PO4 Sponge

Phosphorus Removal - Low & High Level Sources

Phosphorus (P) is a contaminant in streams and lakes that can degrade water bodies, especially when excessive. It contributes to growth of cyanobacteria (blue-green algae) 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.

In addition to removal of P for ecological reasons, P is also a non-renewable resource and the economic recovery is desirable. Phosphate ions removed during regeneration of PO4 Sponge can be recovered using various precipitation or concentration approaches.

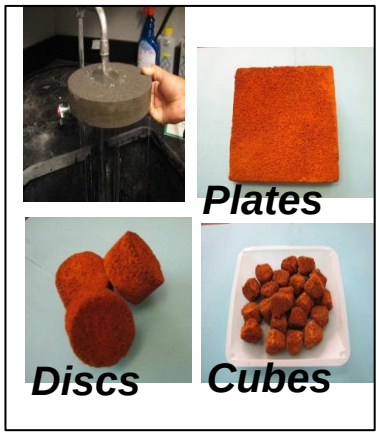
Value Offered by PO4 Sponge

- **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

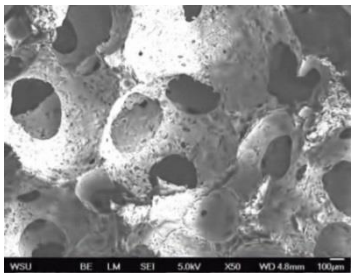
PO4 Sponge products can be made in different shapes and sizes. This provides flexibility for use of the product in systems designed for a variety of applications. This highly porous material is made with iron powder and other minerals bonded together. Nanocrystals of iron oxyhydroxide are chemically grown on pore surfaces, which increase the surface area of from 15 -20 m^2/gr for the iron foam to over 100 m^2/gr. The interconnected, hierarchical pores in this product allow water to readily flow into or through the media with a low pressure drop.

PO4 Sponge products have been under development since 2007 and P absorption in even early products compared favorably with other sorbents.

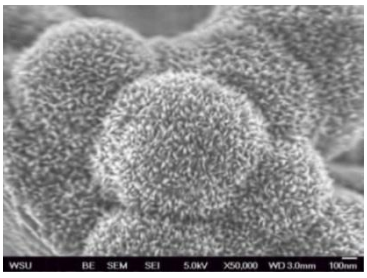


Since 2011, major improvements in product properties and manufacturing and regeneration operations have occurred. Interest in the product is high and MetaMateria is currently working with several organizations to commercialize the technology in various applications.

PO4 Sponge contains iron-oxyhydroxide (FeOOH) acicular crystals (20-60 nm) grown on the pore surfaces. Iron is known to remove P but this is significantly enhanced by the high concentration of the FeOOH nano-crystals, which are sites for PO4 sorption. The nano-iron is 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.



Interconnecting pore structure



Surfaces with 20-70 nm crystals

PO4 Sponge absorbs more P per Kg of media than natural materials and other manufactured products. This can be seen the Table (mg-P per kg-media) and bar graph shown below. Capacity of various products and materials are shown, including an early version of the PO4 Sponge material. As seen, capacity to absorb P is markedly improved over other products shown in the Table below.

Sorption Media	mg-P/Kg
PO4 Sponge - Meta	
High > 5mg/L	80,000
Low < 2 mg/L	25,000
Iron Ore (Hematite)	1,430
Iron Slag	420
Crushed Red Bricks	510
LECA (expanded clay)	800
Activated Fe Alumina	17,100
Filtra-D	2,500
Phostec	7,000

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. 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 adsorbs 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 and is being evaluated for various applications, ranging from 1,000 – 500,000 gallons/day and with phosphorus concentrations up to 125 mg/L. Some examples of lab and field test data are shown to illustrate performance of PO4 Sponge to capture P.

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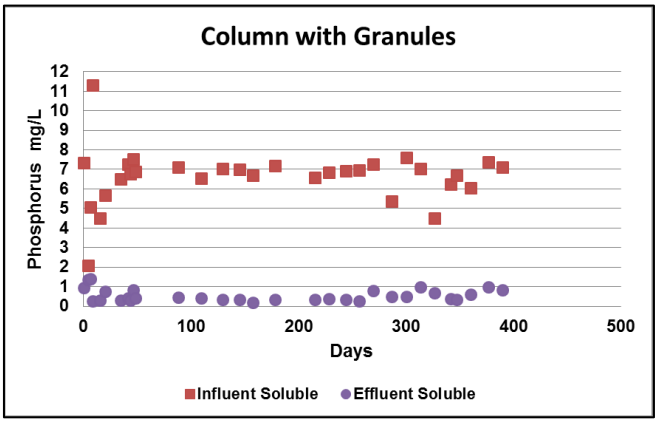
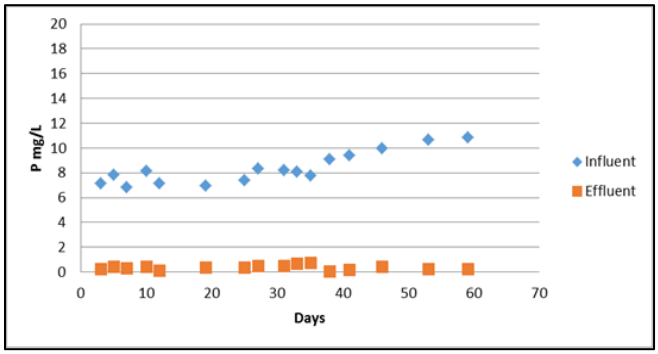
Single pass through columns of granular PO4 Sponge has shown that P is continuosly removed over long periods, as compared to some product. Graph at the right shows results with actual septic water having ~7 mg/L of P of soluble phosphorus and a 3 hour contact time. Effluent P remained below 1 mg/L for 400 days and then continued to sorb P for another 220 days. Total P sorbed exceeded 73 g-P/Kg.



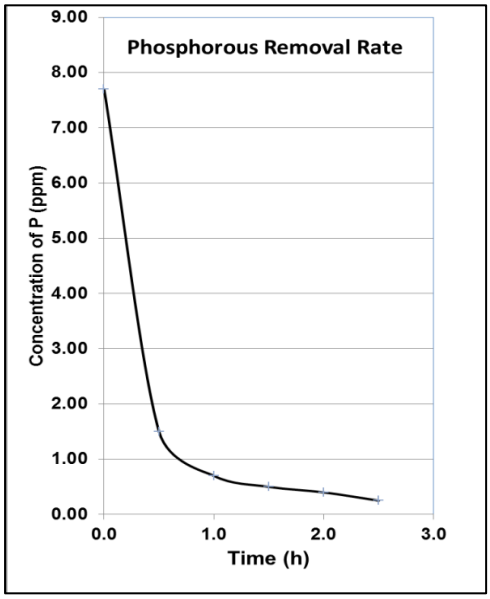
P removal results are shown where discharge water from community septic system passed through a PO4 sponge cartridge (24" long x 6" dia.) at a 1.5 hour EBCT. P influent of 8-11 mg/L effluent P remained under 0.3 mg/L for the 60 day test.

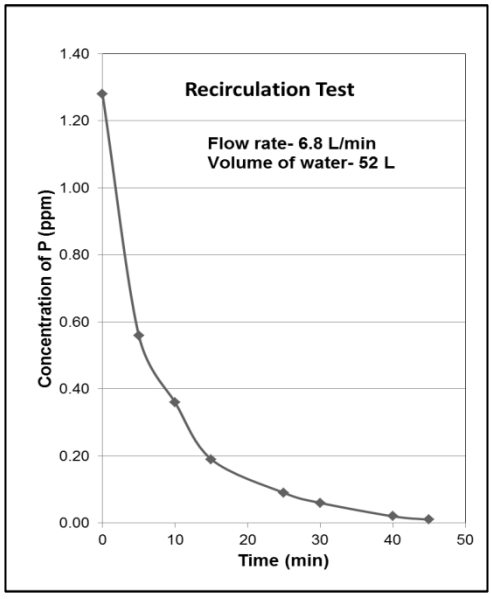


Municipal Waste Water was collected and tested to examine In a separate field test using municipal waste water, PO4 Sponge kept P below 1 mg/L for over 10 months. P adsorbed depends on concentration and lab testings indicates absorption ranging from 15 to >100 g-P/kg.

Examples of water recycled through PO4 Sponge are shown in the curves below. Water of a particular starting concentration was recycled through a bed of PO4 Sponge (left) and a column containing monoliths (right).

Fast Removal to Low Concentrations occurs with a relatively short hydraulic retention time (HRT) when water is recirculated and remains in contact with media. As shown below, a 60 min HRT lowered P from 8 mg/L to below 1 mg/L and in another hour to 0.2 mg/L. Polishing filters can lower P to below 0.1 mg/L as seen where P is lowered from 1.2 mg/L to below 0.1 mg/L in 25 min and 0.01 ppm in 45 min.

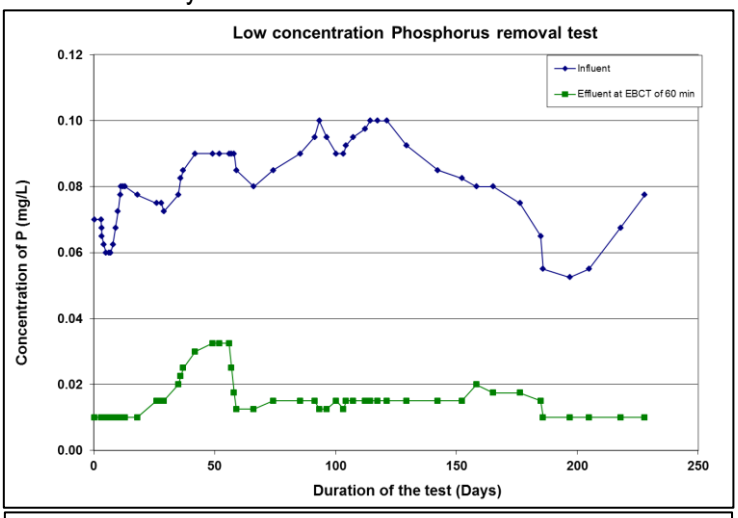




Low Concentration

Single pass testing of PO4 Sponge was also done using ten 36 gram plates in a trough. Water passes through each plate and out in an hour. Time between plates is 6 min at a flow of 10 ml/min.

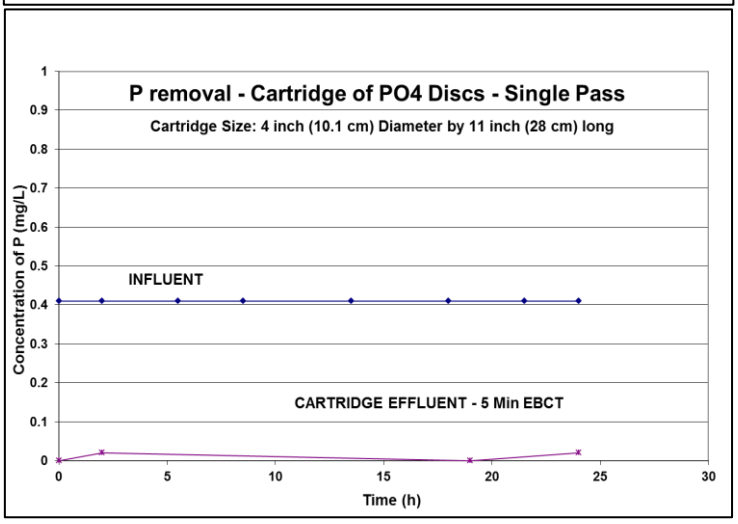
This influent P was chosen because this is similar to P levels found in waterways and agricultural runoff water (0.05 to 0.12 mg/L). As can be seen, P is lowered to below 0.04 mg/L for over 220 days. Readings vary, due to measurement sensitivity in a colorimeter with a limit of ±0.02 mg/L.



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

For another single pass test, discs of PO4 Sponge were packaged in a sealed column (cartridge) and water passed this 10 cm in diameter by 28 cm long cartridge. The graph shows that P remained below 0.02 mg/L while 0.5 L/min of water (5 minute contact time) was passed through the cartridge over 24 hours.

Cartridges, like one shown below, can be made in various sizes and tested with water recycling from a 500 gallon tank. Effluent concentration remained well below 0.1 mg/L. Spikes to increase P in water to 1 mg/L were lowered to below 0.1 within hours. This simulates conditions found in some wetlands and natural swimming pools.



Batch Testing of PO4 Sponge was done using water having a P of 0.84 mg/L. The results below show that >94% of the P was removed in a 2 hour test. 3 different PO4 Sponge materials were tested. Each had a different surface area (69-103m^2/gram). Test used 300 mg of granular material stirred in 100 ml of water (0.84mg/L of P). Phosphorus removed was 94% to 99%.

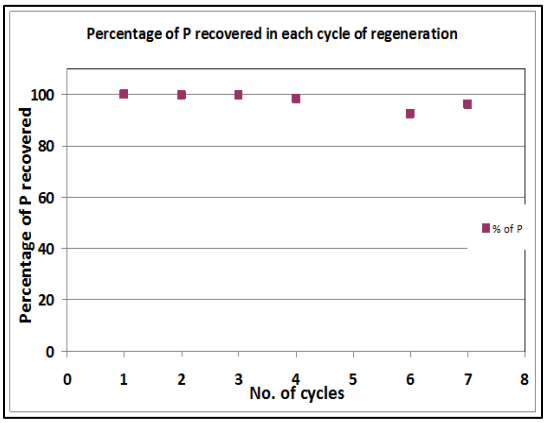
	Initial concentration (mg/L)	Final concentration (mg/L)	Phosphorus removed	
MMT-1	0.84	0.01	0.83	**98.8%**
MMT-2	0.84	0.05	0.79	**94.0%**
MMT-3	0.84	0.03	0.81	**96.4%**

Testing of PO4 Sponge

PO4 Sponge is sold commercially for smaller applications and is being examined in several other applications, where results are encouragingly positive. Field tests of PO4 Sponge are done on-site or use water obtained from commercial sites. Tests include:

- On-Site waste Treatment (septic) Systems containing 6 to 10 mg/L of P
- Municipal waste treatment water ranging from 2 to 6 mg/L (six different sites)
- Industrial waste water (food processing plants) ranging from 75 to 5 mg/L
- Lake and pool water with P below 0.5 mg/L

PO4 Sponge Regeneration allows the product to be used multiple times. Little mechanical or chemical degradation is observed with reuse. It seems feasible to have 15 or more uses. This plot below shows the percentage of P recovered after each regeneration cycle is consistent. Lab testing shows capacities are similar to the starting material, but in use, competing ions, chemistry or other problems may shorten product life. Absorbed PO4 ions are removed during regeneration by circulating a base chemical, such as a sodium hydroxide solution through the PO4 Sponge cartridge or bed for several hours. It can be done *in-situ* or the product (cartridge) can be replaced and treated at a central location.



PO4 Sponge Cost

Lower capital and operating costs can make this product economically valuable for many applications, where alternatives are more costly or more complex. The average price for PO4 Sponge declines with reuse, since regeneration costs are much less than the initial product. Pricing for this product will also decline as demand and volume production increases. MetaMateria estimates a highly automated approach will drop the average price by 85% with 15 uses, likely to under $1/Kg. For many applications requiring removal of P at low concentrations, PO4 Sponge provides an especially attractive and simpler approach than available with other technologies. While the cost to remove a Kg of P depends upon many factors, for smaller waste water treatment operations, PO4 Sponge will offer a less complicated approach that is expected to compete well with chemical and crystallization (e.g. struvite) approaches and with other sorbent products.

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
- No sludge generated
- 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:
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