Accepted Manuscript

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PII: S0048-9697(17)33061-9
DOI: doi:[10.1016/j.scitotenv.2017.11.003](https://doi.org/10.1016/j.scitotenv.2017.11.003)
Reference: STOTEN 24567

To appear in: *Science of the Total Environment*

Received date: 20 July 2017
Revised date: 30 October 2017
Accepted date: 1 November 2017

Please cite this article as: Josune Olabarrieta, Oihane Monzón, Yolanda Belaustegi, Jon-Iñaki Alvarez, Saioa Zorita , Removal of TiO₂ nanoparticles from water by low pressure pilot plant filtration. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Stoten(2017), doi:[10.1016/j.scitotenv.2017.11.003](https://doi.org/10.1016/j.scitotenv.2017.11.003)

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Removal of TiO₂ nanoparticles from water by low pressure pilot plant filtration

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Abstract

Rising use of nanoparticles in manufacturing as well as in commercial products bring issues related to environmental release and human exposure. A large amount of TiO₂ nanoparticles will eventually reach wastewater treatment plants. Low pressure membrane filtration has been suggested as a feasible treatment of water streams. This study investigated first at laboratory scale the influence of: i) membrane material, ii) pore size and iii) water chemistry on nTiO₂ removal. TiO₂ retention was governed by the cake layer formation mechanism and significant retention of nanoparticles was observed even for filters having considerably larger pores than nTiO₂. PVDF showed a great potential for nTiO₂ rejection. Additionally, filtration pilot plant experiments were carried out using PVDF membranes (0.03 and 0.4 µm pore size). The release of nTiO₂ in the pilot scale filtration system was always above the instrumental detection limit (>1.5 µg/L) and in most cases below 100 µg/L regardless of the pore size and applied conditions. The nTiO₂ membrane breakthrough predominantly occurred in the first few minutes after backwashes and ceased when the cake layer was formed. Ultrafiltration and microfiltration were comparable with rejection of nTiO₂ above 95% at similar permeate flow rates. Nevertheless, ultrafiltration is more promising than microfiltration because it allowed longer operation times between backwash cycles.

Keywords:

Microfiltration
Ultrafiltration
Nanoparticle
Separation
Cake formation
Environmental release

1. Introduction

Nanomaterials, with one or more external dimensions in the size range of 1-100 nm, generally exhibit novel properties (*e.g.* add extra strength to the material or increase chemical reactivity) compared to the same material without nanoscale features. Thus, they potentiate a range of enhanced technologies. As a result, at present, nanomaterials have become part of our daily life and there are already a broad range of nanoparticles (NPs) incorporated in a variety of industrial applications and commercial products, namely in cosmetics, the agri-food industry, coatings, construction, environmental remediation, etc., as listed by the Woodrow Wilson database (Vance *et al.*, 2015). In this database TiO₂ is the second (after silver) most frequently advertised nanomaterial component in consumer products.

On the other hand, it is suspected that nanomaterials may pose a risk to the public health and the environment. The risk associated to a material mainly depends on the toxicity and exposure of the material. Not all NPs have shown negative effects on the public health at present environmental concentrations, yet there are a number of articles demonstrating their potential threat. A wide exposure to TiO₂ NPs has shown negative effects on mice such as genotoxicity, inflammation and reproductive and liver metabolic dysfunction (Ema *et al.*, 2010; Gao *et al.*, 2012; Shin *et al.*, 2010; Yang *et al.*, 2017). Furthermore, NPs may accumulate or react with aquatic organisms causing adverse effects (Amiano *et al.*, 2012; Handy *et al.*, 2008; Singh, 2015). Thus, they are a great concern for regulators, industry and the public.

Environmental exposure to nanomaterials is inevitable. For example through sunscreen application to the skin, pharmaceutical ingestion, and also through the release of nanomaterials embedded in commercial products (Al-Kattan *et al.*, 2014; Bossa *et al.*, 2016, Olabarrieta *et al.*, 2014) or direct use of NPs for environment remediation (Di Paola *et al.*, 2012; Karn *et al.*, 2009). Wastewater effluents have been pointed as a probable point source of NPs. Gottschalk *et al.* (2009) estimated through modeling that a major fraction of the released NPs will end up in soil and surface water (*ca* 24%). On the other hand, Kiser *et al.* (2009) determined that wastewater treatment plant (WWTP) effluents discharge about 5-15 µg/L Ti particles (presumably TiO₂) with a size below 700 nm. These values are in the same range of the median (16.3 µg/L of nTiO₂) predicted concentrations in the WWTP effluent for the year 2014 in Europe (Sun *et al.*, 2016). The same authors estimate that the concentrations in natural compartments are around 2.2 µg/L and 2.9 µg/Kg for surface water and natural and urban soil, respectively. This amount of nanomaterials that will reach our treatment plants and the natural compartments is expected to increase as the nanotechnology market grows.

Filtration has attracted attention as a technology that could confine engineered NPs. Studies using common types of filtration media (mainly sand filtration) used in WWTPs highlighted the ineffective quantitative removal of NPs. Rottman *et al.* (2013) showed that solution chemistry and choice of filtration media had a strong impact on the retention of nano-TiO₂ (nTiO₂) during porous media filtration. In the tested conditions (30-bed volumes) only diatomaceous earth displayed quantitative retention of a 50 mg/L nTiO₂ in ultrapure water while 0 and 20% of the NPs were capture by sand and activated carbon respectively. Furthermore, water contaminants showed that this retention could be diminished. Thus, polymeric based membrane technologies are considered more promising technology to trap NPs in WWTPs.

Presently there are few laboratory scale studies available that investigate the use of polymeric membranes for removing NPs from aqueous media. These investigations have mainly focused on the understanding of removal mechanisms and the influence of several parameters such as pore size, water chemistry and particle type and size. Lipp *et al.* (2009) studied nanopolystyrene fouling and breakthrough during low-pressure membrane filtration. Under the tested conditions, polystyrene NP concentration did not impact the breakthrough of NPs through polymeric membranes. Conversely, NP size (21-73 nm) and membrane pore size (20-100 nm) influenced the nanopolystyrene release which ranged from 1 to 84%. Abbot Chalew *et al.* (2013) evaluated Aeroxide TiO₂, silver and ZnO nanoparticle release through flat sheet polyvinylidene fluoride (PVDF) microfiltration (0.45 μ m pore size) and ceramic ultrafiltration (0.02 μ m) membranes using various water matrices. Ultrafiltration was more effective, but still up to 5% of Ti breakthrough was observed. On the contrary, breakthroughs from microfiltration were < 20% Ti from all waters except groundwater and synthetic freshwater with natural organic matter. Ladner *et al.* (2012) investigated the interaction of functionalized NPs (silver, titanium dioxide and gold) with membranes of different materials and pores (*ca* 2 nm to 200 nm). The authors observed that: i) positively charged NPs displayed higher rejection (99%) by negatively charged membranes than by negatively charged NPs, ii) no significant retention behavior difference was observed for five different polymeric membranes (polysulfone, polyether-sulfone, cellulose acetate, polyvinylidene fluoride and nylon), iii) NPs were generally well rejected by membranes with pores smaller than NP size and in some cases by membranes with larger pores. This last conclusion was corroborated by Floris *et al.* (2016). In this work, even though high rejection (99%) of nC60 fullerene could be achieved using dead-end ultrafiltration, a small fraction was detected in the permeate sample (*ca* 8 μ g/L). Equivalent rejection percentage (99%) was obtained with microfiltration membrane of 200 nm pore, but only 10% of the fullerenes could be removed when utilizing a 500 nm pore membrane. The authors also focused on the hydraulic backwash cleaning procedure to mimic separation in real industrial water treatment plant. While the water permeability decreased over 5 filtration cycles for microfiltration, it remained almost constant for ultrafiltration. This suggested that 200 nm pore membrane, compared to 18 nm pore size membrane, is more susceptible to pore entrapment and pore narrowing. The main proposed removal mechanisms were size exclusion, a combination of external and internal deposition and adhesion between nC60 and the membrane material for 20, 200 and 500 nm pore membranes respectively. Van Koetsem *et al.* (2017) also studied how various filtering techniques (paper, micro and ultrafiltration) and aqueous matrix composition influence the retention of nano citrate coated Ag and CeO₂. As in Lander *et al.* (2012) and Floris *et al.* (2016), high retention percentages were observed even for membranes with significantly larger pore size than the NPs diameter. However, when a small amount of salt (i.e. 2 mM NaCl) was added to ultrapure water, the retention efficiency generally declined for CeO₂ whereas for Ag it increased, probably as a result of NP aggregation. Authors also observed that removal efficiency of NPs from water increased with decreasing initial NP concentration.

Although the aforementioned investigations provided valuable information on the interactions between NPs and polymeric membranes, the conclusions are difficult to extrapolate to real filtration water treatment plants because none of the studies were performed i) under typical full-scale conditions such as a constant flux operating mode, ii) using a real water matrix and iii) using commercial hollow fiber cartridges. To bridge this gap between laboratory and full scale filtration plants, the present study focuses on

the fate of engineered TiO₂ NPs in a filtration pilot plant using tap water. In order to attain this goal, this work evaluated the removal efficiency of nTiO₂, first at laboratory scale, with five different polymeric materials, various nominal pore sizes ranging from 0.025 to 0.45 µm as well as various water matrices. In addition, the retention of NPs was examined using micro and ultrafiltration in a pilot plant. In particular, the method of operation, e.g. dead-end versus crossflow filtration was assessed with discrete and continuous sampling between membrane backwashing.

2. Materials and Methods

2.1 Materials

The selected titanium dioxide NP was Aeroxide P25 (nanoparticle diameter: 21 nm; surface area: 50 m²/g, crystallinity: 80% anatase-20% rutile according to manufacturer) from Evonik (Essen, Germany). Sodium bicarbonate and humic acid salt (HA) were obtained from Sigma-Aldrich (Steinheim, Germany).

Reagent water was obtained from a Milli-Q Purification system (Millipore Corp., Bedford, MA, USA). Tap water was collected in spring of 2011 and 2012. The characteristics of this water type were: pH: 7.9-8; conductivity: 220-250 µS/cm, TOC: 0.8-1.6 mg/L. A grab water sample (pH: 8.1, conductivity: 407 µS/cm, TOC: 4.7 mg/L) from Asua river (near Zamudio, Spain) was collected on the 3rd September 2011. Two treated sewage water effluent samples were collected in the spring of 2011: WWTP 1 (pH: 7.5, conductivity: 8.0 mS/cm, chemical oxygen demand: 23.6 mg O₂/L), and WWTP 2 (pH: 7.5, conductivity: 818 µS/cm, TOC: 27.1 mg/L, chemical oxygen demand: 7.6 mg O₂/L). The sewage water was filtered through a GF/F (0.7 µm pore) Whatman (Dassel, Germany) glass fibre filter. River and wastewater samples were frozen at -18°C for posterior analysis.

2.2 Nanoparticle concentration determination

Nanoparticle concentration in the permeate water was measured using inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a Variant 710 ICP-OES with an axial torch configuration. TiO₂ NP samples were digested with 2% HNO₃. Samples were processed within one week. The method's detection limit for nTiO₂ was 1.5 µg/L. The recovery ratio was 66.7%, thus a correction factor of 1.5 was applied in the calculations of NP concentration to compensate for the partial digestion of nTiO₂. (Accuracy of the method after applying the correction factor was 97.7% and precision as RSD was 6% at 20 µg/L nTiO₂).

2.3 Aggregate size and Z-potential

The size of nano-TiO₂ (P25) aggregates in various suspensions was measured using a Dynamic Light Scattering (DLS) instrument, Zetasizer Nano-ZS (Malvern Instruments, Malvern, UK). The CONTIN algorithm was used to convert intensity autocorrelation functions to intensity-weighted hydrodynamic aggregate diameter distributions on the basis of the Stokes-Einstein relationship for spherical particles. All DLS analyses were carried out in triplicates at 25 °C. To ensure a representative sample for the aliquot subjected to DLS analysis, suspensions were stirred at 700 rpm for at least 2 min prior to extracting an aliquot for DLS analysis. The TiO₂ sample concentration was 2 mg/L

(pilot plant) or 1 g/L (laboratory scale setup) in order to have the same conditions as in the filtration experiments. TiO₂ suspensions were prepared under all tested experimental conditions (ultrapure water at different pHs, using HAs, salts and real waters). Multi narrow mode was used as a model to analyse the suspension. The values are averaged in triplicate over 11 runs. ξ -potential measurements were carried out using a Malvern Zetasizer Nano-ZS using a high concentration cuvette (Malvern, ZEN1010) at 25 °C. This technique is based on the Doppler displacement of light due to NPs. Samples were prepared in an identical manner as for the DLS experiments.

2.4 Laboratory scale membrane set-up

A semi-tangential laboratory scale filtration apparatus (Millipore), shown in (**Figure S1A**) was used in the microfiltration experiments. A flat membrane (17.35 cm² surface area) was placed in the module, 75 mL suspension containing 1 g/L nTiO₂ was added to the feed tank which was continuously stirred during the filtration process. The microfiltration experiments were carried out at a pressure of 2 bars unless otherwise stated, using an air compressor.

Five different membrane materials from Millipore were tested: Nylon, Polyethersulfone (PES), Mixed Cellulose Esters (MCE), hydrophilic Polyvinylidene Fluoride (PVDF) and hydrophilic Polytetrafluoroethylene (PTFE). Each material was tested using two different pore sizes, ranging from 0.025 μ m (often considered the borderline between micro- and ultrafiltration) to 0.45 μ m.

2.5 Pilot-plant

The pilot plant consisted of a 1000 L feed tank connected to the tap water supply, a pump, two membrane modules that could be operated simultaneously or individually, a dosimeter for the NPs, a chemically enhanced backwash (CEB) and cleaning in place (CIP) system and a Programmable Logic Controller (PLC) as observed in **Figure S1B** and represented schematically in **Figure 1**. The pilot plant also included a 500 μ m pre-filter, a flow meter, an inlet and outlet pressure controller, a thermometer and a manual valve to control the retentate water flow in cross flow filtration mode. The plant was designed to treat a maximum of 1500 L/h in dead-end or tangential (also known as cross flow) filtration modes.

[Figure 1]

Two PVDF hollow fibre membrane modules were tested: i) a 0.4 μ m microfiltration module from Porous Fibers (Leioa, Spain) with a surface area of 6.6 m² giving a recommended filtrate flux of 50-100 L/m²/h and ii) a 0.03 μ m ultrafiltration module from Dow (Michigan, USA) with a surface area of 33 m² giving a recommended filtrate flux between 40-120 L/m²/h. Other membrane parameters can be found in the Supplementary Information (**Table S1**).

Seven experiments were performed in constant flow mode which are summarized in **Table 1**.

[Table 1]

Twenty-four hour filtration tests were performed in each case. nTiO₂ concentration in the inlet and outlet was evaluated by discrete (also known as grab) and continuous sampling. Since high fouling was observed with the microfiltration module, backwashes were set every 30 min, acidic cleaning with H₂SO₄ to combat inorganic fouling was performed every 8 h and basic cleaning with NaOH to decrease organic fouling was done every 12 h. For the ultrafiltration hollow fibre module, acidic and basic cleaning cycles were identical to microfiltration. However, since the pressure was constant over longer periods of time with the ultrafiltration system, backwashes were set every 45 min.

2.6 Scanning electron microscopy

The morphology of the membranes and the nTiO₂-membrane interaction were elucidated by Scanning Electronic Microscopy (SEM), with a Quanta 200 unit (FEI, USA) operated at an accelerating voltage of 15 kV. Energy-dispersive X-ray spectroscopy measurements (Adjustable EDAX Detecting Unit 132-10 for Quanta 200, FEI, USA) were performed to identify the NPs presence in the membranes and to evaluate their spatial distribution in the filters.

3. Results

3.1 Laboratory filtration

This first block of experiments was designed to evaluate a variety of polymeric membrane materials and pore sizes typically used in water and wastewater treatment. The goal of these tests was to identify the optimum material to be tested in the pilot plant. Furthermore, the impact of matrix composition utilizing model components was assessed.

3.1.1 Polymeric membrane material and pore selection

This section aims at comparing and evaluating the polymeric membrane materials and pore sizes in terms of nTiO₂ release. In this manner, better systems can be designed to minimize NP release and therefore exposure. Five different materials were tested: nylon, PTFE, PVDF, PES and MCE. A suspension of 1 g/L nTiO₂ in ultrapure water was passed through the filters at a pressure of 2 bars. All materials except nylon gave a clear permeate water. The average concentration of nTiO₂ in the nylon permeate was determined to be 2.8 and 6.1 mg/L for membranes with a pore size of 0.22 and 0.45 µm, respectively. Nylon was then excluded from further testing since its performance was significantly worse than the other materials. As observed in **Table 2** the nTiO₂ concentration in the permeate water for the other materials was very close to the method detection limit demonstrating the suitability of all of them when working with ultrapure water suspensions. No big differences in NP release were observed between pore sizes and materials.

[Table 2]

At the beginning of the permeation experiment, average flow rate of the permeate water through the membrane was higher for PES material and decreased in the order: PTFE > PVDF > MCE (for comparable pore sizes) (see **Table 2**). Permeate flow rate decreased in time and after 2 min it leveled off to a constant value of ~40 mL/min for all materials. MCE on the other hand gave much slower filtration but more homogeneous flow (See **Figure S2**). The decrease of flow rate over time is related to NP fouling and occurred

even if the feed side was under continuous stirring. Flow rate was mainly influenced by membrane material and to a lesser extent by pore size. nTiO₂ release was not correlated with water flow rate.

Based on the presented results it was decided to continue the investigation with PVDF 0.22 µm, PES 0.22 µm and PES 0.45 µm materials. Compared to PTFE, these materials are more frequently used in industrial applications. MCE was excluded due to the resulting lower flux and lower implementation in water treatment plants. As the pore size was not apparently a relevant parameter, 0.22 µm (and 0.45 µm in few tests) pore size membranes were chosen for the following experiments.

3.1.2 Synthetic water tests

The nTiO₂ suspension stability and aggregation depends on the aqueous matrix components. Hence our interest in studying the influence of more complex water matrices on NPs filtration. Humic acids (HAs) and bicarbonate were chosen as model aqueous compounds. HAs are naturally occurring organic compounds from organic matter decomposition (Ghabbour and Davis, 2001). This group of compounds has been found to stabilize nTiO₂ suspensions (Luo *et al.*, 2016a; Zhu *et al.*, 2014) and on the other hand, they are known membrane foulants (Zhao *et al.*, 2016). Bicarbonate is an inorganic chemical that forms part of the aquatic carbon cycle and is responsible to a great extent for the pH of natural waters.

Figure 2 shows the nTiO₂ concentration in the permeate water when filtering 75 mL suspensions containing 1 g/L NP through PVDF 0.22 µm, PES 0.22 µm and PES 0.45 µm. Membrane batches were also evaluated in triplicates. From this set of experiments, the difference in membrane material ability to retain NPs became obvious. This implies that the size exclusion mechanism (membrane pore size) is less relevant to NP removal mechanism than material-NP interaction since PVDF showed a better performance than PES for all tested synthetic waters and 0.22 µm and 0.45 µm PES membranes presented similar NP release.

[Figure 2]

SEM observations of the dry nTiO₂ cake crevices suggested higher nTiO₂ adhesion to the PVDF membrane (See **Figure 3**). This higher adhesion of nTiO₂ to PVDF compared to PES could come from its preferential interaction with high electronegative groups such as fluorine (Ye *et al.*, 2011; Luo *et al.*, 2016b) instead of formation of hydrogen bonds between Ti-OH groups on nTiO₂ and O element from S=O in the PES chain (Guo and Kim, 2017). It can also be observed that the PVDF polymeric membrane surface was more homogeneous. This was translated in smaller variations in the results obtained by PVDF polymeric membranes as seen in Figure 2. The greater homogeneity of PVDF material together with its preferential interaction with nTiO₂ could explain its higher performance when processing suspensions in synthetic matrices. Significant differences were observed between membrane batches, highlighting the importance of robust membrane production.

[Figure 3]

Despite the retention of NPs still being very high ($> 99.7\%$), water matrix showed an important effect increasing up to 750-fold the NP release compared to ultrapure water. The presence of bicarbonate led to higher permeability of the NPs compared to humic acid. The mixture of the two compounds presented a synergistic negative effect reaching $2250 \mu\text{g/L}$ nTiO₂ in the permeate when filtering through $0.45 \mu\text{m}$ pore. These differences in NP breakthrough cannot only be explained by previously presented removal mechanisms (Lander *et al.*, 2012) such as NP adhesion or aggregation/stabilization phenomena (Luo *et al.*, 2016a; Zhu *et al.*, 2014). Besides, the role of cake formation has to be taken into consideration. As filtration of NPs proceeds, cake build-up around the mouth of the pores will occur. It is believed that once the cake is fully developed, surface porosity and/or irregular pore size distribution effect could be neglected. Then the size of the interstices of the cake layer itself takes over the role in determining the size of particle retained. Hence the cake acts as a second membrane (Boerlage *et al.*, 2002).

The hypothetical removal mechanisms based on cake formation and adsorption are summarized in **Figure S3**. High nTiO₂ (ζ -potential: $+31.2 \text{ mV}$) adsorption affinity to negatively charged membranes (e.g. -17 mV and -22 mV surface charge of PVDF and PES, respectively according to Lander *et al.* (2012)) would be the main retention mechanism in ultrapure water. On the contrary in the presence of NaHCO₃, with hydrodynamic aggregate diameter comparable to ultrapure water ($317 \pm 11 \text{ nm}$), nTiO₂ would be negatively charged (ζ -potential: -24.5 mV for 100 ppm NaHCO₃ and -31.5 mV for 250 ppm NaHCO₃) diminishing adhesion to the membrane and thus increasing nTiO₂ breakthrough. Based on ζ -potential, cake layer formation rate would be expected to be similar as both dispersion stabilities are comparable. No influence on the stability of the suspensions was observed due to an increase on ionic strength (IS), which was low (up to 0.003M) in all solutions.

Likewise, the combination of HAs+NaHCO₃ would induce high electrostatic repulsion between the negatively charged polymeric membrane and TiO₂ aggregates (ζ -potential: -39.2 mV in 7 ppm HA+ 250 ppm NaHCO₃ aqueous media, average hydrodynamic aggregate diameter: $831 \pm 14 \text{ nm}$). Nevertheless, this fact alone cannot account for the high breakthrough compared to bare NaHCO₃ solution. One hypothesis is that the cake formation in the presence of both HA+NaHCO₃ would be slower (See Section 3.2.1) and looser. This phenomenon is probably due to steric effects and consequently, creation of larger voids allowing the free NP or small aggregate fraction to pass the cake layer reaching the pores of the membrane. Similar theories have previously been described (Kang *et al.* 2010; Zhao *et al.* 2016).

It has to be noted that an increase in average mean hydrodynamic diameter (given as Z-average) would result in higher aggregate size if a unimodal distribution is present, thus one would expect that aggregates would be easier to remove by size exclusion. However, in the dispersions used in this work, bimodal (See Figure 4S) or even multimodal distributions were generally observed. In these cases, an increased average mean hydrodynamic diameter mostly represents a shift of intensity between larger and smaller fraction aggregates. This means that in experiments with HAs+NaHCO₃ solutions, despite the mean hydrodynamic diameter of nTiO₂ being larger; there is still a minor fraction of small aggregates that could permeate through the pores of the membranes if cake layer voids are sufficiently large and electrostatic repulsions between NPs and membrane are present. This would be the case for nTiO₂ in HAs+NaHCO₃ solutions.

Consequently, mean average hydrodynamic diameter as Z-average may not be necessarily a representative parameter to understand filtration mechanisms.

The presence of HAs did not greatly vary NP breakthrough as compared to ultrapure water and their influence on TiO_2 removal is less obvious. HAs added to bare nTiO_2 suspension in water would coat the surface of nTiO_2 aggregates, increasing the steric hindrance and thus stabilizing the aggregates. Yet this phenomenon is more complex (Loosli *et al.* 2013). While nTiO_2 is positively charged (ζ -potential: +31.2 mV) in ultrapure water, HAs are negatively charged. Increasing the amount of HA concentration in nTiO_2 dispersions causes charge inversion, leading to stabilization of TiO_2 . However, at surface charge neutralization, nTiO_2 rapidly forms aggregates. In this work, a charge inversion was observed in the studied HA concentrations. Consequently, the key NP removal mechanisms may vary in the presence of different HA concentrations. For 1 ppm HA dispersion (Average hydrodynamic diameter of: 359 ± 31 nm, ζ -potential: +28.1 mV), adsorption affinity between membrane and nTiO_2 as a removal mechanism may play a vital role. On the other hand, when adding 7 ppm of HAs, adhesion affinity is not likely to be of utmost importance in nTiO_2 removal, as aggregates became negatively charged (ζ -potential: -14.7 mV). The lower dispersion stability may increase the rate of cake formation, avoiding NP breakthrough. Nevertheless, there is a need for further investigations to elucidate the relation between water matrix and NP cake formation and structure and NP transport through the membrane.

Despite NPs being smaller than the pores, they can be removed because of adsorption to membrane surfaces, electrostatic interaction and/or cake rejection. However, it became evident that $0.45 \mu\text{m}$ pore sizes may not be adequate to quantitatively remove NPs when introducing naturally occurring compounds. Significant variations in permeate concentration were observed with $0.45 \mu\text{m}$ PES material as well as differences between membrane batches. Thus, this membrane was excluded from further testing.

3.1.3 Environmental water tests

In order to validate the results obtained with modelled compounds, real water suspensions were processed. Results presented in **Figure 4** confirm the superiority of PVDF material over PES for retaining nTiO_2 in environmental matrices. Despite the presence of humic acids and bicarbonate salt in environmental matrices, nTiO_2 release was not comparable to the observations in synthetic waters. This was expected for several reasons: i) higher ionic strength is predictable, resulting in very large aggregates (over $3 \mu\text{m}$ Z-average diameter, whereas in synthetic water, Z-average diameter did not exceed 900 nm) and rapid sedimentation, ii) lower ζ -potential (ranging -5.1 to -10 mV) was observed and iii) other compounds not previously taken into consideration are present. Fortunately, nTiO_2 concentration in the permeate water did not reach $100 \mu\text{g/L}$ for environmental waters, while in synthetic waters, the nTiO_2 ranged from a few hundred $\mu\text{g/L}$ to a couple of mg/L . This is probably due to quicker and/or denser cake formation, higher adsorption affinity to the membrane, plus a lower fraction of small aggregates would be present in the water. This indicates that the aqueous matrix composition may be a relevant parameter in any filtration study as it highly influences nTiO_2 retention and therefore filtration efficiency.

[Figure 4]

3.2 Pilot plant filtration

Laboratory scale experiments were conducted with the aim of elucidating the best polymeric material to be used in a pilot plant. PVDF material was chosen for the pilot plant experiments because of its superior performance over PES in terms of nTiO₂ retention. The objectives of running pilot plant experiments were to i) elucidate the nTiO₂ release in more realistic conditions, ii) study the difference in nTiO₂ retention between ultra- and microfiltration and iii) investigate the difference in filtration performance using dead-end and cross flow filtration modes of operation. The release of nTiO₂ was evaluated both by discrete and continuous sampling. Due to practical issues, tap water was used as water matrix in this set of experiments. Besides, concerns over the possibility that NPs might pose a threat to drinking water supplies have recently arisen (Troester *et al.*, 2016).

3.2.1 Discrete sampling

When working in a filtration plant, water is continuously filtered until the membrane modules become saturated as a result of the accumulation of solids on the membrane surface. This fouling leads to a decrease in the filtration performance. To prevent fouling and thus increase the lifetime of the membrane, backwash or chemical cleanings are regularly performed. Therefore, a preliminary set of experiments were performed to study the nTiO₂ release over time between backwashes. Backwashes are in most cases performed every 45 and 60 min, but can be performed every 20 min for a few hours. For the microfiltration cartridge, it was necessary to backwash the membrane every 30 min due to pressure increase, probably as a result of pore entrapment and pore narrowing. The pressure when working with the ultrafiltration cartridge did not vary for at least 60 min. However, in order not to have big differences between both cartridge modules, for the ultrafiltration module, the backwashes were carried out every 45 min.

Sampling was performed between the backwash cleanings as follows. Discrete permeate water samples were taken every 5 min during the first 30/45 min after backwash cleanings to evaluate the nTiO₂ release over time. The results from the different tests are presented in **Figure 5**. Generally, nTiO₂ concentration in the permeate water decreased over time showing that nTiO₂ release mainly happens in the first 10 minutes until the cake is formed, which acts as the main barrier to NP release. The retention cut-off of the cake has been reported as a tenth of the membrane pore (Boerlage *et al.*, 2002), thus in our case the micro and ultrafiltration membranes would retain NPs above 45 and 3 nm respectively, once the cake is formed. No substantial differences were observed between micro and ultrafiltration, probably because of the greater influence of the cake formation in the nTiO₂ cut-off than the membrane pore size. When HA+NaHCO₃ were added, the high breakthrough of the nanoparticles extended over time compared to the other test conditions. As previously described, this may be due to a looser or retarded cake formation and lower affinity between NPs and membrane material. All experiments follow the same pattern except for experiment G, where an increase of nTiO₂ concentration was observed in the second sampling time. The reason for this remains unclear.

[Figure 5]

Permeate discrete samples were also taken over a period of 24 h at fix times *i.e.* without taking into account the backwash times (**Table S2**). The concentration of TiO₂ in the permeate water was below 100 µg/L except for two samples in experiment H. These results corroborate the observed effect described in Section 3.1 where the presence of extra amount of humic acids and bicarbonate seemed to increase the concentration of nTiO₂ in the permeate water, most likely as a result of cake layer structure variation. It was also observed (**Figure S4**) that the high diameter aggregates (350-1100 nm) decreased in the permeate while the low aggregate population (50-150 nm) increased, resulting in lower Z-average diameter size aggregates in the permeate. Still, large aggregate size (200-800 nm) could be observed in the permeate, possibly as a result of a re-aggregation process after filtration. However, what these results highlight is that higher amounts of small aggregates will reach the environment. This fraction is of great importance as it is associated with higher mobility and ecotoxicity of NPs.

3.2.2 Continuous sampling

Discrete (or grab) sampling may lead to under or overestimation of nTiO₂ concentration in water. Hence, it was necessary to complete the obtained information by quantifying the average nTiO₂ concentration in the permeate water between backwashes. Two to four sampling replicates were set to study the reproducibility of the measurements. Results can be seen in **Table 3**.

[Table 3]

In microfiltration tests (30 min sampling), the increase in flow rate, and thus in applied pressure, slightly increased the transport of nTiO₂ through the membrane, which lay within the expected observations. Cross-flow filtration (inlet flow: 1300 L/h, permeate flow: 1000 L/h) rejection results are similar to dead-end filtration at 1300 L/h. It was observed that for the dead-end operation mode for microfiltration, after the first filtration the nTiO₂ the breakthrough increased and was constant thereafter.

Sampling time for the ultrafiltration experiments was set at 30 and 45 min, in order to compare with microfiltration and to see the differences between the two sampling times. Surprisingly ultrafiltration did not decrease the average nTiO₂ release. However, feed pressure was constant and lower than with microfiltration which means that the run time between backwashes and cleanings could be extended by at least 15 min. This is of utmost importance, as our previous results from **Figure 5** indicated that breakthrough of nTiO₂ mainly occurs within the first few minutes after the backwash step. The more frequently that backwashes or cleanings are needed, the higher NP release may be. For this reason, ultrafiltration would be recommended for NP separation.

For most of the experiments, as for discrete samples, the nTiO₂ permeate concentration was below 100 µg/L with retention above 95%. Two exceptions are observed for the ultrafiltration cartridge at a flow of 800 L/h. These results were obtained after the membrane cartridge was not used for a long time. We believe that the membrane may not have been stored with enough preservative solution, leading to biofouling, which could not be completely removed when the membrane was cleaned before use. These rejection results below 90% are not representative of usual operating mode, but highlight the great influence of biofouling on NP release to the environment.

To sum up, nTiO₂ release was slightly influenced by flow rate or applied pressure in microfiltration, whilst no big differences were observed for ultrafiltration.

4. Conclusion

Due to the potential effects of NPs in the environment, there is a need to study the suitability of water treatment separations methods to remove them. In this investigation, the suitability of micro- and ultrafiltration to retain nTiO₂ was evaluated. In microfiltration, at laboratory scale, water matrix had more influence on nTiO₂ release than the polymeric material and pore size.

The findings of this study emphasize the release of nTiO₂ in a pilot scale filtration system, where nTiO₂ concentration in permeate water was always above the instrumental detection limit ($>1.5 \mu\text{g/L}$) and in most cases below $100 \mu\text{g/L}$, regardless of pore size and applied conditions. The NP retention rate was generally above 95%, but this implies that up to a few grams per day (*ca* 2.25 g) of NPs could be released when treating 31.2 m^3 of tap water with *ca* 2 mg/L nTiO₂. nTiO₂ release predominantly occurs in the first minutes after the membrane cartridge is cleaned, which is related to cake layer formation. Furthermore, the release of nTiO₂ is likely to happen not only during filtration but also during membrane cleaning steps, which could represent the major fraction of nTiO₂ release. To minimize nTiO₂ release during cleaning steps, it is recommended to use ultrafiltration membranes and to recycle the used water, or treat it via *e.g.* evaporation-immobilization.

Future experimental and theoretical work is needed to elucidate key parameters in the transport of nTiO₂ through a polymeric membrane and cake formation, as surprisingly, a reduction of the membrane pore size did not increase the rejection efficiency of the filtration system. This work should focus on identifying nTiO₂-membrane material interactions. In addition, understanding cake structure and composition vs. water matrix is relevant to comprehend the transport of NPs through the cake layer and polymeric membranes. All this information will help to develop appropriate NP removal processes in water systems.

Acknowledgement

Authors are grateful to Fluytec for the grant of the pilot plant during the study. Authors are thankful to Oana Cristina David for her critical reading. We also thank Rory Nolan for English proofreading. This work was funded by the Provincial Government of Bizkaia (6-12-TK-2010-0013).

ACCEPTED MANUSCRIPT

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Figure caption

Figure 1. Schematic representation of the pilot plant for constant flux filtration experiments. CEB= chemically enhanced backwash, AEB = aerated enhanced backwash

Figure 2. n-TiO₂ concentration (µg/L) in the permeate water using PVDF and PES microfiltration membrane using various synthetic waters; a) humic acids, b) sodium bicarbonate c) humic acids+ sodium bicarbonate. Filtration conditions: water volume of 75 mL, 2 bar, 1 g/L nTiO₂ (n=3).

Figure 3. A) SEM micrograph of TiO₂ nanoparticles deposited on a 0.22 µm PVDF membrane at various magnifications: a) 250X, c) 1000X, d) 2500X and e) 5000X. Untreated PVDF membrane structure at 5000X magnification is shown in b. B) SEM micrograph of TiO₂ nanoparticles deposited on a 0.22 µm PES membrane at various magnifications: a) 250X, c) 1000X, d) 2500X and e) 5000X. Untreated PES membrane structure at 5000X magnification is shown in b.

Figure 4. n-TiO₂ concentration (µg/L) in the permeate water using PVDF and PES microfiltration membrane using various natural waters. Filtration conditions: water volume of 75 mL, 2 bar, 1 g/L nTiO₂ (n=3).

Figure 5. n-TiO₂ concentration (µg/L) variation with time in the permeate water between the aerated backwashes. Consecutive 5 min grab samplings were performed using a) PVDF microfiltration and b) PVDF ultrafiltration hollow fiber pilot plant membrane cartridge. Initial nTiO₂ concentration of *ca* 2 mg/L.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Table 1. Operating conditions of filtrations experiments.

Experiment	Type of filtration and pore size	Material	Filtration strategy	Permeate flow	Water type
A	Microfiltration (0.4 μm)	PVD	Dead-end	800 L/h	Tap water
B				1300 L/h	
C			Cross-flow	1000 L/h *	
D	Ultrafiltration (0.03 μm)	F	Dead-end	800 L/h	Tap water + extra 2 mg/L HAS & 100 mg/L NaHCO_3
E				1300 L/h	
F			Cross-flow	1000 L/h *	
G			Dead-end	1300 L/h	

* Retentate flow: 300 L/h

Table 2. n-TiO₂ concentration (µg/L) in the permeate water using various polymeric membrane materials with different pore sizes. Filtration conditions: water volume of 75 mL, 2 bar, 1 g/L n-TiO₂ (n=3).

Polymeric material	Pore diameter (µm)	TiO ₂ concentration (µg/L)	Times concentration > MDL*	Initial water flow (mL/min)
MCE	0.1	1.8	1	56
	0.025	1.6	1	18
PES	0.45	2.4	2	178
	0.22	2.4	3	152
PTFE	0.2	1.7	3	-
	0.1	1.9	2	114
PVDF	0.22	<MDL	0	126
	0.1	2.9	3	96

* MDL (method detection limit) = 1.5 µg/L

Table 3. Pilot plant nanoparticles filtration conditions and results for continuous sampling between membrane backwashes

Membrane characteristics	Flow & filtration strategy	Sampling day	Feed TiO ₂ concentration (mg/L)	Sampling duration (min)	TiO ₂ concentration in permeate water (µg/L)	Retention %
Microfiltration PVDF 0.45 µm	Dead-end 800 L/h	Day 1 Sample 1	1.7±0.4	30	7.0	99.3
		Day 1 Sample 2			24.4	98.6
		Day 2 Sample 3			24.7	98.5
		Day 2 Sample 4			22.9	98.6
	Dead-end 1300 L/h	Day 2 Sample 1	1.9±0.3	30	16.3	99.1
		Day 2 Sample 2			51.5	97.3
		Day 3 Sample 3			59.9	96.8
		Day 3 Sample 4			54.1	97.1
	Cross-flow 1000 L/h	Day 5 Sample 1	1.2	30	32.8	97.3
		Day 5 Sample 2			41.4	96.6
Ultrafiltration PVDF 0.03 µm	Dead-end 800 L/h	Day 3 Sample 1	2.7±0.3	30	360.6	86.6
		Day 3 Sample 2		45	434.5	83.9
		Day 4 Sample 3		30	72.6	97.3
		Day 4		45	64.3	97.6

Sample 4					
Dead-end 1300 L/h	Day 0 Sample 1	1.8	45	40	97.8
	Day 4 Sample 1		45	85.2	95.9
	Day 4 Sample 2	2.1±0.8	30	55.9	97.3
	Day 5 Sample 3		45	108.3	94.8
	Day 5 Sample 1		30	37.0	96.3
	Day 5 Sample 2	1.0±0.1		39.5	96.0
Cross-flow 1000 L/h	Day 5 Sample 3		45	46.4	95.4

Graphical Abstract

Highlights:

- Nano-TiO₂ retention depends strongly on the aqueous media
- The combination of humic acid and bicarbonate highly increased the nano-TiO₂ release
- Nanoparticle rejection was generally above 95% in a filtration pilot plant
- 2.3 g of NPs could be released when treating 31 m³ of tap water with 2 mg/L nTiO₂