**SUPPLEMENTAL INFORMATION**

**Biogenic Iron Oxides for Phosphate Removal**

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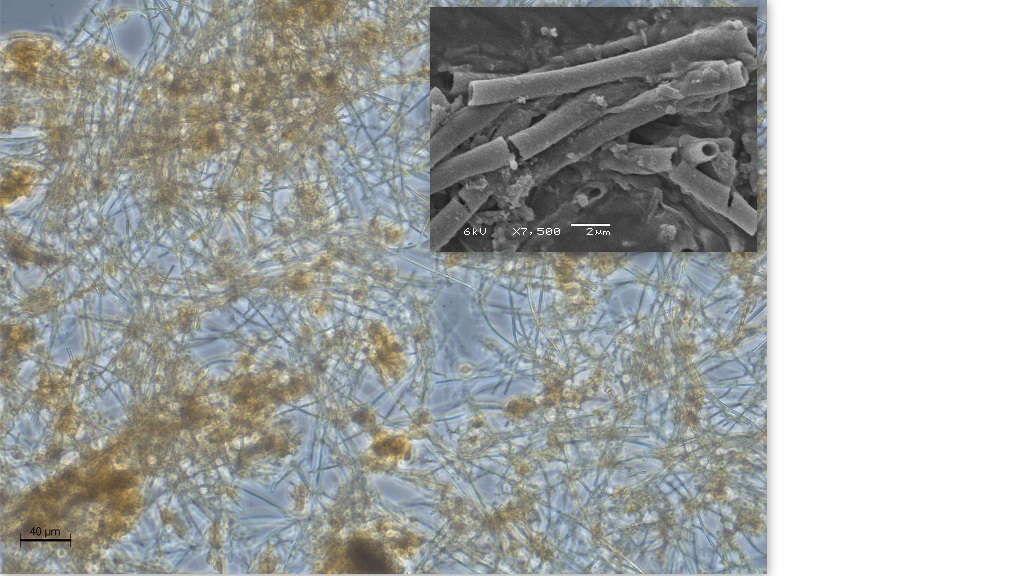
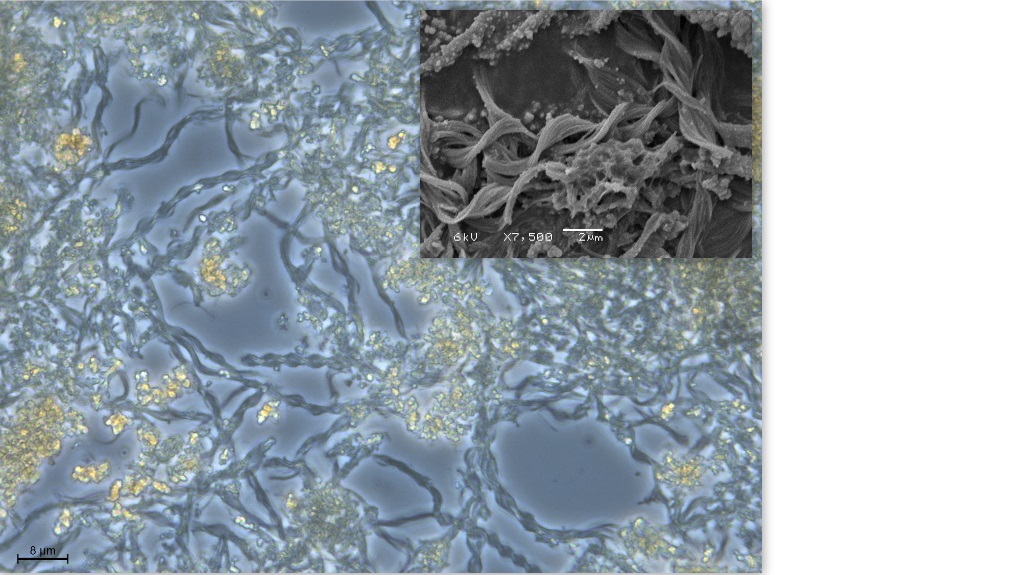
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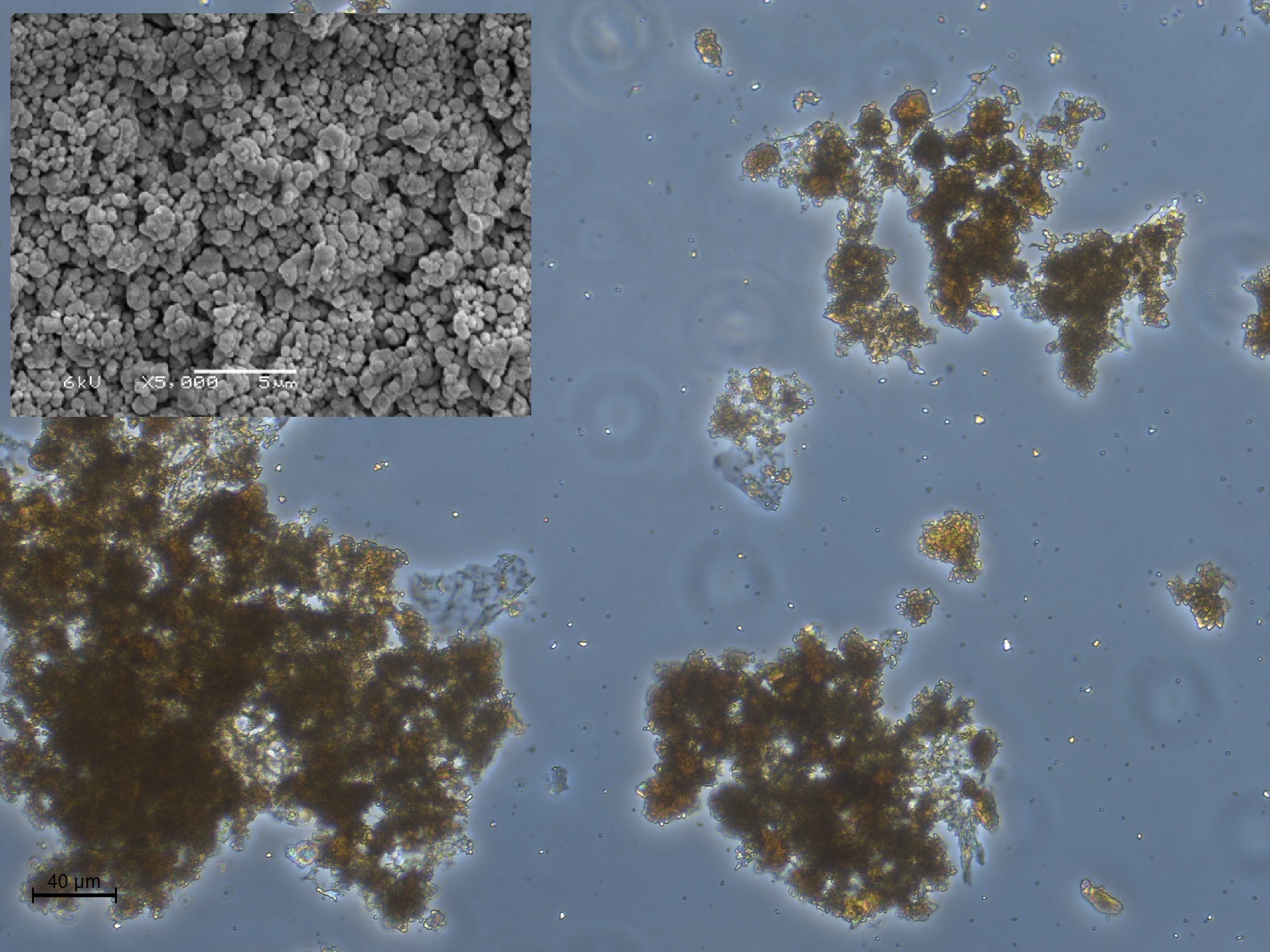
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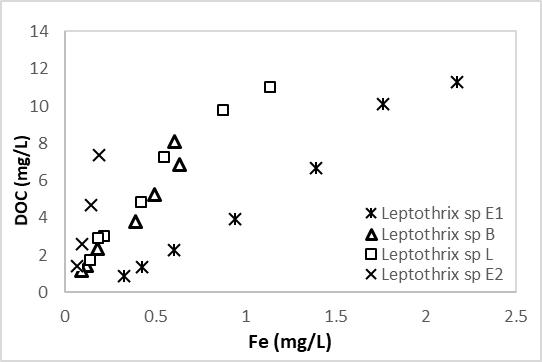
**Contents**

This SI file includes Fig S1, S2, S3 and tables S1 to S5. Total no of pages = 8.

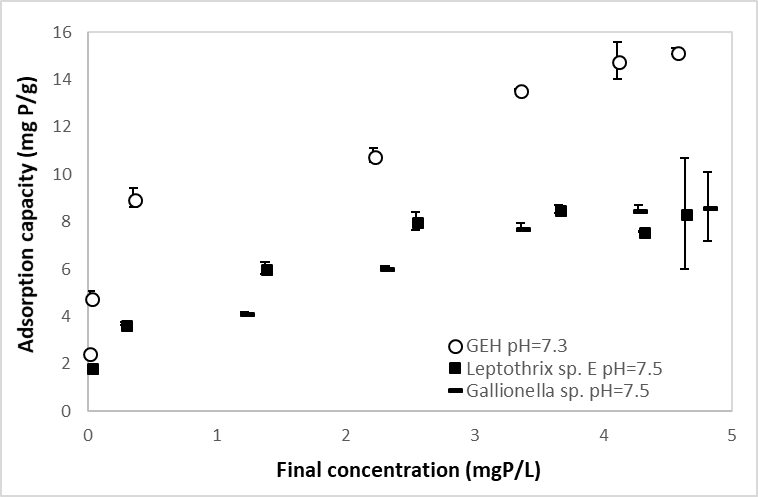
 



**Fig.S1. Light microscopy and SEM images of *Leptothrix* sp. sheats (left), *Gallionella* sp. stalks (right) and** **chemical iron oxide precipitates (ChFeOPrecip) (below). *Leptothrix* sp. is a sheathed filamentous bacterium and form oxyhydroxides as a hollow microtubes. *Gallionella* sp. produce iron oxides, which have the shape of twisted stalks. ChFeOPrecip show common uniform spherical like morphology. SEM image of the granulated ferric hydroxide (GEH) particle surface showing its porous structure [1], which results in a high surface area. Light microscopy photos: on the lelft bar equals 40 µm, on the right equals 8 µm, below equals 40 µm. SEM images: on the lelft and right bars equal 2 µm, below equals 5 µm.**



**Fig.S2. Correlation of DOC and Fe concentrations in the supernatant after isotherms with MQ washed BioFeO of *Leptothrix* sp., where E, B and L letters refer to the sampling locations**



**Fig.S3. Isotherms for MQ washed GEH, *Leptothrix* sp. and *Gallionella* sp. at around pH = 7.5**

Total and volatile solids were calculated according to the equations below:

where,

*A* = weight of dried residue + dish, g,

*B* = weight of dish, g,

*C* = weight of wet sample + dish, g,

*D* = weight of residue + dish after ignition, g.

**Table S1. Characteristics of BioFeO, ChFeOPrecip and GEH prior to phosphate adsorption experiments**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | ***Leptothrix* sp. E non-washed** | ***Leptothrix* sp. E saline- washed** | ***Leptothrix* sp.**  **E, B, L1 MQ washed** | ***Gallionella* sp. MQ washed** | **ChFeOPrecip MQ washed** | **GEH**  **MQ washed** |
| **Fe, mgFe/g** | 237.4 ± 4.0 (n=2) | 204.7 ± 0.4 (n=2) | 235.7 ± 13.0 (n=6) | 390.8 ± 10.3 (n=2) | 339.2 ± 4.3 (n=2) | 566.1 ± 4.9 (n=2) |
| **P, mgP/g** | <0.3 ± 0.1 (n=2) | <0.4 ± 0.0 (n=2) | 3.3 ± 2.6 (n=6) | 31.0 ± 0.3 (n=2) | 10.4 ± 0.4 (n=2) | <0.4 ± 0.0 (n=2) |
| **Ca, mgCa/g** | 25.0 ± 0.2 (n=2) | 3.3 ± 0.1 (n=2) | 10.3 ± 3.4 (n=6) | 31.7 ± 0.4 (n=2) | 35.6 ± 0.2 (n=2) | <0.4 ± 0.0 (n=2) |
| **VS, g/kg TS** | 445.52 ± 61.6 (n=17) | 434.4 ± 12.3 (n=4) | 437.4 ± 72.3 (n=12) | – | 102.3 ± 14.7 (n=4) | – |
| **Fe/P molar ratio** | >337.6 | >291.1 | 39.6 | 7.0 | 18.1 | >805.1 |
| **XRD** | – | – | amorphous | amorphous | – | – |

**1** *Leptothrix* sp., where E, B and L letters refer to the sampling locations

2 AverageVS value of non-washed *Leptothrix* sp. E, B and L

The pseudo-second order kinetic model is described by the following equation:

where,

qt is the adsorption capacity at time t,

k is the rate constant of adsorption (g/mg min),

qe is the adsorption capacity at equilibrium.

The difference between qe determined by fitting with model and qe reached experimentally is a measure of how close the samples were to adsorption equilibrium.

Table S2. Kinetic parameters for the adsorption of phosphate by BioFeO, ChFeOPrecip and GEH

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample** | **qe, mgP/g (fitted)** | **qe, mgP/g (experimental, after 4 days)** | **k, µgP/g min** | **qe reached experimentally in comparison to qe estimated with model (%)** |
| ***Leptothrix* sp.E non-washed** | 10.3 ±0.0 | 10.1 ±0.0 | 7.5 x 10-1 ± 1.1 x 10-1 | 98.0 |
| ***Leptothrix* sp*.* E MQ washed** | 5.4 ± 0.1 | 4.1 ±0.0 | 1.3 x 10-1 ± 1.7 x 10-3 | 75.9 |
| **ChFeOPrecip**  **MQ washed** | 8.2 ± 0.6 | 7.4 ±0.4 | 3.3 x 10-1 ± 1.1 x 10-1 | 90.2 |
| **GEH MQ washed grinded, ≤100 µm** | 10.4 ± 0.0 | 10.0 ±0.05 | 4.3 x 10-1 ± 2.1 x 10-2 | 96.1 |

**Table S3. Portho and Ptotal concentrations in the supernatant after adsorption experiments with BioFeO, Pinitial=5-6 mgP/l (*Leptothrix* sp. from Earnwâld after 7 days, *Leptothrix* sp. from Beetsterzwaag and Lettelbert after 4 days)**

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **TS, g/l** | ***Leptothrix* sp. E non-washed** | | ***Leptothrix* sp. E MQ washed** | | ***Leptothrix* sp. E saline washed** | | ***Leptothrix* sp. B MQ washed** | | ***Leptothrix* sp. L MQ washed** | | ***Gallionella* sp.**  **MQ washed** | |
| **Portho, mg/l** | **Ptotal, mg/l** | **Portho, mg/l** | **Ptotal, mg/l** | **Portho, mg/l** | **Ptotal, mg/l** | **Portho, mg/l** | **Ptotal, mg/l** | **Portho, mg/l** | **Ptotal, mg/l** | Portho, mg/l | Ptotal, mg/l |  |
| **0.2** | - | - | 0.3 ± 0.0 | 0.4 ± 0.0 | 0.1 ± 0.0 | - | 0.1 ± 0.0 | 0.2 ± 0.0 | 0.1 ± 0.0 | 0.2 ± 0.0 | - | - |
| **0.1** | 0.0 ± 0.0 | - | 1.0 ± 0.0 | 1.2 ± 0.0 | 0.5 ± 0.0 | - | 0.6 ± 0.1 | 0.7 ± 0.1 | 0.7 ± 0.3 | 0.8 ± 0.4 | - | - |
| **0.05** | 0.1 ± 0.0 | 0.2 ± 0.0 | 2.2 ± 0.2 | 2.2 ± 0.2 | 1.4 ± 0.0 | 1.8 ± 0.0 | 1.8 ± 0.1 | 1.9 ± 0.1 | 1.5 ± 0.0 | 1.7 ± 0.0 | 1.2 ± 0.0 | 1.2 ± 0.0 |
| **0.025** | 1.1 ± 0.1 | - | 3.5 ± 0.1 | 3.4 ± 0.1 | 2.4 ± 0.1 | 3.0 ± 0.1 | 3.1 ± 0.0 | 3.2 ± 0.0 | 2.9 ± 0.0 | 3.0 ± 0.0 | 2.3 ± 0.0 | 2.2 ± 0.0 |
| **0.0125** | 2.6 ± 0.1 | 2.8 ± 0.0 | 4.2 ± 0.1 | 4.0 ± 0.1 | 3.3 ± 0.0 | 4.0 ± 0.0 | 4.0 ± 0.0 | 4.0 ± 0.1 | 3.8 ± 0.0 | 3.9 ± 0.0 | 3.4 ± 0.0 | 3.1 ± 0.0 |
| **0.00625** | 3.6 ± 0.2 | - | 4.7 ± 0.0 | 4.4 ± 0.0 | 3.7 ± 0.0 | 4.5 ± 0.1 | 4.4 ± 0.0 | 4.4 ± 0.0 | 4.2 ± 0.2 | 4.3 ± 0.2 | 4.3 ± 0.0 | 4.0 ± 0.2 |
| **0.00313** | 4.8 ± 0.1 | - | 4.9 ± 0.0 | 4.6 ± 0.0 | 4.0 ± 0.0 | 5.0 ± 0.0 | 4.6 ± 0.0 | 4.5 ± 0.0 | 4.6 ± 0.0 | 4.6 ± 0.0 | 4.8 ± 0.1 | 4.5 ± 0.2 |

The Langmuir adsorption model is expressed as follows:

Where,

qm = Maximum adsorption capacity (mg P/g),

qe = Adsorption capacity at equilibrium (mg P/g),

Ce = Concentration at equilibrium (mg P/L),

KL = Equilibrium constant for the Langmuir adsorption (L/mg P).

**Table S4.** **Langmuir isotherms constants for the adsorption of phosphate by *Leptothrix* sp and GEH**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample** | **qm, mgP/g dried solids** | **qm,**  **mgP/g Fe** | **Kl,** **L/mgP** | **RMSE1** |
| ***Leptothrix* sp., saline washed (once) not dried**  **by Rentz et al.** **[2]** | 10.8-39.9 | 46.9-165.0 | - | - |
| ***Leptothrix* sp.E non-washed not dried** | 24.7 ± 0.2 | 109.6 ± 1.0 | 3.6 ± 0.1 | 1.7 ± 0.0 |
| **GEH grinded, ≤100 µm MQ washed dried** | 18.0 ± 0.3 | 31.8 ± 0.5 | 12.1 ± 0.8 | 1.3 ± 0.2 |

1RMSE - Root-mean-square error for the fit of experimental data to the isotherms model using non-linear regression.

**Table S5.** **Actual maximum phosphate adsorption capacities observed after 4 days adsorption by BioFeO and GEH**

|  |  |  |  |
| --- | --- | --- | --- |
| **Sample** | **Actual adsorption capacities, mgP/g dried solids** | **Actual adsorption capacities, mgP/g Fe** | **Final P concentration in the solution, mgPortho /l** |
| ***Leptothrix* sp.E non-washed not dried** | 26.0 ± 0.3 | 115.3 ± 1.4 | 5.4 ± 0.0 |
| ***Leptothrix* sp. E MQ washed not dried** | 6.4 ± 1.2 | 27.5 ± 5.2 | 5.1 ± 0.0 |
| ***Leptothrix* sp. E, B, L MQ washed not dried** | 7.3 ± 0.7 | 31.0 ± 3.1 | 4.8 ± 0.3 |
| ***Gallionella* sp*.* MQ washed dried** | 8.7 ± 1.5 | 22.1 ± 3.8 | 4.8 ± 0.1 |
| **GEH grinded (≤100 µm) MQ washed dried** | 19.3 ± 0.1 | 34.1 ± 0.2 | 4.5 ± 0.0 |
| **ChFeOPrecip MQ washed dried** | 12.6 ± 0.3 | 37.2 ± 0.9 | 3.6 ± 0.1 |

**R E F E R E N C E S**

[1]Boels L, Keesman KJ, Witkamp GJ. Adsorption of Phosphonate Antiscalant from Reverse Osmosis Membrane Concentrate onto Granular Ferric Hydroxide. Environ Sci Technol. 2012;46:9638−9645.

[2] Rentz JA, Turner IP, Ullman JL. Removal of phosphorus from solution using biogenic iron oxides. Water Res. 2009;43:2029–2035.