RAPID Sponsors Sustainable Pulp and Paper Research

Manufacturing paper products requires vast quantities of water to produce cellulose pulp from trees. Once the water exits the process, it must be purified for reuse — conventionally, this wastewater is separated from contaminants using steam-fed evaporators.

However, evaporation requires a great deal of energy, and with its enormous paper industry, the U.S. uses about 0.2 quads, *i.e.*, a quadrillion BTUs of energy per year for pulp wastewater recycling. As the world's second largest producer of paper and paperboard, U.S. paper mills house some of the world's most energy-intensive chemical processes.

Globally, the pulp and paper industry is one of the top energy consumers in the industrial sector, accounting for about 6% of total industrial energy consumption.

To reduce this energy load, chemical engineers at the Georgia Institute of Technology, with the support of the Rapid Advancement in Process Intensification Deployment (RAPID) Institute, have developed a novel graphene oxide (GO) membrane that efficiently recycles wastewater from the pulp and paper industry. This work is representative of RAPID's ongoing mission to boost productivity and energy efficiency in manufacturing processes, chiefly by advancing modular chemical process intensification (MCPI) technologies.

Pulping wastewater, known as weak black liquor in the industry, contains organic components such as lignin and hemicellulose, as well as inorganic components. Evaporators remove water from the black liquor, which concentrates the waste stream for easier recovery of chemicals.

Membranes are also capable of separating water from the other components of black liquor. A water-selective membrane, for example, can reduce the energy needed to purify black liquor by removing about 50% of water prior to evaporation.

"The barrier to using membranes for black liquor concentration has been the lack of membranes that are both stable and functional in the harsh chemical composition of black liquor," says Sankar Nair, a chemical engineer at Georgia Tech. "Over the last few years, we have developed a class of nanofiltration membranes that are based on GO, which we found to be chemically and mechanically robust in black liquor conditions." The GO membranes are able to separate water from the large organic compounds present in black liquor, including lignin.

To create the membrane, the chemical engineers began with graphite, a low-cost raw material. They introduced oxygen atoms into the graphite structure, creating GO in the form of stacked, ultra-thin sheets.

In a water-based solvent, they then dispersed the GO and coated them onto polymer layers. Once the solvent was removed through vacuum or evaporation, the GO sheets and polymer self-assembled into a flexible membrane.

In 2017, the Georgia Tech team demonstrated that the GO membranes were chemically stable in black liquor, and that they were able to block dissolved chemicals in black liquor while allowing water to permeate. Next, they manufactured the GO membrane at a larger scale, and discovered that removing some oxygen atoms from the membrane under high pressure made the membrane more stable.

However, while the membrane effectively passed water and blocked lignin, other organic and inorganic materials remained in the purified product. Recently, the team found that inserting conjugated polyaromatic molecules between the GO sheets creates stable membranes that are better at blocking organic and inorganic chemicals. The pore structure can now be tuned to allow researchers to choose which compounds can permeate the membrane.

"With the capability of GO membranes to separate black liquor components in a tunable manner, we can design membrane-based processes that can function under harsh conditions to concentrate the black liquor, recycle water, and also recover streams rich in small organic molecules that can be used as renewable feedstocks for production of biofuels or biobased chemicals," says Nair. "These processes could be retrofitted into a mill in a way that minimizes impacts on the operation of the downstream processes. Thus, pulp and paper mills could become more energy efficient in their core papermaking processes as well as generate possible new revenue streams."

In their next steps, the Georgia Tech team will continue to work closely with RAPID. They have already completed preliminary scaleup of the GO membranes, and are working on extended pilot testing. In addition, the chemical engineers are considering further applications for their GO membranes in biorefineries and other industrial environments.

Wang, Z., *et al.*, "Graphene Oxide Nanofiltration Membranes for Desalination Under Realistic Conditions," *Nature Sustainability*, doi: 10.1038/s41893-020-00674-3 (Jan. 18, 2021).

Update continues on next page