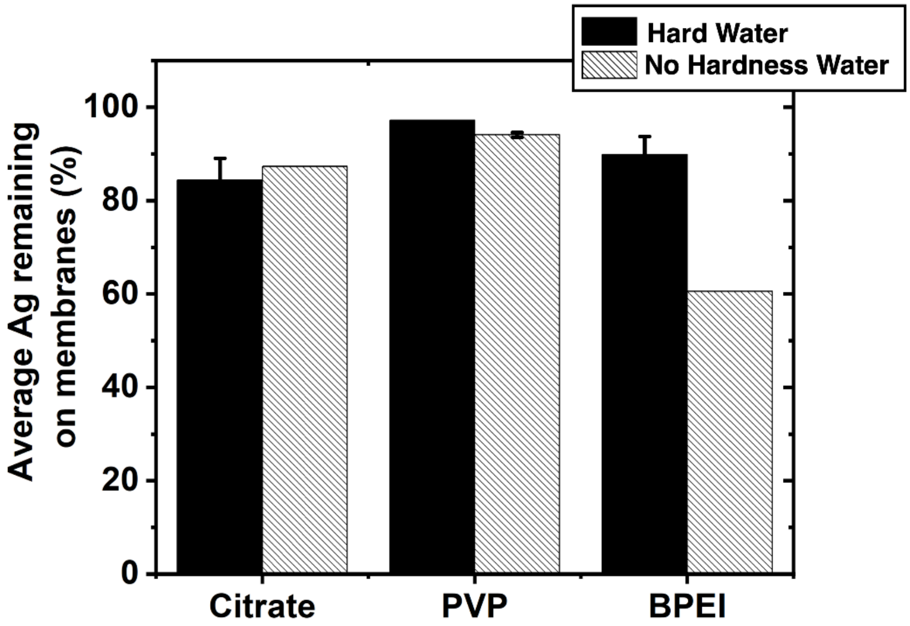

Figure 4. Retention of Ag on membranes after filtering 56.6 mL of water. None of the membranes (even after filtering more water) exhausted the deposited Ag prior to reaching detection limits of Ag by ICP-OES. Error bars included in cases where replicate data were collected and represent standard error.

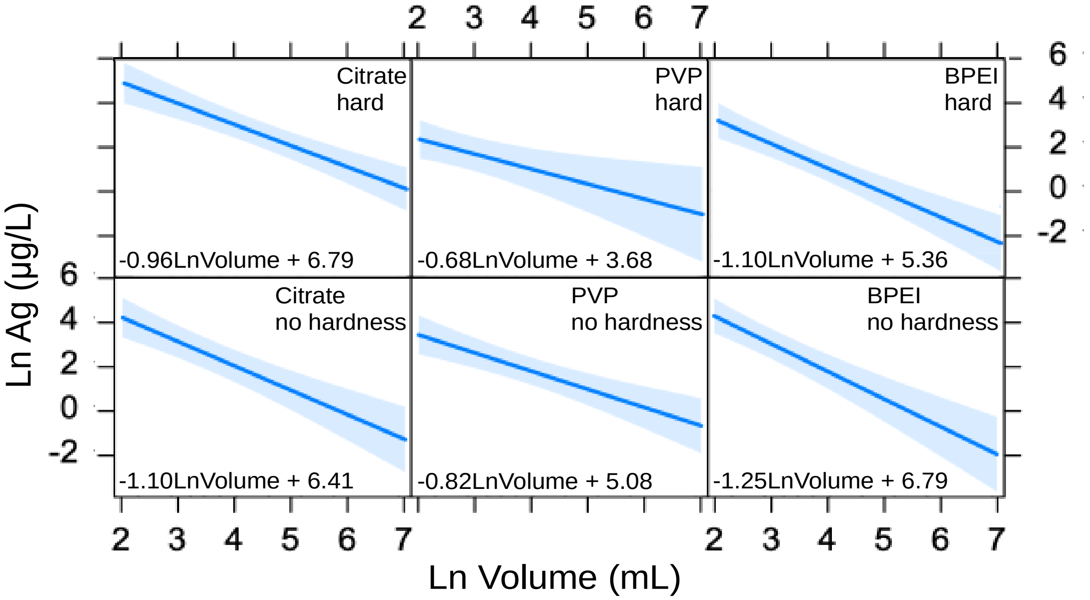

Figure 5. Model results predicting total Ag release from Al_2O_3 membranes coated with different Ag NPs and exposed to different water qualities. Equations are of fixed effects and include 95% confidence intervals.

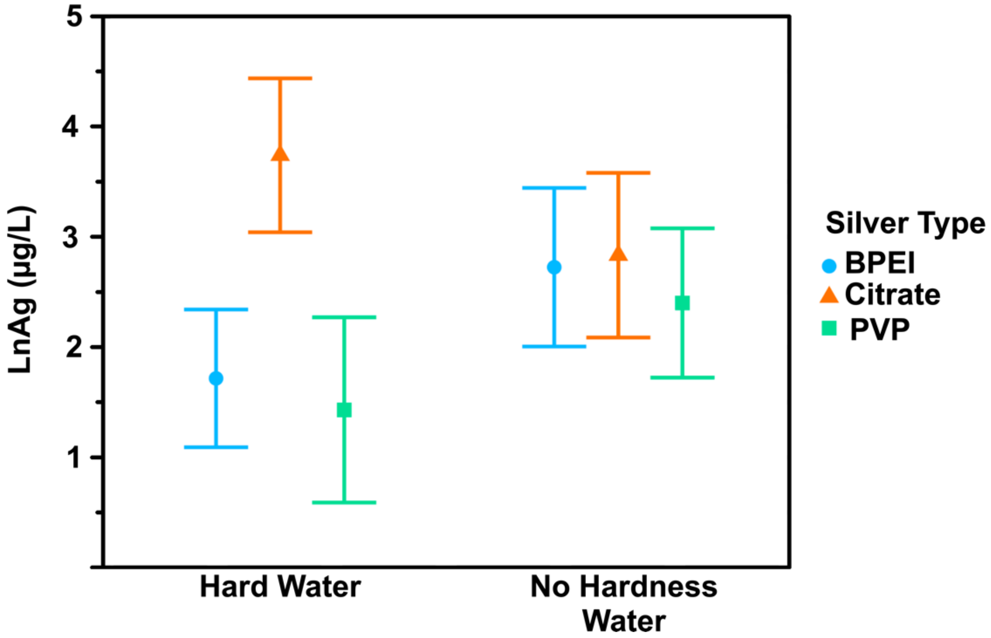

Figure 6. Variation in average total Ag release from Al_2O_3 membranes coated with different Ag NPs and exposed to different water qualities. Error bars represent 95% confidence interval predicted by the model.

3.3. Citrate Ag NP NOM Results

The effect of NOM on citrate Ag NP detachment was also tested using multilevel modeling. Citrate was selected because it is the most prevalently used Ag NP and has dangling carboxyl and hydroxyl groups available for binding to other chemical species [27, 34]. The test conditions simulate 18 days of operation for a treatment unit with 25 m^2 of surface area operated at 170 L/m^2-hr. Figure 7 contains experimental data of representative membranes tested under each water condition. The NOM-containing hard water removes Ag at a higher level and for a longer period than in water without NOM (hard water + NOM p-value = 0.036; no hardness water + NOM p-value = 0.184). The highest overall amount of Ag removed from the ceramic membranes was when they were exposed to water with both NOM and hardness (Figure 8).

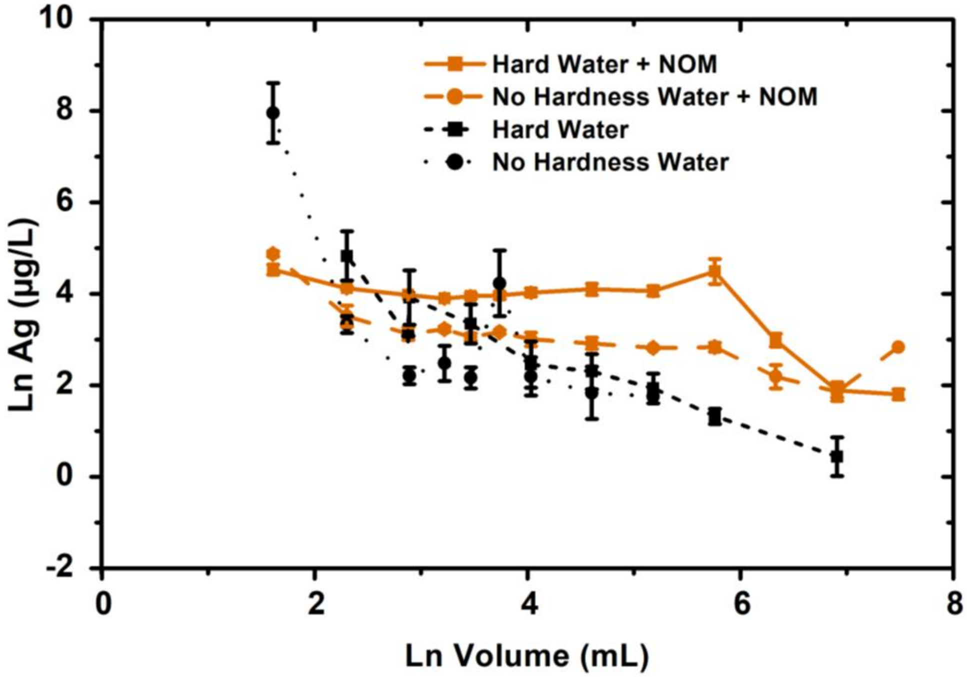

Figure 7. Example of Ag release from citrate AgNP membranes with waters containing different combinations of hardness and natural organic matter (NOM). Error bars represent standard error when effluent Ag was measured from multiple membranes prepared and challenged in the same manner.

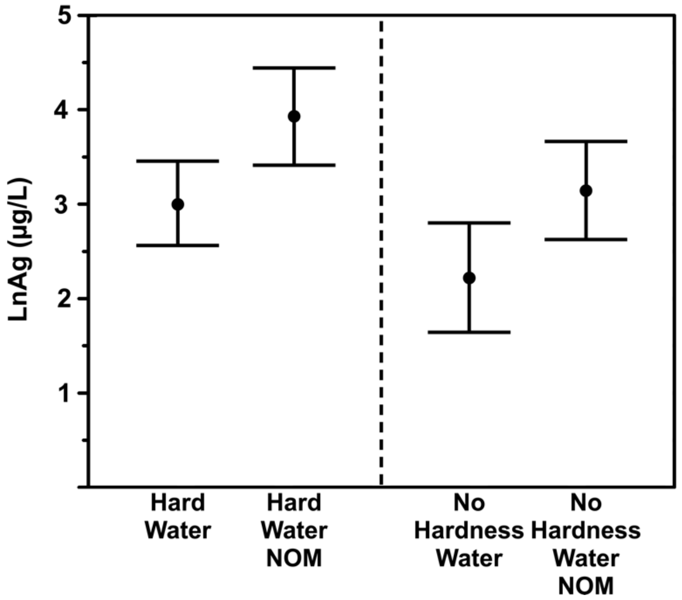

Figure 8. Variation in average total Ag release from Al_2O_3 membranes coated in Ag NPs that were exposed to different water qualities with and without NOM. Error bars represent 95% confidence interval predicted by the model.

3.4. Zeta Potential

The electrical double layer plays a significant role in the attachment of particles to flat surfaces [35-37]. This phenomenon has been documented for attachment of Ag NPs to Anodiscs [26] and also provides insight into why differences in Ag release were observed in this research. Table 2 contains zeta potential values measured for the Ag NPs suspended in the same water compositions used during the filtration tests. Changes to the electrical double layer occurred due to the presence of filtration water conditions that were different than deposition water conditions.

Table 2: Ag NP Zeta Potential at Filtration Water Conditions

Nanoparticle-Water	Zeta Potential (mV)
Citrate-Ag Hard Water + NOM	-19.5
Citrate-Ag Hard Water	-20.1
Citrate-Ag No Hardness Water + NOM	-23.0
Citrate-Ag No Hardness Water	-19.4
PVP-Ag Hard Water + NOM	-5.1
PVP-Ag Hard Water	-3.8
PVP-Ag No Hardness Water + NOM	-7.6
PVP-Ag No Hardness Water	-5.1
BPEI-Ag Hard Water + NOM	-4.9
BPEI-Ag Hard Water	24.4
BPEI-Ag No Hardness Water + NOM	10.1
BPEI-Ag No Hardness Water	19.8

During deposition onto the membranes, citrate Ag NPs had a zeta potential of -23.4 mV, PVP Ag NPs -9.8 mV, and BPEI Ag NPs 33.8 mV [26]. The magnesium, carbonate, and pH differences in the filtration waters provide different effects on the Ag NPs' zeta potential values. Filtration waters produced a slightly less negative zeta potential value for both PVP (Hard: -3.8 mV, Not Hard: -5.1 mV) and citrate Ag NPs (Hard: -20.1 mV, Not Hard: -19.4 mV) than during attachment conditions. Filtration conditions also reduced the zeta potential for BPEI Ag NPs (Hard: 24.4 mV, Not Hard: 19.8 mV) compared to the original deposition conditions. The smaller zeta potential changes for citrate Ag NPs from attachment conditions helps explain why the initial release from PVP and BPEI Ag NPs more strongly depended on silver-water type interactions.

Since the Ag NPs rest on the surface of the Anodiscs, it is expected that the change in the Ag NP zeta potentials would control the initial release of Ag. However, the Ag NPs deposited do not completely cover the surface of the membrane, so it is likely that changes to the Anodisc surface potential also impact the initial and sustained release of Ag NPs. The membrane has a positive surface potential of 14.5 mV for citrate and PVP Ag NP deposition conditions and -24.4 mV for BPEI Ag NP deposition. Although the zeta potential of the membrane was not measured under the different water conditions, at the pH values of both water conditions, it is expected that the Anodisc will have a negative surface potential. This charge difference should lead to a greater release of citrate and PVP Ag NPs than BPEI Ag NPs because the signs of the particles and the membranes switch from being opposite signs during deposition to like signs during filtration (i.e., unstable conditions). This expectation was borne out with observations (Figure 3 B, D, and F x-intercepts). Filtration experiments were only performed using NOM for citrate Ag NPs. NOM decreased the zeta potential of the citrate Ag NPs, but it does so to differing degrees for water with and without hardness and that difference contributes to varied release under these two water conditions.

4. Conclusions

- A multilevel model, based on extensive experimentation, is an effective tool to estimate the release of Ag NPs from ceramic membranes as a function of volume of water filtered. Equations were developed to predict the amount of Ag released for three types of Ag NPs experiencing “hard” and “not hard” water conditions. For the development of the model, several packages in the opensource software R were effectively utilized (i.e., *lme4*, *lmerTest*, and *effects*). This approach can be used by a wide variety of researchers to develop models with nested data and offers a free option for advanced statistical analysis for those with limited financial resources.

- Ag NPs are not created equal; stabilizing agents impact attachment and detachment to/from membrane surfaces. Both water type (via the interaction term) and Ag type (i.e., the stabilizing chemical attached to the Ag NPs) were significant explanatory variables in describing the release of Ag from Al_2O_3 ceramic membranes.

- The data suggest that Ag release will diminish before the consumption of the Ag on the membrane. This trend means that any decrease in bacterial removal over the lifespan of a membrane element used in these water conditions is likely due to the Ag being inaccessible for contact with the bacteria, not due to a lack of Ag on the membrane.

- As explained using changes in zeta potential values between deposition and filtration conditions, PVP and BPEI Ag NPs were more susceptible to changes in initial release from Al_2O_3 ceramic membranes than citrate Ag NPs for hard vs. not hard water. On the other hand, the change in zeta potential of the membrane between deposition and filtration conditions contributed to more sustained release for citrate and PVP Ag NPs than BPEI Ag NPs.

- Results agree with previous granular media research findings that the electrical double layer plays a role in Ag detachment. Hardness and NOM prolong the release of silver over time, but have lower initial amounts released. In general, for greatest retention of Ag, membranes should be operated at pH values where the membrane and particle have opposite sign surface potentials, with soft water, and no NOM.

- Even with the inclusion of Ag type and water type, a significant amount of unexplained variation remains in the proposed multilevel model. Future work should focus on including more factors until this variation is insignificant. Adding NOM for all types of Ag NP membranes, isolating the effects of hardness and pH, and/or including a term that captures the zeta potential of the Ag and of the membrane with changing water conditions are all reasonable next steps. Loss of Ag during cleaning procedures is another important area for future research as is further work to determine for which types of ceramics cation exchange processes dominate over DLVO interactions.

Associated Content

Supporting Information

Supporting Information contains details of parameter estimates and significance testing for the unconditional and continual modeling results. The Supporting Information is available free of charge on the ACS Publication website at DOI:

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Notes

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References

[1] M. Lee, Z. Wu, K. Li, Advances in ceramic membranes for water treatment, in: Advances in Membrane Technologies for Water Treatment, Elsevier, 2015, pp. 43-82.

[2] J. Kim, B. Van der Bruggen, The use of nanoparticles in polymeric and ceramic membrane structures: review of manufacturing procedures and performance improvement for water treatment, Environmental pollution, 158 (2010) 2335-2349.

[3] M. Baghbanzadeh, D. Rana, C.Q. Lan, T. Matsuura, Effects of Inorganic Nano-Additives on Properties and Performance of Polymeric Membranes in Water Treatment, Separation & Purification Reviews, 45 (2015) 141-167.

[4] E. Bet-moushoul, Y. Mansourpanah, K. Farhadi, M. Tabatabaei, TiO2 nanocomposite based polymeric membranes: A review on performance improvement for various applications in chemical engineering processes, Chemical Engineering Journal, 283 (2016) 29-46.

[5] A. Giwa, N. Akther, V. Dufour, S.W. Hasan, A critical review on recent polymeric and nano-enhanced membranes for reverse osmosis, RSC Adv., 6 (2016) 8134-8163.

[6] F. Diagne, R. Malaisamy, V. Boddie, R.D. Holbrook, B. Eribo, K.L. Jones, Polyelectrolyte and silver nanoparticle modification of microfiltration membranes to mitigate organic and bacterial fouling, Environmental science & technology, 46 (2012) 4025-4033.

[7] M. Zhang, K. Zhang, B. De Gusseme, W. Verstraete, R. Field, The antibacterial and anti-biofouling performance of biogenic silver nanoparticles by Lactobacillus fermentum, Biofouling, 30 (2014) 347-357.

[8] M. Ben-Sasson, X. Lu, E. Bar-Zeev, K.R. Zodrow, S. Nejati, G. Qi, E.P. Giannelis, M. Elimelech, In situ formation of silver nanoparticles on thin-film composite reverse osmosis membranes for biofouling mitigation, Water research, 62 (2014) 260-270.

[9] K. Zodrow, L. Brunet, S. Mahendra, D. Li, A. Zhang, Q. Li, P.J. Alvarez, Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show improved biofouling resistance and virus removal, Water research, 43 (2009) 715-723.

[10] M.S. Rahaman, H. Thérien-Aubin, M. Ben-Sasson, C.K. Ober, M. Nielsen, M. Elimelech, Control of biofouling on reverse osmosis polyamide membranes modified with biocidal nanoparticles and antifouling polymer brushes, Journal of Materials Chemistry B, 2 (2014) 1724.

[11] B.A. Bolto, Z. Xie, Recent Developments in Fouling Minimization of Membranes Modifed with Silver Nanoparticles, Journal of Membrane Science and Research, 4 (2018) 111-120.

[12] S. Agnihotri, S. Mukherji, S. Mukherji, Impact of background water quality on disinfection performance and silver release of immobilized silver nanoparticles: Modeling disinfection kinetics, bactericidal mechanism and aggregation behavior, Chemical Engineering Journal, 372 (2019) 684-696.

[13] A.M. El Badawy, R.G. Silva, B. Morris, K.G. Scheckel, M.T. Suidan, T.M. Tolaymat, Surface charge-dependent toxicity of silver nanoparticles, Environmental science & technology, 45 (2010) 283-287.

[14] D.P. Stankus, S.E. Lohse, J.E. Hutchison, J.A. Nason, Interactions between natural organic matter and gold nanoparticles stabilized with different organic capping agents, Environmental science & technology, 45 (2010) 3238-3244.

[15] K.A. Huynh, K.L. Chen, Aggregation kinetics of citrate and polyvinylpyrrolidone coated silver nanoparticles in monovalent and divalent electrolyte solutions, Environmental science & technology, 45 (2011) 5564-5571.

[16] S. Lin, Y. Cheng, J. Liu, M.R. Wiesner, Polymeric coatings on silver nanoparticles hinder autoaggregation but enhance attachment to uncoated surfaces, Langmuir, 28 (2012) 4178-4186.

[17] T. Silva, L.R. Pokhrel, B. Dubey, T.M. Tolaymat, K.J. Maier, X. Liu, Particle size, surface charge and concentration dependent ecotoxicity of three organo-coated silver nanoparticles: comparison between general linear model-predicted and observed toxicity, Science of the Total Environment, 468 (2014) 968-976.

[18] C.M.W. Group, Best practice recommendations for local manufacturing of ceramic pot filters for household water treatment, Center for Disease Control and Prevention, (2011).

[19] A.R. Bielefeldt, M.W. Stewart, E. Mansfield, R. Scott Summers, J.N. Ryan, Effects of chlorine and other water quality parameters on the release of silver nanoparticles from a ceramic surface, Water research, 47 (2013) 4032-4039.

[20] J. Rayner, H. Zhang, J. Schubert, P. Lennon, D. Lantagne, V. Oyanedel-Craver, Laboratory investigation into the effect of silver application on the bacterial removal efficacy of filter material for use on locally produced ceramic water filters for household drinking water treatment, ACS Sustainable Chemistry & Engineering, 1 (2013) 737-745.

[21] A.M. Mittelman, D.S. Lantagne, J. Rayner, K.D. Pennell, Silver dissolution and release from ceramic water filters, Environmental science & technology, 49 (2015) 8515-8522.

[22] A.M. Mikelonis, D.F. Lawler, P. Passalacqua, Multilevel modeling of retention and disinfection efficacy of silver nanoparticles on ceramic water filters, Science of The Total Environment, 566 (2016) 368-377.

[23] R. Sullivan, M. Erickson, V. Oyanedel-Craver, Understanding the microbiological, organic and inorganic contaminant removal capacity of ceramic water filters doped with different silver nanoparticles, Environmental Science: Nano, 4 (2017) 2348-2355.

[24] G. van Erven Cabala, W. Acchar, Silver nanoparticle surface functionalized alumina filters for disinfection of potable water, Materials Today: Proceedings, 2 (2015) 321-330.

[25] Y. Lv, H. Liu, Z. Wang, S. Liu, L. Hao, Y. Sang, D. Liu, J. Wang, R. Boughton, Silver nanoparticle-decorated porous ceramic composite for water treatment, Journal of Membrane Science, 331 (2009) 50-56.

[26] A.M. Mikelonis, S. Youn, D.F. Lawler, DLVO Approximation Methods for Predicting the Attachment of Silver Nanoparticles to Ceramic Membranes, Langmuir, 32 (2016) 1723-1731.

[27] T.M. Tolaymat, A.M. El Badawy, A. Genaidy, K.G. Scheckel, T.P. Luxton, M. Suidan, An evidence-based environmental perspective of manufactured silver nanoparticle in syntheses and applications: a systematic review and critical appraisal of peer-reviewed scientific papers, Science of the Total Environment, 408 (2010) 999-1006.

[28] D. Bates, M. Maechler, B. Bolker, S. Walker, Linear Mixed-Effects Models using 'Eigen' and S4, in: Package 'lme4', R, 2019.

[29] A. Kuznetsova, P.B. Brockhoff, R.H.B. Christensen, lmerTest package: tests in linear mixed effects models, Journal of Statistical Software, 82 (2017).

[30] M.J. Gurka, Selecting the best linear mixed model under REML, The American Statistician, 60 (2006) 19-26.

[31] S.W. Raudenbush, A.S. Bryk, Hierarchical linear models: Applications and data analysis methods, Sage, 2002.

[32] W.H.O. (WHO), Guidelines for Drinking-Water Quality 4th ed., WHO chronicle, 38 (2011) 104-108.

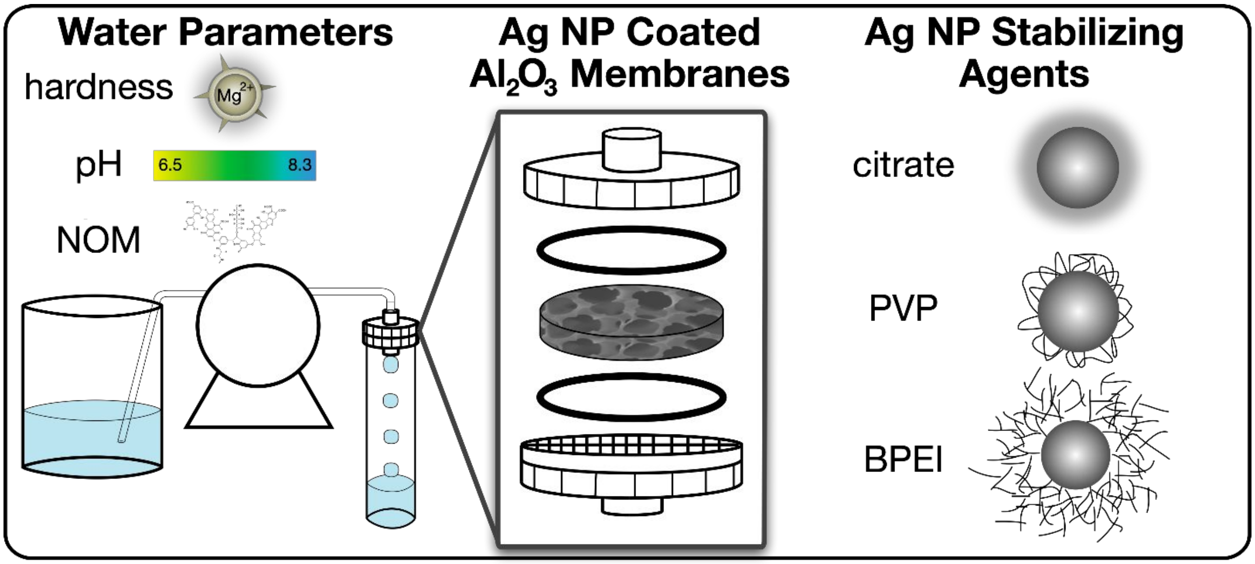
[33] I. Kim, T. Zhu, S. Youn, D.F. Lawler, Polymer-Capped Nanoparticle Transport in Granular Media Filtration: Deviation from the Colloidal Filtration Model, in, American Society of Civil Engineers, 2017.

[34] J.-W. Park, Interfacial properties of asymmetrically functionalized citrate-stabilized gold and silver nanoparticles related to molecular adsorption, in, The University of Utah, ProQuest Dissertations and Theses, 2013, pp. 298.

[35] R. Hogg, T.W. Healy, D. Fuerstenau, Mutual coagulation of colloidal dispersions, Transactions of the Faraday Society, 62 (1966) 1638-1651.

[36] M. Elimelech, J. Gregory, X. Jia, Particle deposition and aggregation: measurement, modelling and simulation, Butterworth-Heinemann, 2013.

[37] C. Van Oss, R. Giese, P.M. Costanzo, DLVO and non-DLVO interactions in hectorite, Clays Clay Miner, 38 (1990) 151-159.



Multilevel statistical model developed to demonstrate stabilizing agent impact on detachment of silver nanoparticles from ceramic water treatment membranes.