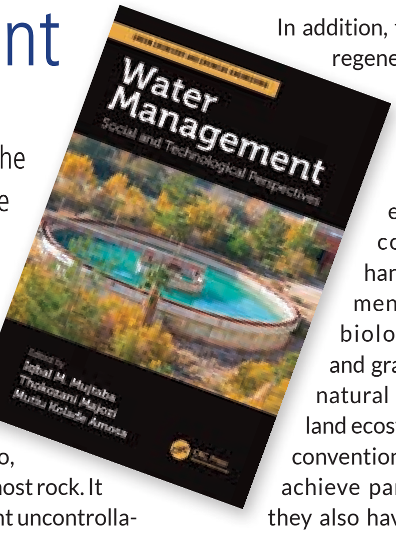
# **Mixed matrix membranes:** Promising materials for AMD treatment

By Michael O Daramola

Water is connected to almost everything on earth. In South Africa, the words 'mining' and 'water' lead one to think about acid mine drainage (AMD). This month we feature an opinion piece by Professor Michael Daramola on membrane technology to treat AMD. The views expressed in this article are his own, informed by experience, literature review and other expert opinion pieces.




A major sanitation and water pollution challenge associated with the mining industry is acid mine drainage (AMD), which forms when sulphide rocks are exposed to air and water for prolonged periods. The formation of acid mine drainage is a natural process, but reactions are caused by exposing sulphide-containing rocks to the environment through mining operations and are often catalysed by bacterial activity. The natural process of AMD formation takes close to 15 years in the absence of bacteria, for ferric iron to produce acid, but the presence of bacteria shortens this reaction time.

Typical characteristics of AMD are very low pH and high concentrations of metals and sulphates. If left untreated, AMD has the significant negative environmental impact of mineralisation of affected areas and acidification of receiving ground and surface waters. The solubility of transition metals is greater in low pH media, hence AMD carries with it high concentrations of metals such as Al, As, and Mg and other transition metals such as Cu, Zn, Pb, Co, Mn and Cd, depending on the host rock. It enters the aquatic environment uncontrollably, posing a threat to humans, domesticated animals and the ecosystem.

## Conventional treatment processes: active and passive treatment

Active treatment involves neutralising the acidity with alkaline substances such as lime to trigger precipitation of metal hydroxide, which is easily be removed by sedimentation. Furthermore, ion exchange technology – which explores the advantage of oppositely charged pollutants and employs solid resins to remove cations and anions from solutions – has also been proposed as a treatment method. A high metal ion uptake capability of this resin makes ion exchange an attractive technology, but it is a preferred technology for low metal ion concentrations and becomes very expensive when dealing with high concentrations of metal ions in solutions.

In addition, the resins need to be regenerated when exhausted by chemicals and this regeneration can produce secondary pollution and elevate operational costs. On the other hand, the passive treatment of AMD relies on biological, geochemical and gravitation processes in natural or constructed wetland ecosystems. Furthermore, conventional methods can only achieve partial treatment, and they also have the disadvantages of producing sludge, requiring high-energy consumption and frequent maintenance.

Therefore, growing global demand for clean water and increasing environmental concerns, warrant the need to search for more sustainable and environmentally friendly technologies for metal ion removal from mining wastewater. There is a great need for water recycling and efficiency of water recycling will depend strongly, amongst other factors, on the performance of existing water treatment techniques and processes to provide potable and clean water for the use of the human race without posing environmental hazards.

Potable water coupled with good sanitation should be affordable by all, which is the sixth of the sustainable development goals (SDG): Clean water and sanitation for all.

## Membrane technology

In the search for alternative technologies, membrane technology has proven to be a promising option. Membrane technology, due to its easy operation, inexpensiveness, high separation efficiency and low energy consumption, has emerged as a promising substitute to conventional methods for AMD treatment.

A membrane is a thin layer of semi-permeable material that separates substances when a driving force is applied across it in a selective manner. Mechanical strength, thermal stability and chemical resistance of a membrane form part of the significant characteristics that define a good membrane and they are highly dependent on the properties of the materials of construction.

Most common pressure-driven membrane processes, which are distinguished by pore sizes, are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). But pure polymer membranes have poor chemical resistance, poor mechanical strength and poor thermal stability when compared to inorganic membranes.

*In the search for alternative technologies for AMD water treatment, membrane-based technology has proven to be a promising option.*

In terms of chemical resistance, mechanical property and thermal stability, zeolite-based membranes (inorganic) display better performance when compared to polymeric membranes, but the cost of the ceramic supports employed in fabricating zeolite-based membranes is very high, contributing to very high overall costs of zeolite-based membranes. In addition, they are very fragile and brittle, making handling during module assembly difficult.

In addition, technology for fabricating commercial zeolite membranes is still at the developmental stage, while technology for commercial production of polymeric membranes is mature, with their applications in a series of industrial processes. To overcome these shortcomings of zeolite membranes, mixed matrix membranes have been proposed.

Mixed matrix membranes (MMMs) are composite membranes containing inorganic fillers (eg, zeolite crystals/nano materials) within the matrix of polymer membranes. Mixed matrix membranes consist of inorganic fillers fabricated within a polymeric matrix and aim to take great advantage of the processability, durability, permeability and selectivity of polymers by offering the advantage of a unique surface chemistry and good mechanical properties.

The presence of crystals within the polymer chains improves separation performance, mechanical strength and thermal stability of polymeric membranes. However, chemical structure of the inorganic fillers, type of inorganic fillers and surface chemistry are mitigating factors to obtaining high quality MMMs. Examples of these membranes, which have been synthesised and tested for the treatment of AMD, are chitosan-infused and sodalite-infused polymer membranes.

Chitosan-based membranes are preferred as membrane materials for the removal of metal ions from solutions due to the ease of separation after processing, high adsorption capacity, faster kinetics, better reusability and biodegradability after use. In addition, the presence of functionalities such as amine ($-NH_2$) and hydroxyl (-OH) in the chitosan molecules, provides a basis for interaction with other materials, thereby making it a promising material for AMD treatment.

Polyvinyl alcohol (PVA)/chitosan composite membranes have been examined for the removal of cobalt ions ($Co^{2+}$) from radioactive wastewater. In comparison with other adsorbents, the PVA/ chitosan (magnetic) composite beads used in the membrane resulted in its very high adsorption capacity.

In the same vein, performance of microporous chitosan/polyethylene glycol mixed matrix membrane during adsorptive removal of iron and manganese from wastewater has been reported. According to the authors, the membranes displayed very good performance for the removal of iron and manganese ions from the wastewater sample tested and they are re-usable.

Recently, a report on the synthesis and performance evaluation of hydroxy sodalite/ polyether sulfone (HS/PES) mixed matrix membrane for acid mine drainage (AMD) treatment was published by Daramola and his co-workers from Wits University. The authors investigated the use of HS crystals as a filler in PES to fabricate HS/PES membranes, which were tested by the treatment of real AMD. The membrane displayed very good selectivity to lead ions ($Pb^{2+}$, about 60%). In addition, the authors demonstrated, based on experimental results, that loading HS crystals within the PES polymer matrix enhanced the performance (selectivity and flux) of pure PES membranes.

In addition, the authors observed, based on the characterisation of the synthesised HS/PES membrane that the fractional free volume within the PES polymer matrix decreased with an increase in HS loading. As far as could be ascertained, this was the first open report on the application of HS-infused polymer mixed matrix membrane for AMD treatment.

Despite vast research efforts in the development of membrane materials, especially mixed matrix membranes, for water and wastewater treatment, the expected progress in the field is hampered by some challenges mitigating the quick development of these membranes for industrial applications. Two commonly known difficulties associated with membrane operation are concentration polarisation and fouling.

Membrane fouling is a more serious concern than concentration polarisation but both need to be prevented in membrane system operations. During a membrane separation process, a natural consequence of semi-permeability and selectivity of a membrane results in accumulation of rejected solutes or particles on the membrane surface. This process, which is reversible, is called concentration polarisation.

Another challenge in the development of mixed matrix membranes (eg, HS/PES membranes) for mining wastewater treatment, is the low membrane flux and membrane reproducibility. Development of dependable and proven robust synthesis techniques for the fabrication of reproducible membranes with high selectivity to metal ions from mining wastewater (eg, AMD), is essential for commercialising mixed matrix membranes for industrial application. In addition, developing ultra-thin membrane (about 1.0 µm in thickness) could enhance the membrane flux without compromising the selectivity.

For industrial application, a tubular configuration is preferred to the flat-sheet configuration, and enhancement of the surface area-to-volume ratio of the tubular configuration could be instrumental in enhancing the performance and throughput of these membranes in industry.

Instead of casting the membrane precursor solution into flat-sheet membranes (as is commonly done), the precursor solution could be made into fibres using an electrospinning technique. Furthermore, parametric optimisation and operational stability studies of the performance of these membranes using various real mining wastewater might be necessary to benchmark their performance and integrity against other commercially available membrane materials/systems. ❑

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