**Supplementary Text 1**

***Standard curve for Mn(II) by EPR spectroscopy***

A calibration curve for Mn(II) was plotted by use of EPR spectroscopy, following the procedure described below. A 100 µM Mn(II) stock solution was first prepared by dissolving 0.1618 g of manganese(II) chloride dihydrate salt (≥ 99%; Emsure grade, Merck) in 100 ml Milli-Q ultrapure water (ASTM Type-1, 18.2 MΩ-cm). From this stock solution, various concentrations of Mn(II) standards ranging from 10 nM to 50 µM were prepared by appropriate dilutions. The Mn(II) standard solutions tested were 10 nM, 100 nM, 1 µM, 5 µM, 10 µM, 25 µM, 50 µM and 100 µM. For analysis, 0.4 ml of the standard solution was transferred into quartz EPR flat cell (Wilmad Glass; 0.5 ml capacity) using a micropipette and EPR spectra were recorded in the paramagnetic range characteristic of Mn. A standard calibration curve was plotted by depicting a relationship between the calculated area of the EPR signal and the Mn(II) concentration. The fourth EPR peak at ~ 3510 Gauss from the lower field side was considered for the area calculation as it represents the one that is least effected by second order effects (Chiswell and Mokthar 1986). The area of the fourth EPR signal was determined using a simple equation, I x ΔH2, where I is the amplitude of peak and ΔH stands for the peak-to-peak linewidth (Olivie-Lauquet et al.1999).

**Supplementary Text 2**

***XPS spectra of C 1s, O 1s and P 2p***

Supplementary Figure 5 presents the decomposition of C 1s, O 1s and P 2p XPS spectra. The carbon 1s spectrum decomposed into four peaks. The peaks at 284.8 ± 0.2 eV, 286.0 ± 0.2 eV, 287.0 ± 0.2 eV and 289.9 ± 0.2 eV correspond to carbon singly bonded to carbon and hydrogen (C-C, C-H), carbon singly bonded to oxygen (C-O), carbon doubly bonded to oxygen (C=O) and carbonate carbon (CO32-), respectively (Pradier et al. 2005; Biesinger et al. 2011). The oxygen 1s spectrum decomposed into five peaks. The peaks at 530.0 ± 0.2 eV, 531.0 ± 0.2 eV, 531.35 ± 0.2 eV, 532.0 ± 0.2 eV and 532. 7 ± 0.2 eV correspond to metal oxides (through microbial oxidation), oxygen in carbonates, oxygen in organic carbonyl group (C=O), oxygen in phosphates (P-O bond), and oxygen in organic C-O bond, respectively (Biesinger et al. 2011; Wu et al. 2016; Ahmad et al. 2017). The phosphorus 2p spectrum decomposed into two peaks at 133.12 ± 0.2 eV and 134.0 ± 0.2 eV, relating to phosphates in the 2p3/2 and 2p1/2 regions, respectively (Xie et al. 2017).

**Additional References:**

Ahmad Z, Najeeb MA, Shakoor RA, Alashraf A, Al-Muhtaseb SA, Soliman A, Nazeeruddin MK. 2017. Instability in CH3NH3PbI3 perovskite solar cells due to elemental migration and chemical composition changes. Sci Rep. 7:15406.

Olivie-Lauquet G, Allard T, Benedetti M, Muller JP. 1999. Chemical distribution of trivalent iron in riverine material from a tropical ecosystem: A quantitative EPR study. Water Res. 33:2726–2734.

Pradier CM, Rubio C, Poleunis C, Bertrand P, Marcus P, Compere C. 2005. Surface characterization of three marine bacterial strains by Fourier Transform IR, X-ray photoelectron spectroscopy, and time-of-flight secondary-ion mass spectrometry, correlation with adhesion on stainless steel surfaces. J Phy Chem B. 109:9540–9549.

Wu X, Zhao G, Wang X, Liu W, Liu W. 2016. Treelike polymeric phosphate esters grafted onto graphene oxide and its tribological properties in polyalkylene glycol for steel/steel contact at elevated temperature. RSC Adv. 6:47824–47832.

Xie Q, Li Y, Lv Z, Zhou H, Yang X, Chen J, Guo H. 2017. Effective adsorption and removal of phosphate from aqueous solutions and eutrophic water by Fe-based MOFs of MIL-101. Sci Rep. 7:3316.

Supplementary Figure 1



Supplementary Figure 2



Supplementary Figure 3



Supplementary Figure 4



Supplementary Figure 5

**Carbon 1s**



**Oxygen 1s**



**Phosphorus 2p**



Supplementary Figure 6

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Supplementary Figure 7



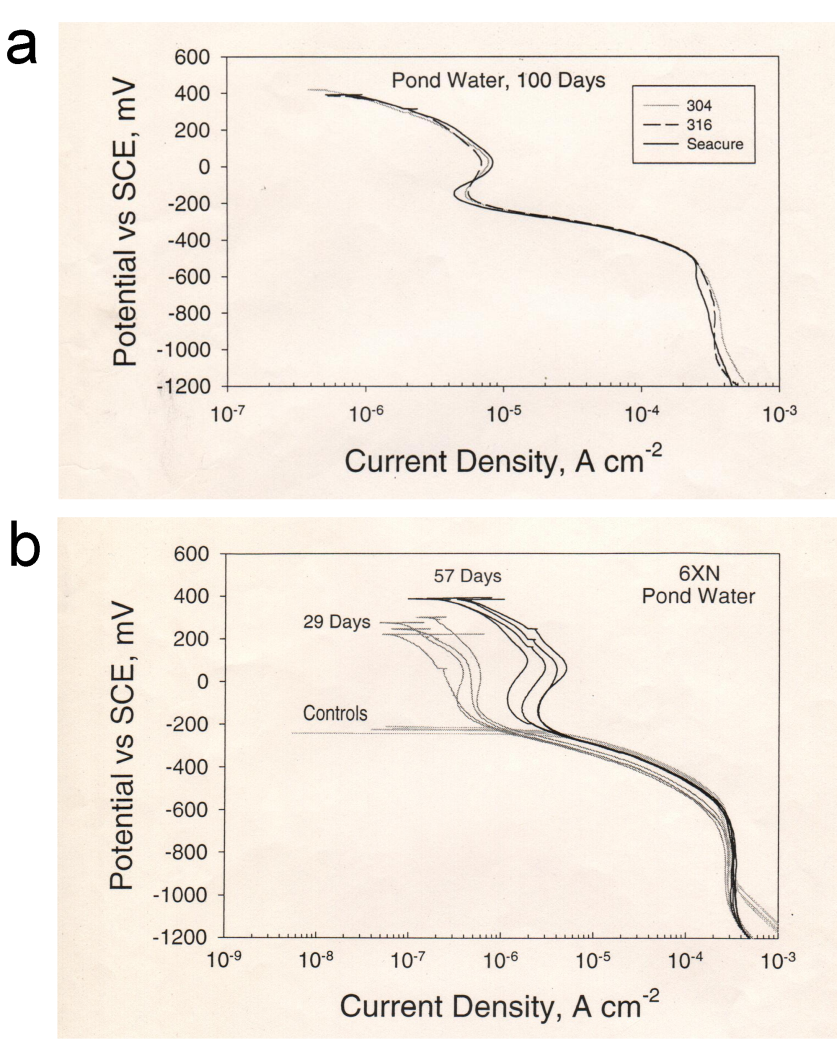
Supplementary Figure 8



Supplementary Figure 9



Supplementary Figure 10



Supplementary Figure 11



Supplementary Figure 12



Supplementary Table 1

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Spectrum number | Scan area (µm) | Elemental composition (wt %) | | | | | | | | | | | |
|  |  | C | O | Na | Al | Si | P | K | Ca | Cr | Mn | Fe | Zn |
| 1 | 10 x 10 | 12.13 | 57.67 | 9.26 | 0.13 | 0.84 | 6.01 | 1.81 | 0.78 | 0.35 | 6.20 | 2.61 | 1.79 |
| 2 | 10 x 10 | 18.07 | 48.07 | 6.36 | 0.13 | 0.53 | 6.25 | 2.30 | 0.88 | 0.51 | 8.86 | 3.28 | 3.03 |
| 3 | 10 x 10 | 8.03 | 54.34 | 9.24 | 0.09 | 0.33 | 9.25 | 2.98 | 0.74 | 0.44 | 7.09 | 2.92 | 1.59 |
| 4 | 10 x 10 | 8.14 | 39.89 | 8.09 | 0.00 | 1.16 | 9.11 | 4.27 | 1.31 | 1.05 | 15.33 | 5.80 | 5.92 |
| 5 | 1 x 1 | 18.47 | 50.51 | 8.07 | 0.00 | 0.36 | 7.14 | 2.21 | 0.82 | 0.26 | 7.30 | 2.49 | 2.23 |
| 6 | 1 x 1 | 14.89 | 47.55 | 8.68 | 0.27 | 2.73 | 6.04 | 1.86 | 1.70 | 0.49 | 7.17 | 3.24 | 2.66 |
| 7 | 1 x 1 | 21.48 | 44.78 | 7.72 | 0.26 | 1.17 | 6.89 | 1.96 | 1.12 | 0.45 | 5.17 | 6.21 | 2.73 |
| 8 | 1 x 1 | 8.67 | 50.10 | 11.20 | 0.00 | 0.30 | 8.92 | 2.41 | 0.97 | 0.00 | 9.55 | 3.35 | 2.84 |
| 9 | 1 x 1 | 17.26 | 39.64 | 9.01 | 0.00 | 0.48 | 11.12 | 4.13 | 0.78 | 0.79 | 7.72 | 7.59 | 1.53 |
| 10 | 1 x 1 | 14.16 | 29.38 | 7.38 | 0.00 | 0.57 | 10.92 | 4.38 | 1.86 | 0.93 | 17.46 | 6.61 | 6.08 |
| Average & SD | | 14.13 ± 4.78 | 46.19 ± 8.19 | 8.50 ± 1.31 | 0.08 ± 0.10 | 0.84 ± 0.73 | 8.16 ± 1.95 | 2.83 ± 1.04 | 1.09 ± 0.40 | 0.52 ± 0.31 | 9.18 ± 4.02 | 4.41 ± 1.91 | 3.04 ± 1.64 |

Supplementary Table 2

|  |  |  |  |
| --- | --- | --- | --- |
| Compounds | Oxidation  state | Binding  energy (eV) | FWHM |
| MnO | Mn(II) | 640.77 ± 0.1 | 2.82 |
| Mn2O3 | Mn(III) | 641.22 ± 0.1 | 2.51 |
| MnO2 | Mn(IV) | 642.05 ± 0.1 | 2.28 |

Supplementary Table 3

|  |  |  |  |
| --- | --- | --- | --- |
| Species | Binding energy (eV) | FWHM | Atomic concentration (%) |
| Mn(II) | 640.80 ± 0.2 | 1.49 | 10.12 |
| Mn(III) | 641.26 ± 0.2 | 2.15 | 14.16 |
| Mn(IV) | 642.11 ± 0.2 | 2.62 | 75.72 |

Supplementary Table 4

(a)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Reference | Location | Exposure environment | Substratum | Reduction potential (V *vs* SCE) | Scan rate (mV sec-1) |
| Motoda et al. 1990 | Shizuoka prefecture, Japan | Estuary | S31600 | –0.05 | 0.33 |
| Dickinson et al. 1996 | Bozeman, MT, USA | Stream | S31600 | –0.1 | 0.16 |
| Dexter and LaFontaine 1998 | Lewes, DE, USA | Estuary | N08367 | 0.0 | 0.16 |
| Eashwar and Dexter 1998 | Lewes, DE, USA | Pond | S30400, S31600 and S44660 | 0.0 | 0.16 |
| Lewandowski et al. 2002 | Bozeman, MT, USA | Creek | S31600 | 0.0 | 0.16 |
| Marconnet et al. 2008 | Paris, France | Siene River | S31600 | –0.4 | 5.0 |
| Strom and Dexter 2009 | Lewes, DE, USA | Estuary | Chromium (99.96 %) | 0.2 and 0.0 | 0.16 |

(b)

|  |  |  |  |
| --- | --- | --- | --- |
| Reference | Standard | Concentration | Reduction potential (V *vs* SCE) |
| Ruppel et al. 2001 | Polymeric MnO2 | ~ 0.4 µmol cm-2 of MnO2 | 0.1 |
| Lewandowski et al. 2002 | Electroplated MnO2 | Not mentioned | 0.0 |
| Strom and Dexter 2009 | Polymeric MnO2 | 0.3 µmol cm-2 of MnO2 | 0.19 |
| Strom and Dexter 2009 | Synthetic Mn(III) complex | 490 ± 10 µmol of Mn | –0.04 |

Supplementary Table 5

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Immersion time (days) | Peak current density (µA cm-2) | Exchange current density (µA cm-2 ) | Measured reduction potential (Vmeas) | Calculated reduction potential (Vcal) |
| 14 | 4.51 | 0.41 | 0.067 | 0.227 |
| 30 | 10.63 | 0.67 | –0.005 | 0.218 |
| 62 | 33.70 | 1.29 | –0.078 | 0.205 |
| 95 | 132 | 2.60 | –0.198 | 0.188 |

Peak current density, exchange current density and measured reduction potential (Vmeas) are obtained from cathodic polarization data shown in Figure 7a.   
Calculated reduction potential (Vcal) is obtained using Butler-Volmer equation (Bard and Faulkner 2001) assuming a two-electron reduction from MnO2 to Mn(II); standard equilibrium potential for this system at pH 8.0 and with 90% of MnOx as MnO2 (based on XPS data in Figure 5b) is taken as 0.290 V *vs* SCE from Pourbaix diagram for manganese (Liang 1973).

**References**

Bard AJ, Faulkner LR. 2001. Electrochemical methods: Fundamentals and applications. 2nd ed. New York (NY): Wiley.

Liang CC. 1973. Manganese. In: Bard AJ, editor. Encyclopedia of electrochemistry of the elements. Vol. 1. New York (NY): Marcel Dekker; p. 348–398.

**Captions for Supplementary Figures**

**Supplementary Figure 1.** EDX spectra of biomounds characteristic of the natural biofilms formed in natural pond water obtained at 10 different sample locations. Spectra 1 to 4 were taken over 10 µm x 10 µm sample areas and spectra 5 to 10 over 1 x 1 µm sample areas.

**Supplementary Figure 2.** XPS high resolution C 1s spectra acquired on manganese oxide (MnO) standard as a function of etch time.

**Supplementary Figure 3.** XPS high resolution Mn 2p spectra for three monovalent manganese oxide standards. The binding energies for Mn 2p3/2 state of MnO [Mn(II)], Mn2O3 [Mn(III)] and MnO2 [Mn(IV)] are 640.77 ± 0.1 eV, 641.22 ± 0.1 eV and 642.05 ± 0.1 eV respectively. The Mn 2p spectrum of MnO [Mn(II)] displays characteristic satellite peaks for Mn 2p3/2 and Mn 2p1/2 states.

**Supplementary Figure 4.** Extrapolation of standard binding energies of manganese oxides with those of the freshwater biofilm sample to establish the best fit for Mn(II), Mn(III) and Mn(IV).

**Supplementary Figure 5.** XPS high resolution spectra exemplifying the C 1s, O 1s, and P 2p regions of the biomound mentioned in Figure 5.

**Supplementary Figure 6.** EPR spectra and the standard calibration curve for Mn(II). **(a)** EPR spectra for Mn(II) standards in the range from 1 µM to 100 µM showing strengthening of the sextet structure with concentration. **(b)** Calibration curve for Mn(II) based on the area of the fourth EPR signal (see Supplementary Text 2), demonstrating a high level of statistical validity. The 1 µM data was ignored here in view of difficulty in the calculation of the area from the fourth EPR signal.

**Supplementary Figure 7.** Selected EPR spectra plotted from Kim et al. (2011), consisting of synthetic Mn oxide (δ-MnO2), bacterial Mn oxides (*Bacillus* spore SG-1 and *Erythrobacter* SD-21) and field samples of freshwater and marine Mn nodules. The linewidth, designated by ΔH, is indicated for each spectrum.

**Supplementary Figure 8.** EPR spectra and ΔH values for biofilm, particulate matter and Mn(II) standard in this work. EPR spectra for biofilm and particulate matter show a perfect match and are also similar to particulate matter from Seine estuary by Boughriet et al. (1992).

**Supplementary Figure 9.** Cathodic polarization curves on UNS S30400, S31600 and S44660 stainless steels in pond water after 37 d revealing no discernible variation in the character of the curves among the three alloys.

**Supplementary Figure 10.** Cathodic polarization curves on UNS S30400, S31600 and S44660 stainless steels (labelled as 304, 316 and seacure in the image, respectively) obtained after biofilm development in a freshwater pond (100 d) located in Lewes, Delaware (USA) revealing no discernible variation in the character of the curves among the three alloys.

**Supplementary Figure 11.** Repetitive polarization curves recorded by Strom and Dexter (2009) showing the cathodic behaviour of a chromium coupon in Delaware estuarine waters. The two reduction peaks noticed by the investigators are highlighted.

**Supplementary Figure 12.** Cathodic polarizationbehaviour of a grade 316 (UNS S31600) coupon exposed to the natural pond water for 146 days. Note the occurrence of two reduction peaks (indicated by arrows) as reported by Strom and Dexter (2009).

**Captions for Supplementary Tables**

**Supplementary Table 1.** Elemental composition of natural freshwater biofilm recorded at 10 biomound locations. Spectra 1 to 4 are for 10 µm x 10 µm scan areas and spectra 5 to 10 for 1 x 1 µm scan areas. Average and standard deviation (SD) data for each element are shown at the bottom of the respective columns.

**Supplementary Table 2.** Binding energy and FWHM values of Mn 2p3/2 for manganese oxide standards.

**Supplementary Table 3.** Mn 2p3/2 binding energy and FWHM of pond water biofilm sample with atomic concentration (%) of Mn.

**Supplementary Table 4.** Literature references where manganese oxide reduction peak has been recorded by investigators in (a) natural biofilms at different geographic sites in various types of aquatic environments, and (b) various synthetic Mn oxide coatings under laboratory conditions.

**Supplementary Table 5.** Summary of electrochemical data relating to the cathodic polarization curves presented in Figure 7a. Here, the measured Mn reduction potential is put adjacent to the theoretical reduction potential calculated according to Butler-Volmer equation. The data show that the experimentally observed reduction potentials are more negative than the calculated values at any point of immersion and become even more negative with time.