

Separation of zinc oxide nanoparticles in water stream by membrane filtration

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ABSTRACT

Zinc oxide (ZnO) nanoparticles are used for the synthesis of various materials. The nanoparticles, when entering into the environment, affect aquatic life. Their antibacterial properties deter the biological treatment process of wastewater treatment plants. The study focuses on the effectiveness of ultrafiltration (UF) membranes for the removal of ZnO nanoparticles. In this study, a commercial membrane was used for the separation of ZnO nanoparticles in the presence of natural organic matter (NOM) and alkalinity. Membrane flux and retention were studied for different concentrations of ZnO (1 mg/L, 10 mg/L, and 100 mg/L). Bare and fouled membranes were studied using a scanning electron microscope (SEM), energy-dispersive X-ray (EDX), and atomic force microscopy (AFM). At higher concentrations (> 10 mg/L), ZnO nanoparticles tend to aggregate and increase in size, resulting in 95 to 98% retention. Further, the presence of NOM and alkalinity enhances particle–particle interactions and thereby promotes nanoparticle aggregation, which shows better retention even at lower concentrations (1–10 mg/L).

Key words | alkalinity, natural organic matter, retention, ultrafiltration, zinc oxide

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INTRODUCTION

Nanoparticles are used in the preparation of a variety of materials due to their extraordinarily large reaction surface, e.g., cosmetics, paints, medicines and drugs, drug delivery systems, super hydrophobic and super hydrophilic surfaces, water treatment applications, electronics, optics, textiles, etc. However, the impact of nanomaterials on living beings is still in the early stage of research. Separate work on the toxicity of these materials on individual species indicates that continuous use of these materials and their discharge into the environment will eventually affect the living population (Angelica *et al.* 2012; Bolis *et al.* 2012; Grimaldi *et al.* 2013). Zinc oxide (ZnO) is one of the toxic nanoparticles tested among silver (Ag), fullerenes and nano copper oxide (nano-CuO), and carbon nanotubes (CNTs), titanium dioxide (TiO₂), and iron oxide (Fe₃O₄) (Kahru & Dobourgier 2010).

ZnO is used for the synthesis of nanocombs, nanorings, nanohelices, nanosprings, nanobelts, nanowires, nanocages, nanosensors, nanocantilevers, sunscreens, cosmetics, coating

applications in optoelectronics, sensors, transducers, and biomedical sciences (Wang 2004; Dange *et al.* 2007). Studies on ZnO nanoparticles in an aquatic environment show that ZnO released into water bodies affects aquatic life, especially if it is in Zn⁺² ions (Bian *et al.* 2011). It reduces the efficiency of the physico-chemical treatment process of coagulation–flocculation in water treatment by providing stability to pollutants (Brar *et al.* 2009; Omar *et al.* 2014). It has antibacterial properties (Huang *et al.* 2008; Li *et al.* 2008) which affect the biological treatment process (Brar *et al.* 2009). Many adverse effects of nanosized ZnO on mammals, plants, phytoplankton, and even human cell lines have been reported (Xia *et al.* 2008; Lin & Xing 2008).

The fate of nanomaterials in natural systems depends on water quality parameters such as pH, ionic strength, and natural organic matter (NOM). As NOM occurs in surface water as complex organic matter at concentrations ranging from 1 mg/L to 100 mg/L (Wall & Choppin 2003), it is important to consider its effect in understanding the fate

of nanomaterials. In most environmental conditions, NOM increases the stability of ZnO nanoparticles in solution by adsorption on the particles resulting in an overall negative charge and double layer repulsion, thereby producing a net energy barrier between the particles. The stabilizing effect of NOM on nanoparticles enhances its mobility and dispersion of already-formed nanoparticle aggregates in natural waters, which increases the toxicity towards aquatic life (Brayner *et al.* 2010; Van Hoecke *et al.* 2011).

As natural water is used as a source of drinking water, this water needs to be free from nanomaterials. Various studies have attempted to understand the removal of nanomaterials from water using different unit processes. Studies on nanoparticles' removal from water includes electro-filtration, chemical and magnetic seeding aggregation, coagulation, and adsorption (Chin *et al.* 2006; Sung *et al.* 2007; Liu *et al.* 2011; Yang *et al.* 2011; Ma *et al.* 2012; Shih *et al.* 2012; Rottman *et al.* 2013). Recently, membrane filtration has been reported for retrieving Ag nanoparticles from wastewater streams (Palencia *et al.* 2014). However, no work has been done on membrane separation of ZnO nanoparticles in water streams. This indicates a knowledge gap, and presents a question to address. The present work studied the effectiveness of the membrane filtration process for the separation of ZnO, and its behavior in the presence of NOM and alkalinity.

MATERIALS AND METHODS

A suspension of ZnO nanoparticles of 5×10^5 mg/L concentration (99% metal base purity) and humic acid were purchased from Sigma Aldrich, India. All other chemicals were of analytical grade and were used as received. Polyethersulfone (PES) membranes (10, 20, 30, 50, and 100 kDa) were obtained from Microdyn-Nadir, Germany.

Different concentrations of ZnO solution (1 mg/L, 10 mg/L, and 100 mg/L) were prepared in double distilled water. The nanoparticles were dispersed for 20 min in an ultrasonicator. Freshly made suspensions were prepared before each experimental run. ZnO completely dissolved around pH 6 and 12 (Dange *et al.* 2007), thus all the experiments were conducted in the pH range of 7 to 11. During the filtration study, after every batch of 60 mL the membrane was washed with distilled water. Real water from the River Yamuna, Delhi and spring

water from Shastradhara, Dehradun were also studied. Membrane flux (L/m^2h) and ZnO retention (%) at different time intervals were determined using stirred ultrafiltration cells (Millipore Amicon, USA). Based on the initial membrane (PES 10 kDa, PES 20 kDa, PES 30 kDa, PES 50 kDa, PES 100 kDa) screening (membrane flux and ZnO retention), P020F (PES 20 kDa) was selected for further studies. The effect of alkalinity (200 mg/L) and NOM (as humic acid, 2 mg/L) on ZnO suspension in water was studied. The concentrations of alkalinity and humic acid were selected based on the composition of natural river water (Zhou & Keller 2010). The results are presented as an average of three independent representations of experiments. Membrane flux and retention were calculated by Equations (1) and (3), respectively, and flux normalized was calculated by Equation (2).

$$\text{Membrane flux (L/m}^2\text{h)} = \frac{\text{(Permeate volume, L)}}{\text{(membrane area, m}^2 \times \text{time, h)}} \quad (1)$$

$$\text{Flux normalized (J/J}_0\text{)} = \frac{\text{Permeate flux (J)}}{\text{Pure water flux (J}_0\text{)}} \quad (2)$$

$$\text{Retention (\%)} = \frac{\{(C_f - C_p) \times 100\}}{C_f} \quad (3)$$

where C_f = Feed ZnO concentration, C_p = Permeate ZnO concentration.

ZnO concentration was measured as Zn^{+2} ions using an atomic absorption spectrophotometer (AAS, Electric Corporation, India), and humic acid concentration was determined using a total organic carbon (TOC) analyzer (Schimadzu TOC-Vcsh, Japan). Alkalinity was studied following *Standard Methods for the Examination of Water and Wastewater* (APHA 2005). Particle size analysis was done using dynamic light scattering (DLS) (Nicomp PSS 380ZLS, USA). Scanning electron microscope (SEM) analysis of the membranes was done by freeze fracturing in liquid N_2 and sputtered with gold (Au) (ZEISS EVO 50, Germany). Energy-dispersive X-ray (EDX) for ZnO deposits of the membrane surface was analyzed with a Bruker-AXS energy dispersive X-ray system (Model QuanTax 200). Membrane surface morphology was studied by atomic force microscopy (AFM) (Bruker Icon Dimension Asyst, India).

The contact angle of the membranes was measured using the sessile drop technique by goniometer (KRÜSS ZSO 100, Germany). The porosity and the pore size of the membranes were determined by the gravimetric method and by the filtration velocity method, respectively (Basri *et al.* 2011).

RESULTS AND DISCUSSION

Membrane characteristics

The porosity and pore size of the membrane were found to be 18% and 0.028 μm , respectively. The contact angle of the membrane was $80.6^\circ \pm 0.6^\circ$. Thus, the membrane is an ultrafilter and hydrophilic. The SEM image of the membrane indicates an asymmetric structure, with a separation layer on top of the support layer (Figure 1).

Membrane filtration of ZnO

Figure 2(a) shows the normalized flux for different concentrations of ZnO (1, 10, and 100 mg/L) at varied time intervals up to 15 h. The flux steadily decreased at all three ZnO concentrations. The flux decreased with increasing ZnO concentrations from 1 mg/L to 10 mg/L and further to 100 mg/L. Such a steady decrease in the flux with time indicates retention of ZnO nanoparticles and fouling of the membranes. The flux reduction is greater for

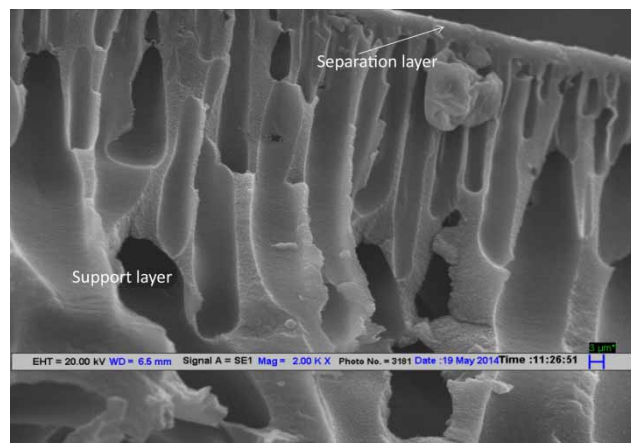


Figure 1 | SEM image of the PES membrane.

higher concentrations of ZnO (100 mg/L). This indicates an increased concentration polarization of the membrane. Figure 2(b) shows the retention of ZnO at different time intervals. As expected, ZnO retention increased with increased concentration, and more than 95% retention was obtained at 10 mg/L and 98% at 100 mg/L. However, only 25% ZnO reduction was obtained at 1 mg ZnO/L. Thus, lower ZnO retention and higher flux at 1 mg/L, compared to 10 mg ZnO/L and 100 mg ZnO/L indicates that the nanoparticles tend to aggregate with increasing concentrations. As a result, these discrete particles in suspension start aggregating into a larger size and offer greater resistance to the movement of water through the membrane. With subsequent filtration, this results in membrane fouling and cake layer formation. A similar observation was noted with Ag nanoparticles' separation through ultrafiltration (Palencia *et al.* 2014).

The point of zero charge (pH_{PZC}) for ZnO nanoparticles is pH 9.3, where ZnO aggregation is at a maximum. Above pH 9.3, ZnO nanoparticles partially aggregate with net negative charge, and below pH 9.3, ZnO nanoparticles partially aggregate with net positive charge (Omar *et al.* 2014). The present study was carried out at pH 7.5, which indicates partial aggregation with net positive charge. Further, the particle size increased from 100 nm during the 15 h filtration study to 185 and 664 nm (e.g., for 100 mg ZnO/L), which are larger particle sizes than the pore size of the membrane. This resulted in size exclusion of the ZnO nanoparticles.

The SEM of the bare and fouled membranes shows the deposition of ZnO as a cake layer on the membrane surface during filtration (Figure 3). It is evident that the cake layer is predominant at higher concentrations of ZnO solutions (10 mg/L to 100 mg/L) than at a lower concentration (1 mg/L). The initial smooth surface of the membrane gets replaced by ZnO flakes (Figure 3). The retention of ZnO on the membrane surface was further confirmed by EDX analysis, where Zn was found in the fouled membranes (Figures 4(c)–4(d)) and not in the bare membrane (Figure 4(a)).

AFM images of the bare membrane and fouled membranes show differences in the surface topography of the membranes (Figure 5). The fouled membranes show an increase in height in comparison to the bare membrane. The surface topography of the fouled membranes increases

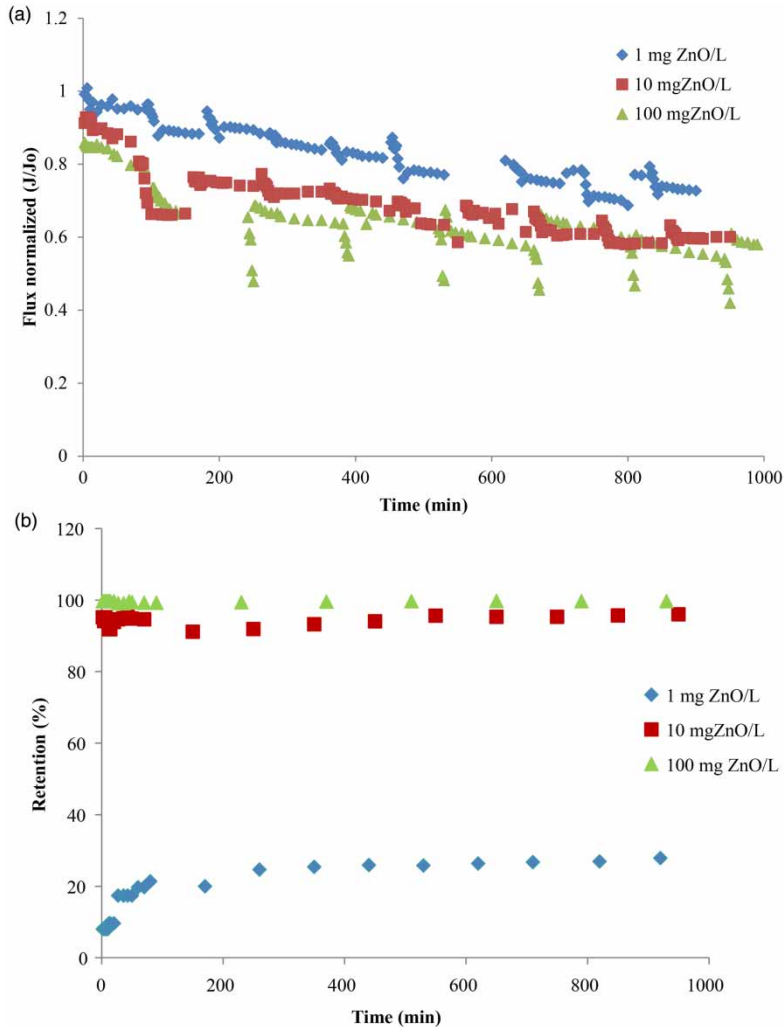


Figure 2 | Flux normalized (J/J_0) (a) and ZnO retention (b) vs time of different concentrations of ZnO (1 mg/L, 10 mg/L, 100 mg/L) at 28 ± 2 °C and pH 7.5.

with increased concentration of ZnO in the solution from 1 mg/L to 100 mg/L. The results obtained in AFM are in accordance with SEM images in Figure 3.

Membrane filtration of ZnO in the presence of NOM and alkalinity

The effect of NOM and alkalinity in membrane filtration of ZnO was studied (Figure 6). Different solutions of ZnO (1, 10, 100 mg/L) with NOM (2 mg/L), and ZnO (1, 10, 100 mg/L) with NOM (2 mg/L) and alkalinity (200 mg/L) were prepared and passed through the membrane. Figure 6(a) with NOM shows that membrane flux decreases with time;

similarly, the presence of NOM and alkalinity in the solution reduces the flux (Figure 6(b)). It is interesting to note that at concentrations of 1 mg/L and 10 mg/L, the change in flux is not much different between the solution with NOM and with NOM and alkalinity. In both the experiments it varies from 0.8 to 0.6. However, at higher concentrations (100 mg/L), the flux reduction is much higher in a solution with NOM and alkalinity compared to a solution with NOM. It indicates that at higher concentrations of ZnO, the nanoparticles destabilize in the presence of alkalinity, where the pH of the solution increases to 9 (pH_{pzc} 9.3). Figures 6(c) and 6(d) show complete ZnO retention for 10 mg/L and 100 mg/L, while the

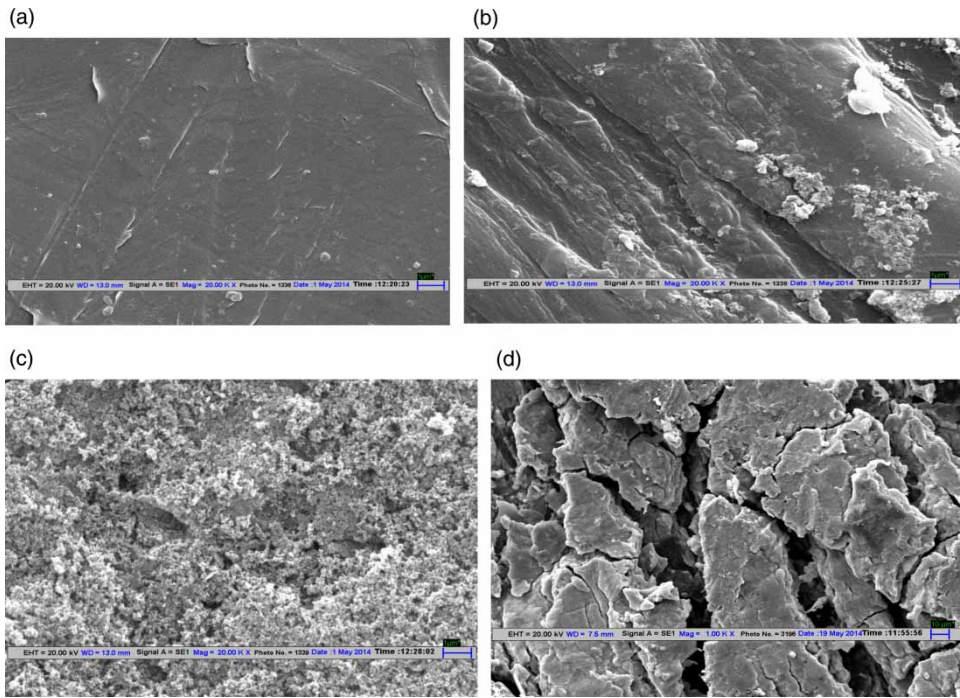


Figure 3 | SEM images of membrane top surface (a), bare membranes and fouled membrane (b) 1 mg ZnO/L, (c) 10 mg ZnO/L, and (d) 100 mg ZnO/L.

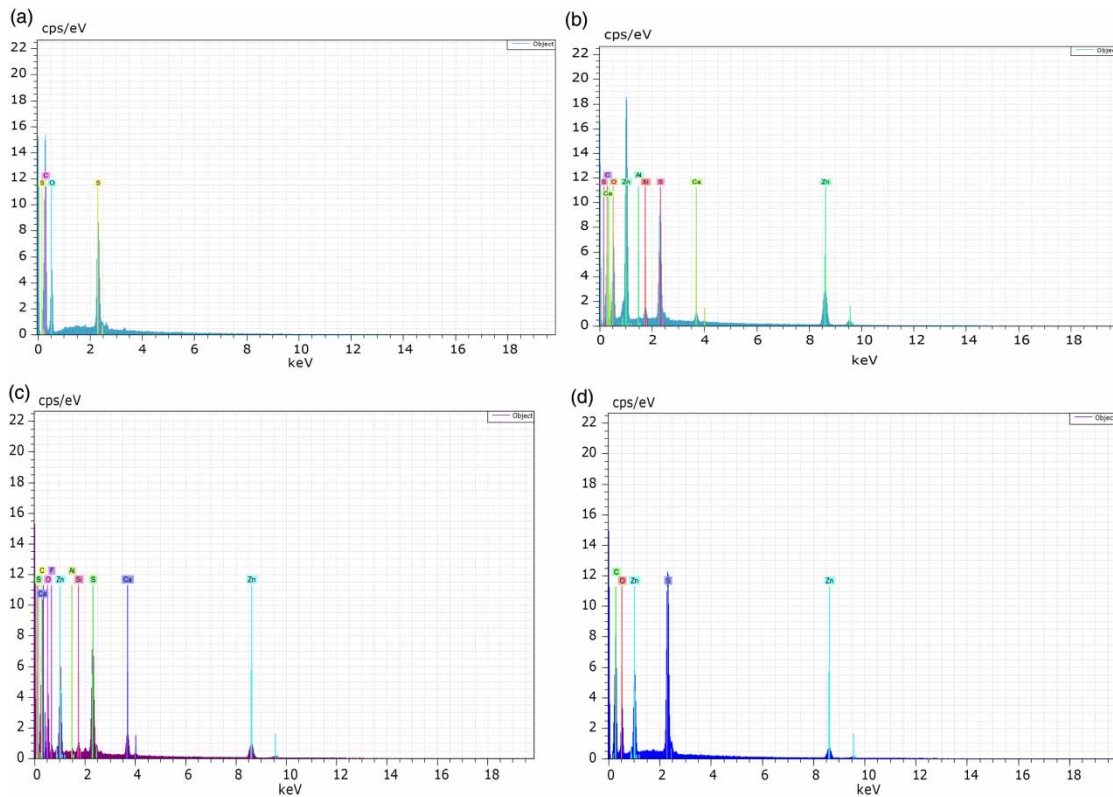


Figure 4 | EDX analysis of ZnO on (a) bare membrane, and fouled membrane (b) 1 mg ZnO/L, (c) 10 mg ZnO/L, and (d) 100 mg ZnO/L.

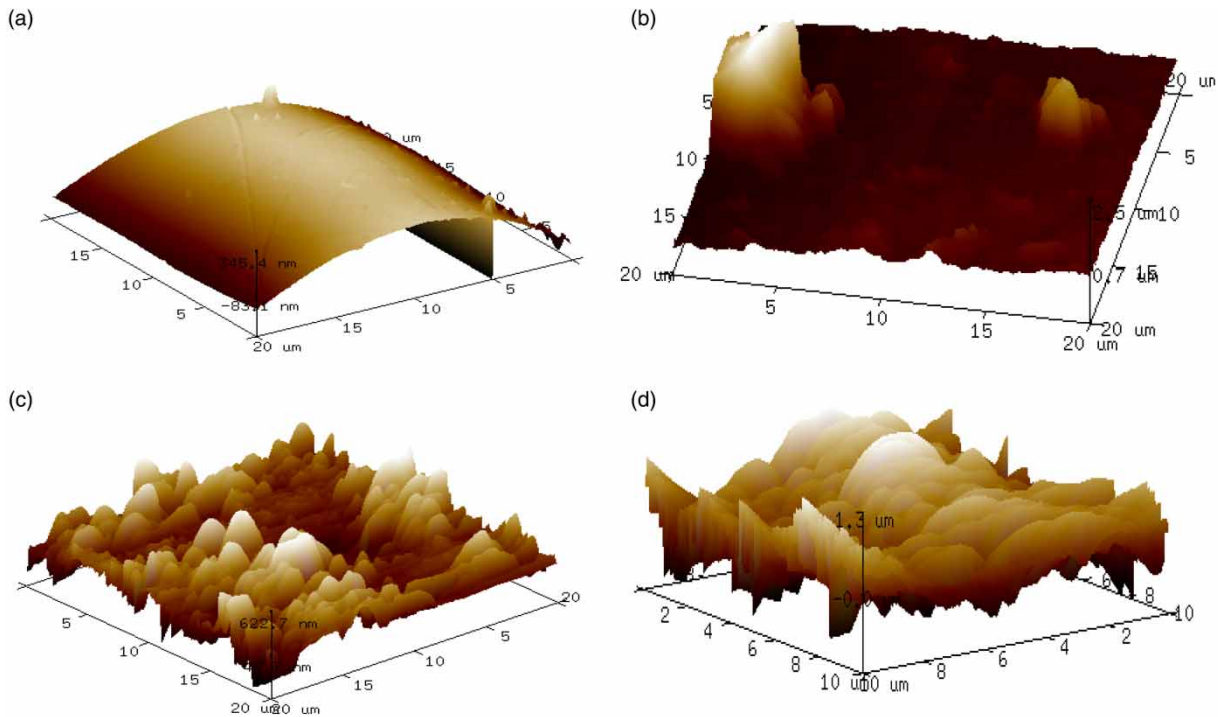


Figure 5 | AFM images of bare membrane (a) and fouled membranes at ZnO concentrations of (b) 1 mg/L, (c) 10 mg/L, and (d) 100 mg/L.

retention increases in 1 mg/L from 25% (Figure 2(b)) to 80%. This indicates that NOM and alkalinity destabilizes the colloidal ZnO nanoparticles, resulting in agglomeration. Such agglomeration, in turn, improves membrane retention.

Studies show that adsorption of NOM onto the oxide nanoparticles' surface occurs according to three mechanisms: first, the high surface area of nanoparticles provides NOM with a large adsorption area (Gu *et al.* 1994; Kang & Xing 2008); second, access of NOM molecules to sites that have low hydrophilicity and low negative charge on the particle surface (Yang *et al.* 2009); third, NOM adsorption onto oxide nanoparticles due to the electrostatic interaction and ligand exchange reactions (Gu *et al.* 1994). The interaction between NOM and ZnO nanoparticles has been found to be the third mechanism (Yang *et al.* 2009). Thus, when the pH of the solution is near to its point of zero charge, the nanoparticles are in the aggregation zone (Omar *et al.* 2014) and NOM acts as a bridge between the ZnO–ZnO nanoparticles, resulting in increased particle size.

In the present study, real water collected from a river (Yamuna River water, Delhi) and spring (Sahastradhara, Dehradun) spiked with 10 ppm ZnO were studied to

understand the effect of NOM and alkalinity, and other dissolved ions on membrane filtration (Supplementary information, available with the online version of this paper). The characteristics of the water are different from each other as the geology of the area is different. The spring water originates in a limestone terrain and the river water flows through a sandstone terrain; furthermore, the river water is contaminated as it flows through the city. A real water filtration study shows little difference to that of synthetic water. However, long-term filtration is necessary to establish the fouling tendency of the membranes with real water.

CONCLUSION

The efficiency of membrane filtration for the retention of ZnO nanoparticles in the presence of NOM and alkalinity was studied. At concentrations greater than 10 mg ZnO/L the nanoparticles tend to aggregate and grow larger than the pore size of the UF membranes. Further, in the presence of NOM and alkalinity, the discrete ZnO nanoparticles aggregate with NOM acting as a bridge between the

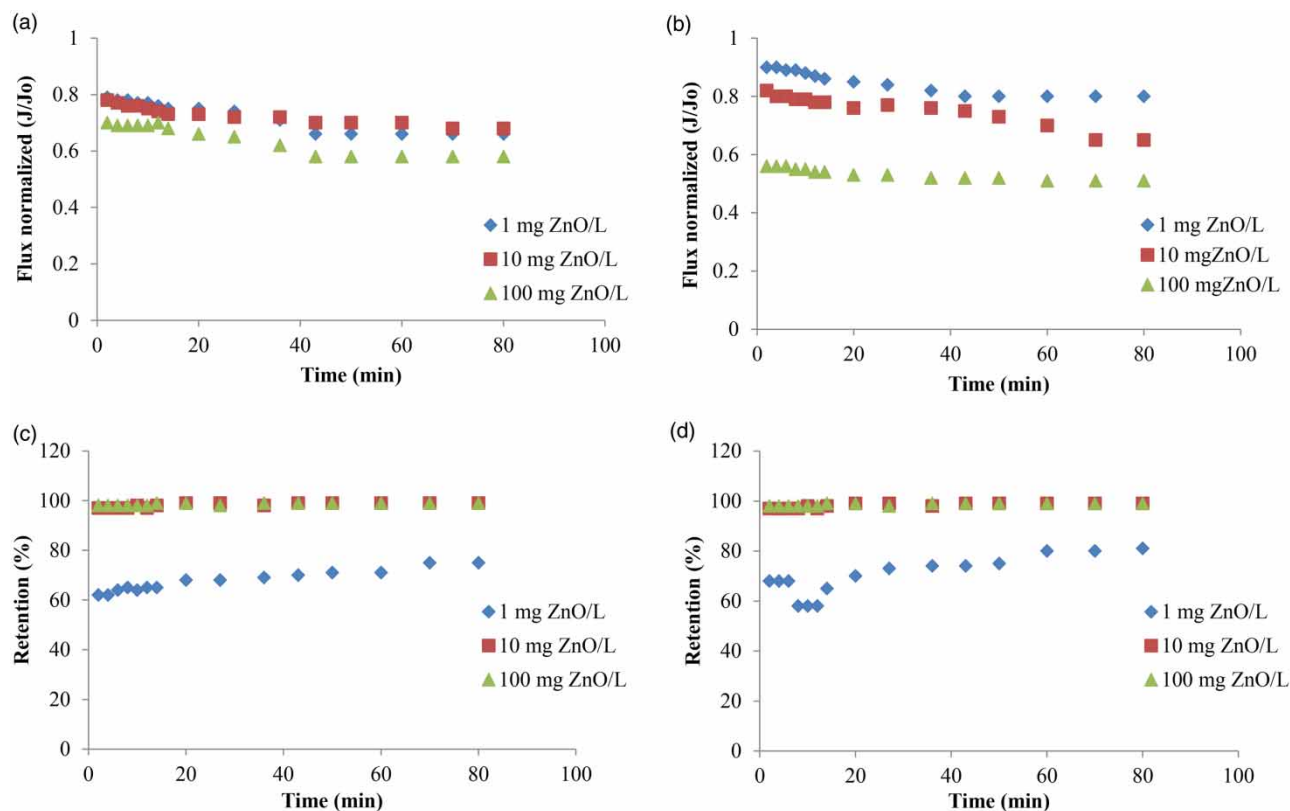


Figure 6 | Membrane flux in the presence of (a) NOM (2 mg/L) and (b) NOM (2 mg/L) + alkalinity (200 mg/L). ZnO retention in the presence of (c) NOM (2 mg/L) and (d) NOM (2 mg/L) + alkalinity (200 mg/L).

ZnO–ZnO particles even at lower concentrations (1 mg/L to 10 mg/L). The study indicates that ZnO nanoparticles can be removed by the membrane filtration process, and this process can be considered as a polishing step during wastewater treatment and as a pre-treatment step during water purification for drinking water. The waste stream containing concentrated ZnO nanoparticles in the water filtration process could be studied to reuse for further applications, e.g., as a photocatalyst in wastewater treatment, paints, and electronic devices.

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