PO4 Sponge

Phosphorus - Low Concentration Removal

Phosphorus (P) is a contaminant found in streams and lakes and waste water. It contributes to biological growth and especially harmful algae blooms and associated toxins, lower water clarity, and depletion of dissolved oxygen, which affects fish and other marine creatures. Each Kg of P discharged into water bodies creates a potential for 100 Kg of algae to grow. Phosphorus comes primarily from agriculture and waste water sources. Over 80% of phosphorous is commercially used for fertilizer, of which world agriculture is highly dependent. Most food products and drinking water contains phosphorus.

MetaMateria’s PO4 Sponge offers an effective way to remove soluble P from water. PO4 Sponge is a unique, porous, high surface area material that contains iron-oxyhydroxide nano-crystals to provide an extremely large number of sites for phosphate ion sorption. The product is simple to use and can be regenerated and reused multiple times, which provides economic advantages.

Value Offered by PO4 Sponge

- Has high capacity to sorb phosphorus (per Kg) than other products
- Capture is effective at both high and low concentrations - values below 0.03 mg/L are achievable
- Can be reused multiple times – Kg of PO4 Sponge can remove > 1 Kg of P, with reuse
- Long Life & Cost Effective removal for many applications
- Water easily flows through porous product
- Phosphorus is removed from capture site – will not re-contaminate water
- Phosphorus can be recovered

PO4 Sponge Product

PO4 Sponge products is made in different shapes and sizes and this provides flexibility for use of the product. This highly porous material is made with iron powder and other minerals bonded together. Nanocrystals of iron oxyhydroxide are chemically grown on pore surfaces, which increase the surface area of from 15 m²/gr for the iron foam to over 100 m²/gr. The interconnected, hierarchical pores allow water to readily flow into or through the media with a low pressure drop.

PO4 Sponge products were under development since 2007. Since 2011, major improvements in product properties and manufacturing and regeneration operations occurred. Interest in the product is high and MetaMateria is working with several organizations to commercialize the technology. Applications for low level P removal include control of bacteria growth, where disinfectants are not desired.

PO4 Sponge contains iron-oxyhydroxide (FeOOH) acicular crystals (20-60 nm) grown on the pore surfaces. The high concentration of the FeOOH nano-crystals enhances sites for PO4 sorption.
The nano-iron represents about 10% of the porous base with a capacity of some 3000 mg-P/gram of Fe when tested at higher P concentrations. Other nano materials, such as La, Mn, Ag or Cu compounds can be added. The interior structure of the product is shown below.

PO4 Sponge absorbs more P per Kg of media than natural materials and other manufactured products, as seen in the Table (mg-P per kg-media). Batch testing shows continuous increases in P absorbed as concentration of P increases. Iron is a reactive material that can also sorb many metal, sulfate and other ions, which can compete with P sorption. Lower capacity exists at concentrations below 0.5 mg/L, but these are estimated to be 15,000 mg-P/Kg of media. Lab testing with silica and nitrate ions show little effect on capacity. Some ions in water, such as calcium can increase phosphorus removal, especially at a lower pH. Capacity to sorb P declines at higher pH values.

### Phosphorus Removal

PO4 Sponge sorbs dissolved reactive phosphorus (DRP) or soluble P not part of biological or other compounds. The PO4 ions in water need to contact the nanomaterial in the porous product. This can be done by passing water through either a bed of product or through a monolith. A portion of the P is quickly sorbed, while additional sorption requires the PO4 ion to move from a higher to lower concentration area, which takes more time. Two approaches are used: (1) single pass and (2) recycle, where a portion of the water exiting product is goes back through the bed or monolith to allow a further reduction in the P remaining in the water. In some cases, a majority of P is removed by recycling and remaining water is passed through a polishing filter to lower P levels even further. PO4 Sponge is sold commercially for various applications.

**Recycling**

Examples are shown where water was recycled through a column of PO4 Sponge monoliths. P is lowered from 1.2 mg/L to below 0.1 mg/L in 25 min and to 0.01 ppm in 45 min.

**Low Concentration**

Single pass testing of PO4 Sponge was done through ten 36 gram plates in a trough. Water passes through each plate. Time between plates is 6 min at a flow of 10 ml/min.
The low P levels are similar to P levels found in waterways and agricultural runoff water (0.05 to 0.12 mg/L). As can be seen, P was lowered to below 0.04 mg/L for over 220 days. Readings vary, due to measurement sensitivity in a colorimeter with a limit of ±0.02 mg/L.

Note that ~68% of P removed to date is by the first PO4 plate, which does not show any sign of saturation.

In another single pass test, discs of PO4 Sponge were packaged in a sealed column (cartridge 10 x 28 cm).

Cartridges, like one shown below, can be made in various sizes.

The graph shows influent P held at 0.4 mg/l and effluent P remained below 0.02 mg/L at a 5 minute contact time for water passed through the cartridge over 24 hours. We have done testing for longer periods by recycling water from a 500 gallon tank. Effluent concentration remained below 0.05 mg/L. In these tests, P in the water was periodically increased to 1 mg/L and time to recovery to lower levels was determined. P was lowered to below 0.1 within a few hours and back to lower levels shown in the graph, typically within 24 hours. This simulates conditions found in some wetlands and natural swimming pools.

Batch Testing of PO4 Sponge was done using water with 0.84 mg/L of P. Results in the table show that >94% of the P was removed in a 2 hour test. Three different PO4 Sponge materials were tested. Each had a surface area ranging from 69-103m²/gram. This Test used 300 mg of granular material stirred in 100 ml of water (0.84mg/L of P). Phosphorus removed was 94% to 99%.

<table>
<thead>
<tr>
<th></th>
<th>Initial concentration (mg/L)</th>
<th>Final concentration (mg/L)</th>
<th>Phosphorus removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMT-1</td>
<td>0.84</td>
<td>0.01</td>
<td>0.83</td>
</tr>
<tr>
<td>MMT-2</td>
<td>0.84</td>
<td>0.05</td>
<td>0.79</td>
</tr>
<tr>
<td>MMT-3</td>
<td>0.84</td>
<td>0.03</td>
<td>0.81</td>
</tr>
</tbody>
</table>

In summary, MetaMateria’s PO4 Sponge offers attractive advantages, whose benefits include:

- Can be economical way to meet regulated values – no chemicals and is a simpler system
- Can maintain phosphorus concentrations as low as 0.01 mg/L
- Excellent approach to meet future regulation targets of 0.1 mg/L (ppm)

For More Information visit www.metamateria.com or contact:
Dr. J. Richard Schorr, CEO jrschorr@metamateria.com or Mr. Timothy Marth, VP tmarth@metamateria.com