Considering energy efficiency in filtration of engineering nanoparticles
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ABSTRACT
Engineering nanoparticles (ENPs) are an integral part of consumer products. Released to the atmosphere or disposed to sewage, ENPs quickly penetrate to surface and ground water sources. An absence of a dedicated ENP-retaining water treatment strategy imposes a potential health threat on drinking water consumers. The threat is met by gearing up an upgrade of treatment systems towards membrane filtration that provides a better barrier to ENP penetration at higher energy costs. The current study compares the energy demand of granular and membrane filtrations, with the retention efficiency of inorganic and organic ENPs. Dedicated experiments with gold and silver nanoparticles, dyed viruses, proteins, polysaccharides, and plasmid DNA showed that the energy demand increases from slow to river bank to rapid sand filtration, and to membrane ultrafiltration (UF). The UF alone consumes on average two times more energy than the entire coagulation–flocculation–sedimentation–sand filtration tray. The differences in retention efficiency however are much less pronounced. The traditional retention tray requires 0.4–0.45 kWh per m$^3$ of effluent (kWh/m$^3$) to provide between 90% and 99% (1 and 2 logs) ENP retention; 1 kWh/m$^3$ on average is needed to secure the retention of 99.9% (3 log) ENPs by UF.

Key words | bacteriophage, energy-efficient filtration process, gold nanoparticle, PES, PVDF

INTRODUCTION
The term engineering nanoparticles, or ENPs, embraces all particles from 1 to 100 nm synthesized intentionally to gain a commercial advantage from unique properties at these dimensions. The properties may lie in engineering, chemical, biological, electronic, optical or other fields. Several examples of commercially available organic ENPs are DNA plasmids (Arkhangelsky et al. 2011), biopolymers such as proteins and polysaccharides (Arkhangelsky et al. 2008), and dyed viruses (Arkhangelsky & Gitis 2008). Well-known inorganic ENPs are carbon nanotubes, composite nanometric catalysts, metals and metal oxides. Several thousand commercial products including personal care products, food storage containers, antimicrobial paints, cleaning supplies, electronic devices, batteries and clothing use ENPs (Reijnders 2006). Unlike natural nanoparticles, ENPs are often extremely reactive and harmful to various forms of life including microorganisms, animals and humans (Frenk et al. 2013).

ENPs enter the environment through several routes. Manufacturing of ENPs can lead to their accidental release into an atmosphere or a receiving water body. An intensive use of fossil fuels in energy production and transportation is a constant source of ENPs in the atmosphere. These volatile ENPs land on surface water or penetrate through soils to aquifers. Routine laundry or the disposal of used ENP-containing products release ENPs directly into sewage. A municipal wastewater treatment plant (WWTP) receives the collected sewage but is unable to treat it. A WWTP treats the entire sewage by a series of physical and biological treatments aimed at reducing the organic and microbiological loads to bearable levels that can be released into the environment. A primary treatment by centrifugation and
Our drinking water contains ENPs. Estimated concentrations of ENPs in water range from 10 μg/L silver and 24.5 μg/L titanium dioxide to dozens of μg/L of modified DNA and viruses (Blaser et al. 2008; Gottschalk et al. 2009). These concentrations will probably increase in the future due to even wider use of ENP-containing products and a continuous development of new ones (Klaine et al. 2008). Potential adverse effects of ENP ingestion with drinking water are yet to be fully discovered. Increased concentrations of inorganic ENPs in liver, kidneys, brain, and blood of rats and mice are reported already (Kim et al. 2008; Park et al. 2010). A parallel study reported DNA damage in mice (Sharma et al. 2012) that led to genotoxicity and genetic mutations in exposed species.

The evaluation of ENP retention by various water treatment processes is far from being complete. Sixty percent of TiO₂ and ZnO metal oxide ENPs were reduced from buffered ultrapure water by alum coagulation and sedimentation (Zhang et al. 2008). More than 99% of SiO₂ nanoparticles were removed by 10 kDa ultrafiltration (UF) membranes (Springer et al. 2015).
These important results however were achieved under sterile laboratory conditions by separate groups of researchers. Here we report the results of long-term strategic research on the attenuation of ENPs of both biological and inorganic origins by typical filtration processes. A physical barrier posed by the filtration is a first line of defense against even wider spread of ENPs in drinking water. Investigated filtration processes included slow sand filtration, river bank filtration, rapid sand filtration and membrane UF. The efficiency of rapid sand filtration was evaluated as a stand-alone process and in a typical tray of coagulation, flocculation, sedimentation and filtration. In a similar approach UF was evaluated with and without coagulation and flocculation stages. The synthesized ENPs included modified viruses, proteins, polysaccharides, plasmid DNA, and gold and silver nanoparticles. All ENPs were prepared in the same laboratory using the same protocols thus making the validity of the comparison unquestionable. The experiments were performed on both laboratory and pilot scales using the same water (Beer-Sheva, Israeli quality).

Filtration efficiency was compared on the basis of energy demand. The energy cost constantly changes and could be a significant component in daily operational expenses (OPEX) of water and WWTPs. A significant part of treatment operations including coagulation, flocculation, sedimentation, and chlorination have very modest energy demands. Filtration however is not a part of the list. Pumps are the main energy-consuming device within a typical filtration operation. The power input of a pump $P$ in the study is determined as the product of feed flow $Q_f$ (m$^3$/h) and applied pressure $Δp$ in bar (Schafer 2001):

$$P = \frac{Q_f \cdot Δp}{η_{pump}}$$

(1)

The calculated power is displayed in kW of electricity per m$^3$ of treated effluent per 1 hour of membrane operation (kWh/m$^3$), and it takes into consideration a 40% $η_{pump}$ overall pump efficiency.

**MATERIALS AND METHODS**

The MS2 (ATCC 15597-B1), phi X174 (ATCC 13706-B1), and T4 (ATCC 11303) bacteriophages and their *Escherichia coli* host cells were purchased from Deutsche Sammlung von Microorganismen und Zellkulturen GmbH (DSMZ, Germany). The viruses were labelled with four different dyes such as rhodamine B (9-(o-carboxyphenyl)-6-(diethylamino)-3H-xanthen-3-ylidene) diethylammonium chloride), fluorescein, FITC (fluorescein-5-isothiocyanate) and 5-DTAF (5-(4,6-dichlorotriazinyl)aminofluorescein). The labelling reaction was performed in the presence of coupling agent DEC (1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride), which was needed for permanent attachment. The mixture was stirred inside a dialysis membrane with MWCO of 6,000 Da to wash out free dye molecules. The membrane dialysis was carried out in distilled water under stirring at 4 °C, until no fluorescence was observed in the rinsing water (approximately 1 week). The purified ENPs were stored at 4 °C in a dark room. Fluorescence measurements were conducted using a TECAN Infinite M200 plate reader equipped with a monochromator. The intensity was reported in the instrument’s Relative Fluorescence Units (RFU). Bovine serum albumin (BSA) and glucose were purchased from Sigma-Aldrich and used as received. A 4.5 kilobase pair (kb) pGEMR and 9.5 kb pHE4-ADR double stranded circular DNA plasmids were synthesized in the laboratory and isolated using a NucleoBond PC 500 isolation kit (Macherey-Nagel, Düren, Germany) (Arkhangelsky et al. 2011).

Monodispersed aquasols of gold ENPs were prepared by reduction of hydrogen tetrachloroaurate with sodium citrate and tannic acid (Turkevich et al. 1951; Slot & Geuze 1985). For instance, 4.0 ml of a 1% solution of trisodium citrate and 5.0 ml of tannic acid were added to 40.0 ml of a 0.01% (w/v) solution of HAuCl$_4$. All chemicals were purchased from Sigma-Aldrich. The mixture was stirred for 5 min under gentle boiling, cooled to room temperature, and stored at 4 °C. The initial gold concentration was 52 mg/L (Arkhangelsky et al. 2012). Monodispersions of silver ENPs were prepared by reduction of silver nitrate with sodium citrate and tannic acid. For instance, 4.0 ml of 1% trisodium citrate, 5.0 ml of tannic acid and 5 ml of 25 mM K$_2$CO$_3$ in 6 ml of deionized water (DIW) were heated up to 60 °C and added to a preheated solution of 1.0 ml of a 1% AgNO$_3$ solution (v/w). The total mixture volume was completed to 100 ml with DIW. The mixture was boiled for 7 min under a gentle stirring. The suspension
was cooled to room temperature and centrifuged for 30 min at 10,000 rpm.

*Slow sand filtration* experiments were performed in a 23 cm long column with an internal diameter of 5.5 cm. The column was wet-packed with uniformly sized quartz sand (Haifa Bay) with a geometric mean diameter of 1.06 mm and a uniformity coefficient of 1.55. The measured filtration porosity $\phi$ was 0.235, and the calculated hydraulic residence time was 25.2 min. Filtration experiments were performed with 0.012, 0.05, 0.085, and 0.12 m/h approach velocities. *River bank filtration* experiments were performed in 10 cm diameter acrylic pipes with a total height of 2.2 m. The influent flowed from a head tank by gravity into downward-sloping pipes that were loosely connected to filtration columns located 2.5 m below the head tank. The filter was filled with 1.6 m exhausted granular activated carbon (GAC, AquaSorb 2000). The GAC had an effective size of 0.8 mm, a uniformity coefficient of 1.7 and a porosity of 0.65. *Rapid sand filtration* experiments were performed inside a 7.6 cm diameter, 80 cm high, transparent Plexiglas filter. The filtration media was Haifa Bay quartz sand with 1.32 mm effective size, 1.55 uniformity coefficient and a porosity of 0.45. The filtration tests were performed at a constant filtration velocity of 10 m/h. *UF experiments* were performed with fresh 30 kDa polyethersulphone (PES-30) and polyvinylidene fluoride (PVDF-30) membranes (Sterlitech Corporation) at 70 L/m²h⁻¹. Filtration was performed in a 150 ml autoclaved stirred cell (magnetic stirring, 400 rpm) equipped with a back-pressure transmembrane pressure (TMP) controller.

**RESULTS AND DISCUSSION**

Figure 2 presents the efficiency of UF membranes in retention of gold ENPs, viruses, proteins, polysaccharides, and plasmid DNA. A typical membrane operation deals with effluent quality vs effluent quantity dilemma. A higher effluent quality is often received at low flux or at low TMP. The low flux/TMP however needs a large membrane surface thus increasing capital expenses (CAPEX). To lower CAPEX, membrane treatment plants are designed to filtrate near the upper limit of the manufacturer’s flux/TMP

![Figure 2](https://iwaponline.com/ws/article-pdf/17/5/1212/409218/ws017051212.pdf)
recommendations. Figure 2 shows that there is an energy price tag attached to that operational decision.

UF membranes are very efficient in virus retention. A 30 kDa UF membrane retains more than 99% T4, MS2 and phi X 174 viruses already at 0.5 bar TMP. The retention slightly decreases with increase in TMP but remains very high. For example, the retention of T4 is 99.98% (LRV of 3.83) at 1 bar TMP and 99.95% (LRV of 3.35) at 5 bars TMP. Comparably high retentions are observed with MS2. Filtration at 1 bar TMP resulted in 99.98% (LRV of 3.82) retention. The 5 bars TMP resulted in 99.8% (LRV of 2.91). A 99.92% (3.15 LRV) retention of phi X 174 at 1 bar and 99.8% (LRV of 2.68) retention at 5 bars TMP are almost identical to the MS2 retention. The energy demand shows an opposite trend. Operation at 1 bar TMP requires 0.18 kWh per m³ of effluent. Five bars TMP require 0.92 kWh/m³, a five times greater difference accompanied by an actual decrease in effluent quality. A similar trend is observed in experiments with pGEMR and pHE4 DNA plasmids. The retention of 99.99% (LRV of 4.9) pGEMR requires only 0.18 kWh/m³. The 99.8% retention was received with application of 0.92 kWh/m³. The trend is obvious. Better retentions are obtained at low fluxes with low energy demands. The operation at high flux/TMP has an hourly energy price tag. An energy-efficient effective retention of ENPs with UF membranes can be executed at 0.2 kWh/m³ or even lower.

Figure 3 depicts the retention of viruses by slow, river bank and rapid sand filtration. All types of granular filtration are plotted on the same axis as a function of approach velocity. MS2 is a classic bacteriophage for a variety of filtration experiments, and its filtration efficiency is well documented.

Slow sand filtration provides more than 80% retention of MS2, and that is the highest efficiency among granular filtration separation processes. Slow sand filtration however is rarely practiced today due to a relatively large footprint. A transition towards more compact river bank filtration decreases the retention efficiency towards 50%. Rapid sand filtration slightly improves the retention efficiency to 60% at 5 and 10 m/h approach velocities. The retention efficiency improves by an average 10% with the addition of coagulation and flocculation stages. Much better retention is obtained in filtration of T4. For the entire flux range the retention is higher than 90%, and there is almost no change with the addition of coagulation and flocculation stages. Sand filtration is very modest in energy demand. The energy is mostly spent on the elevation of the influent above the filter bed, and on the backwash. Slow sand filtration is performed with a 20–30 cm head, and its typical energy demand is below 0.01 kWh/m³. River bank filtration is performed with a 1–2 m head and requires up to 0.1 kWh/m³. Rapid sand filtration is performed with a pressure head up to 4 m and requires up to 0.2 kWh/m³. This allocation includes the energy for a backwash pump. Low and unstable filtrate quality in rapid sand filtration is improved by the addition of coagulation and flocculation stages needed to form bigger and more stable flocs that are better removed by a filter bed. The energy demand for a rapid mixing of coagulant is between 0.2 and 0.4 kWh/m³. An additional operation often associated with rapid sand filtration is the sedimentation needed to settle flocs. The average energy demand
for sedimentation is between $5 \times 10^{-4}$ and $1 \times 10^{-3}$ kWh/m$^3$ (Plappally & Lienhard 2012). Granular sand filtration therefore requires up to 0.2 kWh/m$^3$ for the filtration only or up to 0.5 kWh/m$^3$ for the entire coagulation–flocculation–sedimentation–filtration tray. The energy required for rapid sand filtration is two times lower than the lowest demand for UF membranes. With typical UF fluxes and TMPs the difference increases to three times on average.

Figure 4 displays average energy requirements in rapid sand filtration (left) and UF (right) per treatment stage, and in total. The raw water pumping here considers only pumping from a surface water source (river or lake), not from a groundwater source. The energy demand for the pumping is therefore very modest, between 0.02 and 0.05 kWh/m$^3$, and much lower than the energy required in groundwater pumping (Plappally & Lienhard 2012). Chlorination is the necessary process in any water treatment installation. The energy demand for chlorination is relatively low, just between $2 \times 10^{-5}$ and $2 \times 10^{-3}$ kWh/m$^3$ (Arpke & Hutzler 2006). Except for water recharge practices by Waternet and Dunea in the Netherlands (Gerbens-Leenes 2016), slow sand filtration is not combined with other filtration options and is therefore left out of the figure.

**CONCLUSIONS**

Filtration of ENPs is an energy-demanding operation that results in significant attenuation of ENPs in drinking water. Slow sand filtration, river bank filtration, and rapid sand filtration are operations that can provide between 90% and 99% (one or two logs) efficiency in ENP retention at less than 0.5 kWh/m$^3$. The 99.9% (three logs) ENP retention efficiency provided by UF membranes requires between 0.8 and 1 kWh/m$^3$ energy although it can be effectively performed at less than 0.5 kWh/m$^3$. Filtration is not an absolute barrier against ENPs that will continue to appear in drinking water.

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