

## **Self-cleaning Ceramic Membranes for the Removal of Natural and Synthetic Nanomaterials from Drinking Water Using Hybrid Ozonation-Nanofiltration**

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**Jeonghwan Kim<sup>1,2</sup>, Alla L. Alpatova<sup>1</sup>, Lindsay M. Wright<sup>2</sup>, Thomas L. Deits<sup>3</sup>  
Simon H. R. Davies<sup>1</sup>, Melissa J. Baumann<sup>2</sup>, Volodymyr V. Tarabara<sup>1</sup>, Susan J. Masten<sup>1,4</sup>**

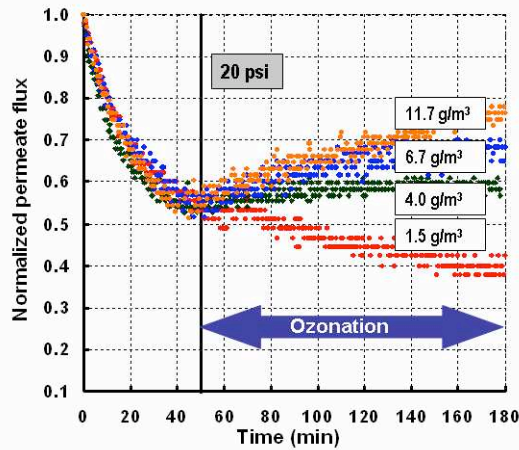
<sup>1</sup>Department of Civil and Environmental Engineering, Michigan State University, East Lansing, MI 48824, USA; <sup>2</sup>Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, USA; <sup>3</sup>Science Department, Lansing Community College, Lansing, MI 48823, USA; <sup>4</sup>Department of Civil Engineering, McMaster University, Hamilton, ON L8S4L7, Canada

### **Motivation and Objectives**

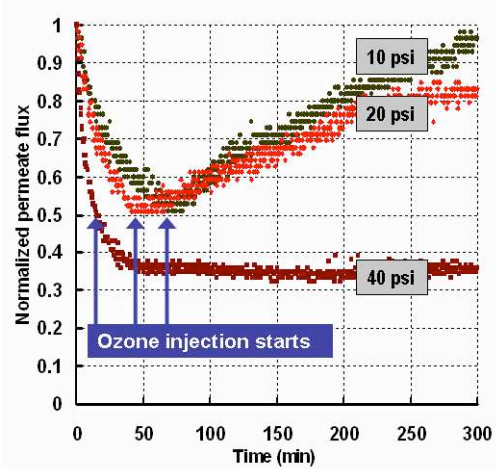
The trademark of the science of the 21<sup>st</sup> century is environmental awareness that dictates a proactive approach to ensuring that novel technologies fit well within the framework of ecologically sustainable development. The recent explosion in nanotechnology research has resulted in the synthesis of a range of novel materials often possessing unique properties that have yet to be fully understood. As environmental scientists, we are asking and looking for answers to the following questions: What will happen when nanomaterials enter our environment? What are their transport pathways and fate in the environment? Should they and how can they be removed from the environment? Which treatment systems are most effective to remove nanomaterials from air and water? The aim of this project is to build a base of fundamental knowledge pertaining to the hybrid ozonation filtration process and to apply this new knowledge to develop an effective water treatment system targeting the removal of nanoparticles from water. Novel high performance membranes, an integral component of the O<sub>3</sub>-NF system, featuring reduced permeability and improved catalytic properties are also being developed [1].

### **Research Activities and Findings**

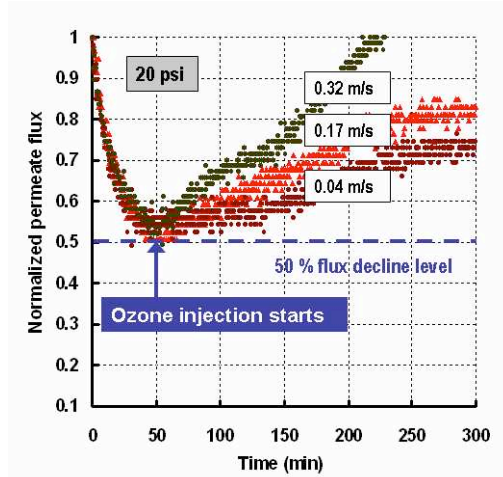
Combined effect of ozonation and hydrodynamic conditions on the permeate flux in the hybrid ozonation-filtration system. Bench-scale, hybrid ozonation/high-pressure membrane filtration apparatus was installed to investigate the effect of ozonation on membrane fouling at Michigan State University. A key feature of the installation is the design and operation of relatively high-pressure membrane filtration system combined with ozonation process. The effects of ozone concentration and hydrodynamic conditions on the permeate flux in a hybrid ozonation-ceramic membrane filtration system treating prefiltered (0.45 μm) natural water (Lake Lansing, MI) were investigated. In one set of experiments, continuous ozonation was initiated after 50% of flux decline was observed. The extent of the permeate flux recovery upon the application of ozone was found to depend on the ozone dosage, transmembrane pressure, and crossflow velocity. Higher recoveries were achieved at greater ozone concentrations, lower transmembrane pressures and higher crossflow velocities (Figures 1-3) [3]. When ozone was continuously applied during the entire fouling experiment, higher permeate fluxes were observed. The difference in the behavior observed in the two sets of experiments suggest that the permeate flux recovery is affected by the accessibility of the oxidants generated at the membrane surface to the materials fouling the surface.



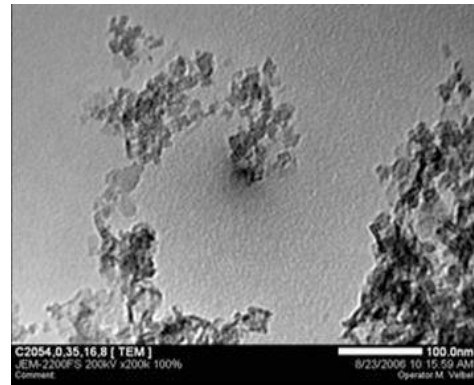
**Figure 1.** Effect of ozone concentration on permeate flux recovery



**Figure 2.** Effect of transmembrane pressure on permeate flux recovery



**Figure 3.** Effect of crossflow velocity on permeate flux recovery

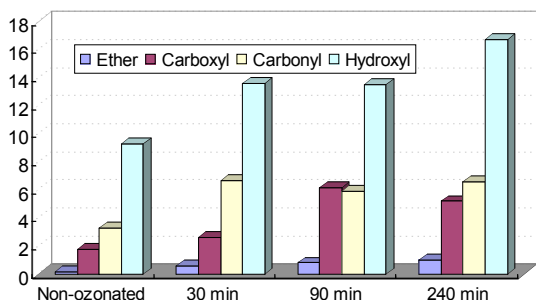


**Figure 4.** Synthesized MnO<sub>2</sub> nanoparticles

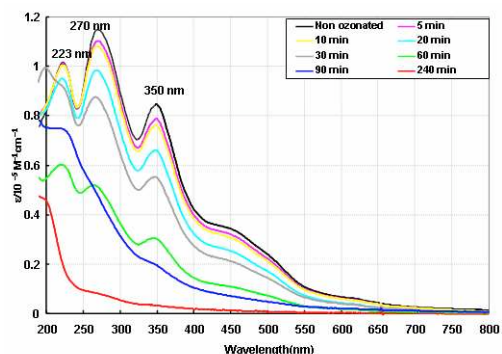
Development of novel ceramic nanofiltration membranes. We have developed a new procedure for the preparation of nanosized Mn oxide particles of near spherical shape using ozone to rapidly oxidize Mn(II) (Fig. 4). Nanoparticulate MnO<sub>2</sub> was selected due to its higher catalytic oxidation capacity with respect to organic matter. We are completing the characterization of the synthesized particles. Work on coating the membrane with the Mn oxide particles is in progress.

Effects of ozonation on physicochemical properties of aqueous colloidal fullerenes. This sub-project focuses on aqueous colloidal fullerenes  $nC_{60}$  as species representative of manufactured nanomaterials with demonstrated cyto- and genotoxicity [2] and a potential of entering water supply. During the first year, physicochemical properties of ozonated  $nC_{60}$  were investigated and compared against properties of non-ozonated  $nC_{60}$ . X-ray photoelectron spectroscopy study revealed that ozonation resulted in significant hydroxylation of  $nC_{60}$  surface

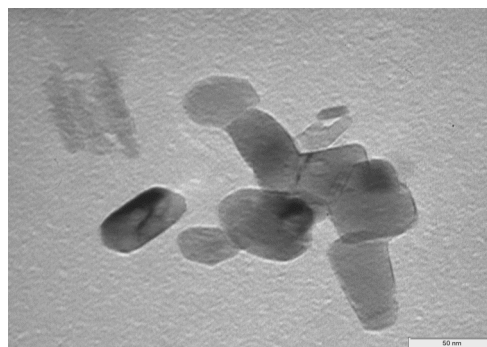
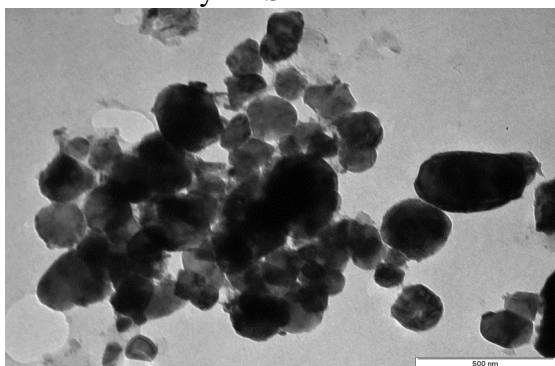
(Fig. 5). The intensity of the peaks at 233 nm, 270 nm, and 350 nm in the UV-vis absorption spectra (Fig. 6) gradually decreased to zero with an increase in the ozonation time. TEM has been used to study the size and morphology of the fullerene clusters.  $nC_{60}$  clusters dispersed in water typically have a size of 20 nm to 400 nm (see Figure 7). After ozonation there is a significant change in the size and morphology of the  $nC_{60}$  particles. As shown in Figure 7 (right), the size of most particles after ozonation is typically less than 50 nm. It can also be seen that  $nC_{60}$  clusters appear that have a rod-like morphology. Studies are also being conducted to measure the decrease in fullerene concentration after ozonation.



**Figure 5.** Percentage of functional groups on the surface of  $nC_{60}$  colloids as a function of ozonation time as estimated by XPS results



**Figure 6.** UV-vis absorption spectra of  $nC_{60}$  suspensions as a function of ozonation time



**Figure 7.** TEM images of  $aqu/nC_{60}$  (produced by extended mixing in water) as prepared (left) and after 45 minutes of ozonation (right)

Results of the present study demonstrated that new type of aqueous colloidal fullerene species were generated by ozonating precursor  $nC_{60}$  suspensions and that colloidal fullerenes can be eliminated from water by prolonged ozonation.

#### References

- [1] For further information about this project link to <http://www.egr.msu.edu/~kimjeo21/> or email Susan Masten [masten@egr.msu.edu](mailto:masten@egr.msu.edu), Simon, Davies [davies@egr.msu.edu](mailto:davies@egr.msu.edu), Melissa Baumann [mbaumann@egr.msu.edu](mailto:mbaumann@egr.msu.edu), Volodymyr Tarabara [tarabara@egr.msu.edu](mailto:tarabara@egr.msu.edu).
- [2] A. Dhawan, J. S. Taurozzi, A. K. Pandey, W. Shan, S. M. Miller and S. A. Hashsham, V. V. Tarabara. Stable Colloidal Dispersions of  $C_{60}$  Fullerenes in Water: Evidence for Genotoxicity, with, *Environ. Sci. Technol.* Research ASAP article, DOI: 10.1021/es0609708. Published on web 10/26/06.

[3] J. Kim, A. L. Alpatova, L. M. Wright, M. J. Baumann, S. H. R. Davies, V. V. Tarabara, S. J. Masten. Combined effect of ozonation and hydrodynamic conditions on the permeate flux in the hybrid ozonation-ultrafiltration process. Submitted to *ACS Spring Meeting*, Chicago, IL, March 25-29, 2007.