Selenium is a naturally occurring and essential nutrient for humans, animals, and some plants; however, selenium also can cause adverse health and reproductive effects when consumed in excess. In nature, selenium is found primarily in organic-rich sedimentary rocks (e.g., petroleum source rock, coal, phosphorites, and carbonaceous shales) and sulfidic ores. Because of its natural occurrence in geologic materials used as industrial feedstocks, selenium often is present in wastewater due to oil and gas extraction, petroleum refining, coal-fired electric power generation, metals mining and processing, and production of phosphate fertilizers. It also is found in wastewater and sludge at wastewater treatment plants. Selenium also may be present in irrigation water and stormwater runoff from agricultural operations located in areas with seleniferous soils.

In mining and coal-fired power plant effluents, selenium is mainly found in the form of selenate (Se [VI]) and selenite, (Se [IV]). Both compounds are toxic to aquatic life; hence, discharge limitations for selenium are becoming increasingly stringent. The U.S. Environmental Protection Agency (EPA) requires selenium concentrations in discharges from coal-fired power stations to be below 12 ppb on a monthly average and 23 ppb as daily maximum. The discharge consent for release into freshwater systems at certain sites is 5 ppb.

Treating selenium

Selenium treatment technologies can be applied either at the source (upstream) or at the end of the pipe (downstream), or both. The species of selenium can change as wastewater moves through different chemical, physical, and biological processes within the facility's treatment plant or process units. The applicable treatment technology required will depend on the species of selenium in the wastewater and discharge requirements.

Selenate and selenite can be reduced biologically to the elemental form of selenium, which makes it virtually insoluble. Particulate elemental selenium can then be separated from the wastewater by traditional liquid–solid separation methods. Biological treatment methods include constructed wetlands and fixed-film bioreactors — using granulated activated carbon as support material for biofilm growth, either as a packed bed or as a fluidized bed — and moving bed biofilm reactors (MBBRs) utilizing a plastic support for biological growth.

Other methods include precipitation with iron salts, ion exchange, zero valent iron, and reverse osmosis.

Although technologies are capable of removing selenium from industrial wastewater, the ability to consistently and reliably remove selenium remains a challenge. Treatment of selenium using these core technologies will require primary, tertiary, and residuals treatment. The effectiveness of selenium treatment is highly dependent on species, concentration, and mass of selenium in wastewater and other water matrix parameters. Therefore, a detailed wastewater characterization including selenium speciation and mass balance would be important to properly evaluate treatment options. An example of this evaluation based on utilizing an MBBR process on both power plant and mining effluent is provided below.

MBBR technology

An MBBR is a biological method to remove selenium that can operate with the same support material for over 20 years, while granulated activated carbon in other biological methods may need to be replaced regularly. The MBBR does not require back-washing; it can tolerate high suspended solids concentrations in the feed and is not subject to clogging. MBBRs also are generally energy-efficient, and individual reactors can be made significantly larger than other bioreactors.

The MBBR process has been used extensively for carbon and nitrogen removal. The process utilizes media made of polyethylene, which has a shape that provides a large protected surface area for biofilm development. Two examples of
MBBR media are shown in Figure 1. K1 is the original media with a protected surface area for biofilm growth of 500 m$^2$/m$^3$ at 100% filling (bulk volume/volume). K5 is a later development that provides 800 m$^2$/m$^3$ at 100% filling. Fillings up to 60% to 65% can be used. Under anoxic conditions, the media are kept in suspension using mechanical mixers.

![Figure 1. Examples of MBBR media: K1 (left) and K5 (right). Credit: Veolia Solutions and Technologies](image)

**Performance evaluation**

Studies were performed on laboratory MBBR models that were continuously fed with industrial wastewater from two sources: flue gas desulfurization (FGD) from a power plant and a coal mine. Carbon sources and nutrients were added in small separate feed streams. Effluent samples were collected and treated in batches with either filtration through 0.2-μm membrane filters or with coagulation and flocculation using ferric chloride and polymer.

The characteristics of the wastewaters treated are summarized in the table.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>FGD effluent</th>
<th>Coal mine effluent</th>
<th>Copper mine effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenate (ppb)</td>
<td>237</td>
<td>-</td>
<td>469</td>
</tr>
<tr>
<td>Selenite (ppb)</td>
<td>&lt;5</td>
<td>-</td>
<td>9.5</td>
</tr>
<tr>
<td>Total Selenium (ppb)</td>
<td>249</td>
<td>38</td>
<td>560</td>
</tr>
<tr>
<td>NO$_3$-N (ppm)</td>
<td>90</td>
<td>23</td>
<td>1.5</td>
</tr>
<tr>
<td>NO$_2$-N (ppm)</td>
<td>0.7</td>
<td>0.02</td>
<td>0.015</td>
</tr>
<tr>
<td>Sulphate (ppm)</td>
<td>2000</td>
<td>420</td>
<td>240</td>
</tr>
<tr>
<td>COD (ppm)</td>
<td>105</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>PO$_4$-P (ppm)</td>
<td>0.11</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>NH$_4$-N (ppm)</td>
<td>3.3</td>
<td>&lt;0.015</td>
<td>&lt;0.015</td>
</tr>
</tbody>
</table>

**Table. Influent characteristics of the tested wastewaters**

**FGD effluent**

Treatment of the FGD effluent containing approximately 250 ppb selenate and 90 ppm NO$_3$-N was studied in a two-stage MBBR with K1 media. Glucose was added as carbon source and the process was operated at 30°C.

The results (Figure 2) show that it was possible to achieve 10–20 ppb of total selenium after chemical treatment. The total selenium concentrations after chemical treatment were consistently lower than that of the filtered samples, which demonstrates that chemical treatment was more efficient than filtration through a 0.2-μm filter for separation of selenium from the effluent.

NO$_3$-N and NO$_2$-N were depleted in the first MBBR, while most of the selenium removal took place in the second reactor.
Coal mine effluent

Treatment of coal mine effluent containing approximately 38 ppb total selenium and 23 ppm NO$_3$-N was studied in another two-stage MBBR using K5 media and Micro C as a carbon source. The process temperature was decreased gradually from 22°C to 6°C during the study, and the total hydraulic retention time was decreased from 30 to 4.5 hours.

The results (Figure 3) show that it was possible to consistently achieve concentrations of less than 5 ppb total selenium after chemical treatment and frequently below the detection limit of 3 ppb. The concentration of NO$_3$-N+ NO$_2$-N was reduced to 0.4 to 1.2 ppm after the first reactor and then further reduced to around 0.2 ppm after the second (Figure 4). Between 50% and 85% of the selenium reduction also occurred in the first reactor, with the second reactor acting mainly as a polishing step for both nitrate and selenium.

**Figure 3.** Total HRT, process temperature, and effluent concentrations of total selenium in coal mine effluent (green triangles represent samples that were below the detection limit, 3 ppb, for total selenium)
A viable treatment option

The results show that MBBR can be a viable solution for biological selenium removal as well as nitrate removal from FGD and mine effluents. By combining the MBBR with traditional chemical treatment, very low effluent selenium concentrations can be reached. With so much focus on the selenium regulations, having a biological solution offers treatment options where they were previously limited, especially in the mining and energy markets.

Note: This article was adapted from a WEFTEC 2014 presentation, “Moving Bed Biofilm Reactor for Selenium Removal from FGD and Mine Effluents,” by Caroline Dale, Maria Ekenberg, Mikael Sjölin, Flemming Wessman, and Jens Morän.