

Supporting Information

**Protection coatings for corrosion control of mild steel using
phenolic polymeric deep eutectic solvents**

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Experimental Part – Formation of poly(DEMs) double protective layer

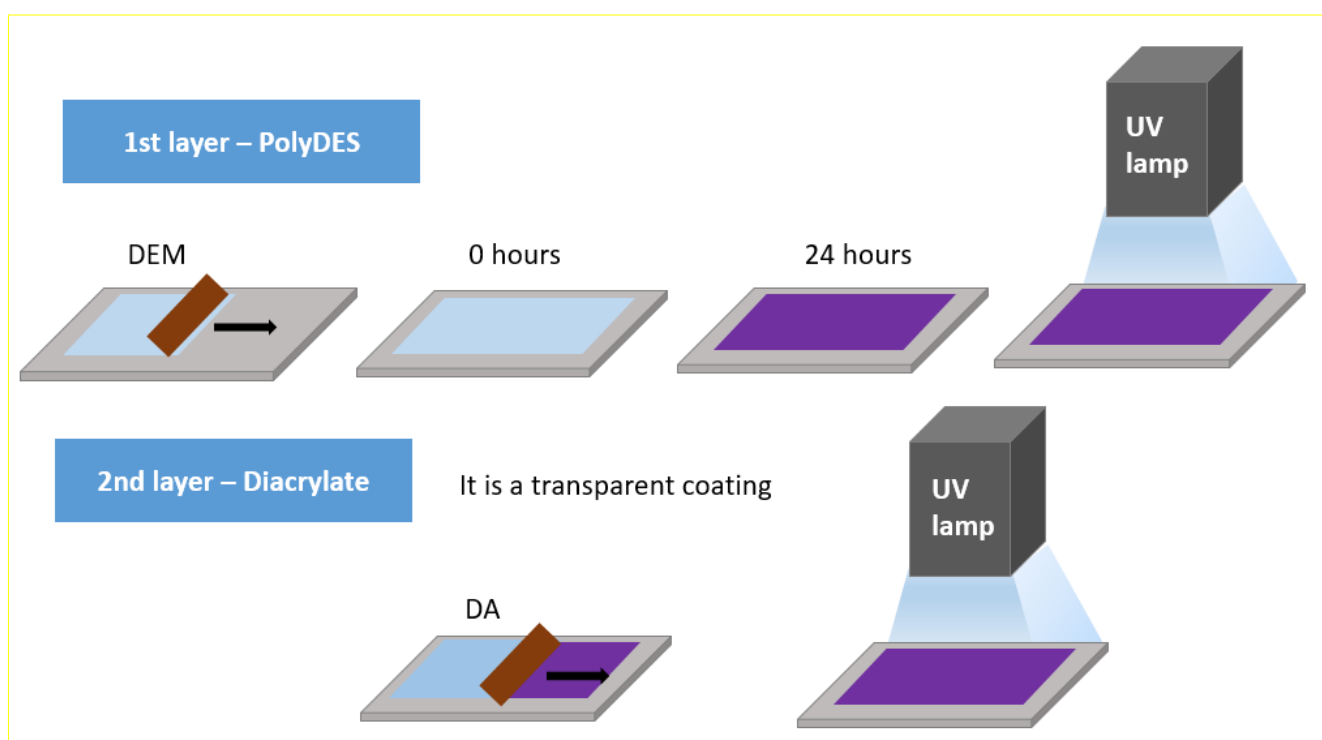


Figure S1. Scheme of the formation of protective coating by Doctor Blade technique.

Characterization of Deep Eutectic Monomers (DEMs)

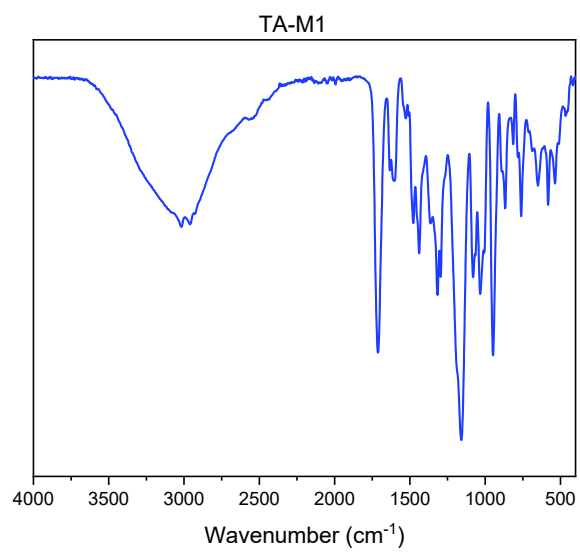


Figure S2. FTIR of TA-M1.

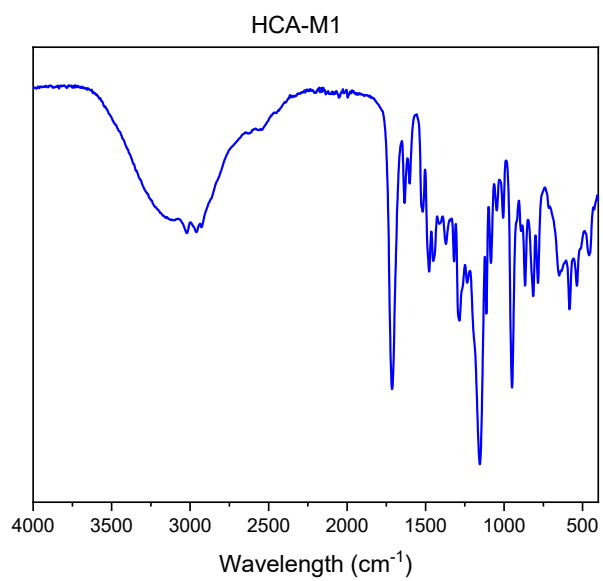


Figure S3. FTIR of HCA-M1.

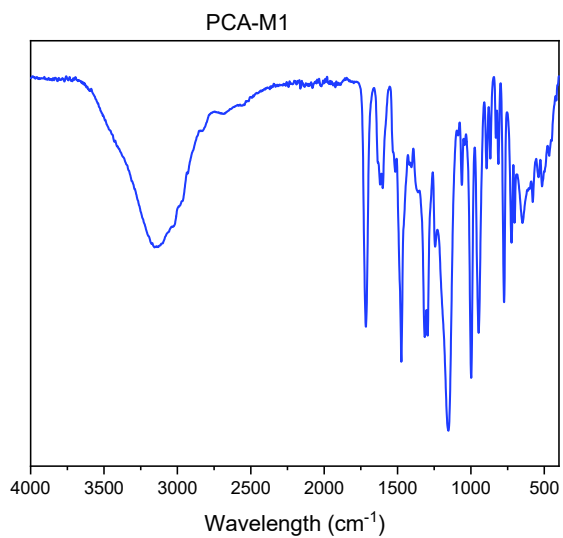


Figure S4. FTIR of PCA-M1.

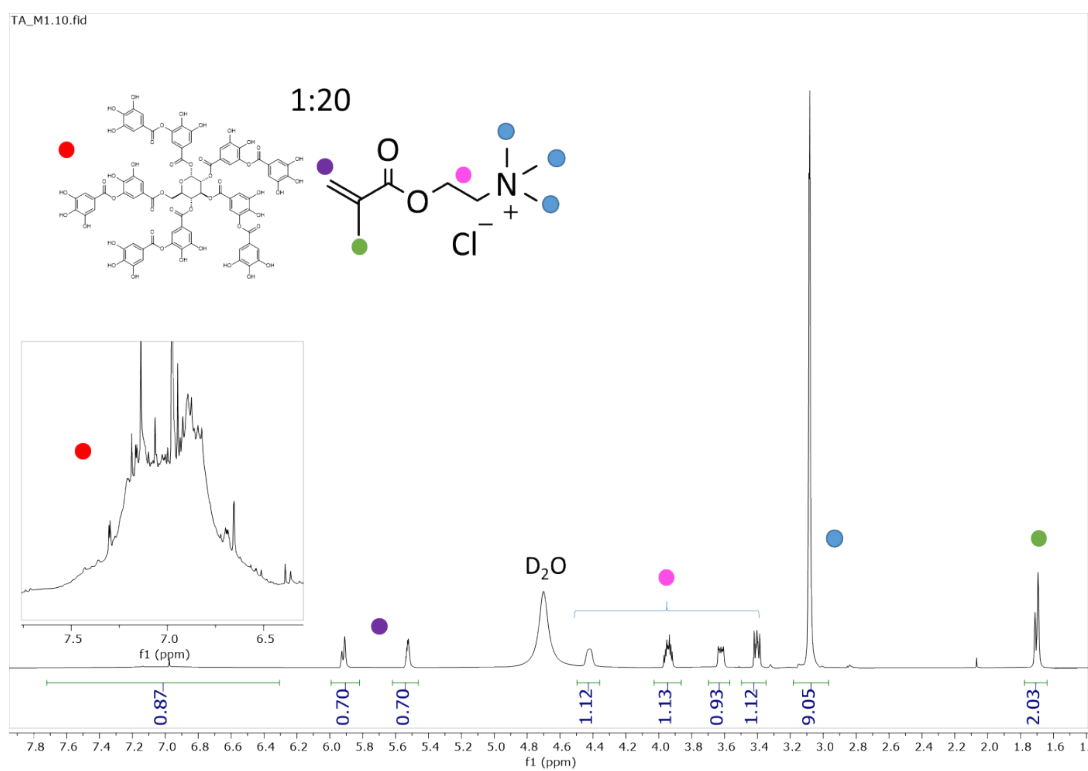


Figure S5. ¹H-NMR of TA-M1.

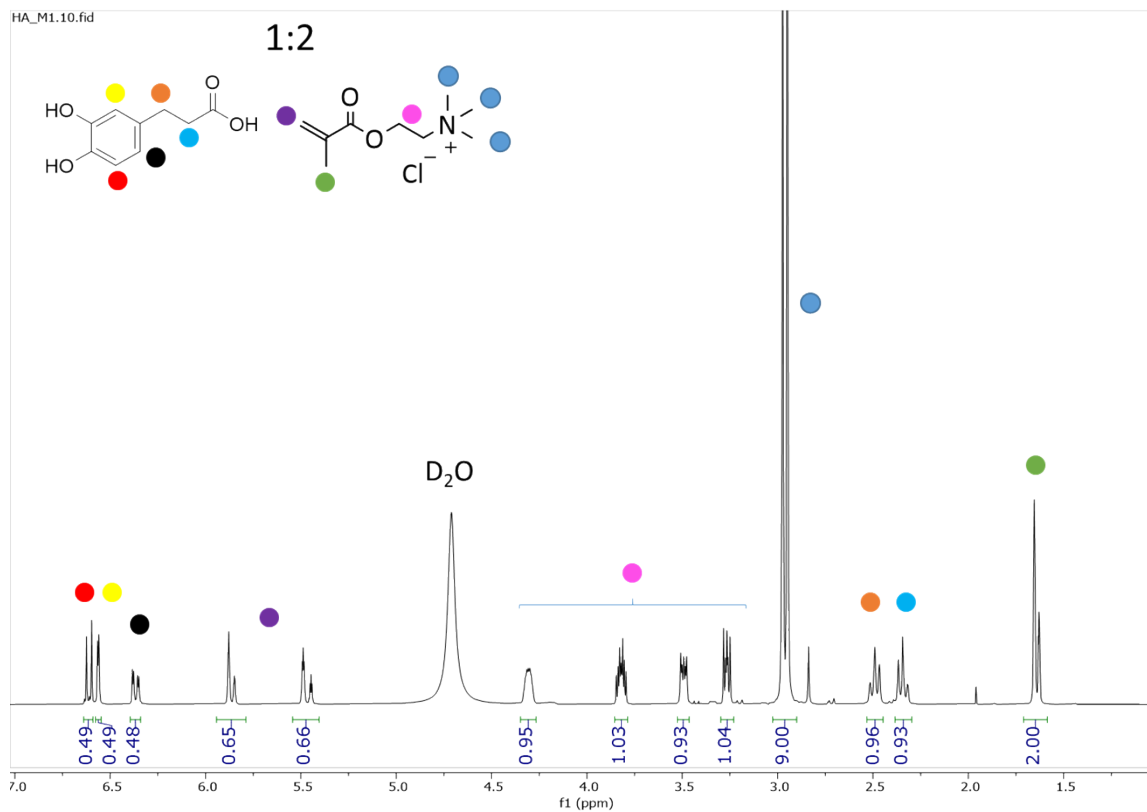


Figure S6. ¹H-NMR of HCA-M1.

Calculated Coating Thickness

Thickness of the applied coatings are measured with a calliper, before and after every layer is applied, by Doctor Blade technique. Table S1 summarizes the average values for the single poly(DEMs) coatings,

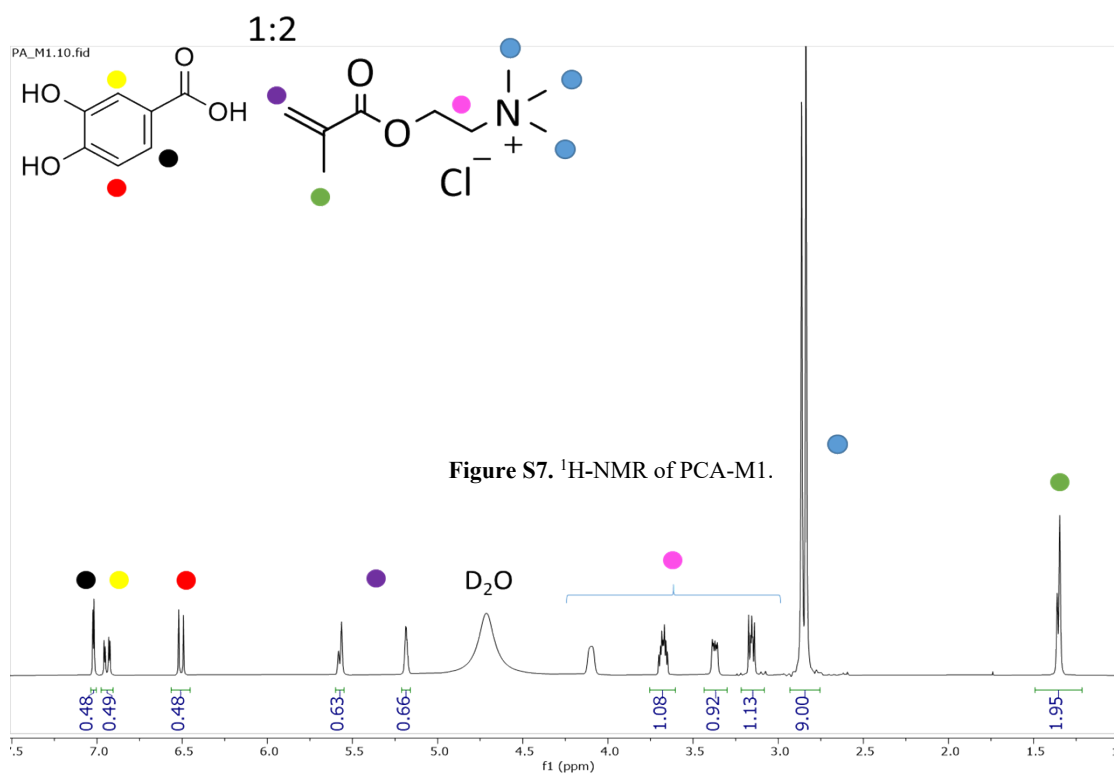


Figure S7. ¹H-NMR of PCA-M1.

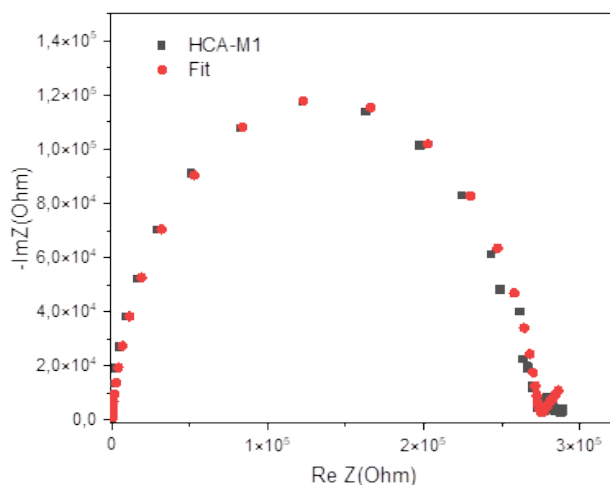
hydrophobic diacrylate coatings and for the double layer coatings, which is the sum of the previous two single coatings. According to the results, TA-M1 coatings is the thickest one, two times higher than other poly(DEMs) probably related to the higher viscosity TA-M1 deep eutectic monomer has due to the bigger HBD group. After UV-polymerization tannic acid based polymer results in an almost solid polymeric coating after the which looks brittle and rigid, whereas the PCA and HCA based polymeric coatings, are fixed to the mild steel surface. In addition, the higher phenolic content per molecule, makes tannic acid based DEM highly viscous, what leads into a more difficult application of the doctor blade technique and consequently, the obtained thicknesses are higher.

Material	Poly(DEM) coating (μm)	DA Coating (μm)	Double layer coating(μm)
TA-M1	85	53	138
PCA-M1	41	52	93
HCA-M1	44	58	106

Table S1. Average thickness of the applied coatings.

Electrochemical Characterization of polymeric coatings

Niquist plots are excluded from main text, because these polymeric coatings show high resistance, what results in a substantial impact on signal attenuation, and therefore, a distortion in obtained meaningless Niquist curves. However, for HCA-M1 polymeric coating at 24 hours, the fitting results are added in the Figure S8 and Table S2 for the Niquist plot. The circuit model was used is shown in Figure S9, where R_e , R_{coat} and R_{ct} correspond to the electrolyte resistance, pore resistance in the coating and charge transfer resistance at the interface respectively. It also presents two capacitive elements, which are fitted as constant phase elements.



First one represents the double layer capacitance at the interface (C_{dl}) and the other represents the coating capacitance (C_{coat}).

Figure S8. Nyquist plot and the corresponding fit for HCA-M1 coating at 24 hours.

Table S2: Resistance values obtained by fitting.

Parameter	Value
R_e	$0,67e^{-12}$ Ohm
R_{pore}	273321 Ohm
R_{ct}	72188 Ohm
C_{coat}	$4,89e^{-9}$ F.s ^(a-1)
C_{dl}	$0,113e^{-9}$ F.s ^(a-1)

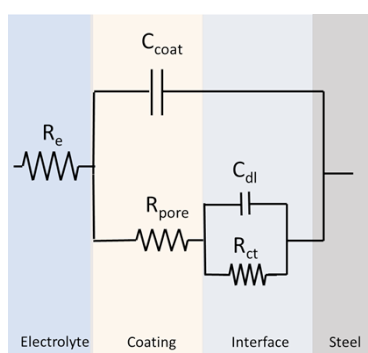


Figure S9. Equivalent circuits used for numerical fitting of EIS data.

Understanding the nature of the complex formation through the use of DES as corrosion inhibitors in aqueous solution

Table S3. Evolution of pH in immersion tests

Sample	Day 0	Day 1	Day 2	Day 7
Blank	6	6	7	6
HCA-M1	3	3	3	3
PCA-M1	4	3	3	4
TA-M1	3	2	2	2

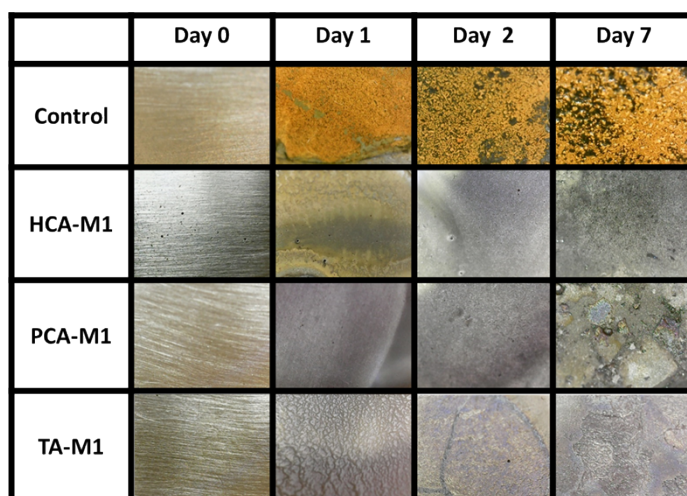


Figure S10. Images of steel immersed in DEM solution, taken by optical microscope.

Polyphenol Deep Eutectic monomers as corrosion inhibitors in aqueous solution

The corrosion of AS1020 steel in the presence of aqueous electrolytes with and without DESs was evaluated using electrochemical impedance spectroscopy and potentiodynamic polarization techniques, as well as, by analyzing the surface corrosion with an optical microscope (**Figure S10**). **Figure S11** shows the Bode plots for the steel samples tested in NaCl and DES solutions. The concentration of DES increased from 3 to 10 mM in the solution. From the electrochemical results, after 24 hours of immersion in the respective solutions, all DESs have a protective effect on the steel surface. The impedance modulus in all cases is higher than the impedance modulus of the steel in 0.1 M NaCl solution, with values about $10^{3.5} \Omega\text{cm}^2$, while the impedance modulus of the control material is around $10^{2.95} \Omega\text{cm}^2$. The concentration of DESs has no significant effect on the electrochemical response.

The corrosion protection is also reflected in the potentiodynamic polarization curves (**Figure S11**). The values of the corrosion parameters calculated from the polarization curves, such as the corrosion current density (I_{corr}), corrosion potential (E_{corr}), and corrosion efficiency, are listed in **Table S4** at 25°C and a concentration of 10 mM DES.

From the data shown in **Table S4**, it is clear that the effect of adding 10mM DESs and forming a complex of DES-Fe on the mild steel surface shows a lower corrosion current of the mild steel in this aggressive medium. It is reflected in the corrosion inhibition efficiency value of about around 50% for TA -M1 and 30% for HCA-M1 and PCA-M1, respectively. This is in good agreement with the corrosion protection behavior shown in the optical images.

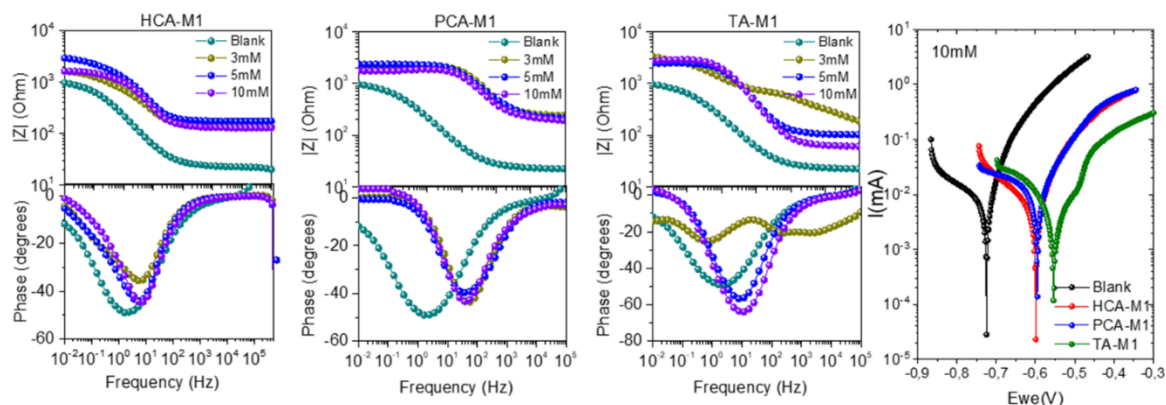


Figure S11. a) Bode plots for HCA-M1 b) Bode plots for PCA-M1 c) Bode plots for PCA-M1 d) Polarization Curves for all the DEMs in solution.

Table S4. Results of corrosion current densities (I_{corr}), corrosion potential (E_{corr}) and corrosion efficiency (% η).

Sample	E_{corr} (mV)	I_{corr} (μA)	% η
Steel	-725	1.89	-
HCA-M1	-596	1.33	30%
PCA-M1	-594	1.38	26%
TA-M1	-552	0.97	48%

Quantification of the dissolved iron ions

In DEMs immersion tests, there is no coating applied in the surface and consequently, the iron concentration leached from the steel surface to the solution is much higher. Tannic acid based solutions show the lowest iron concentration, which can be related to the fastest complexation of the phenolic solution with the iron ions, in the top of the steel surface, forming a purple layer (**Figure 7**) that blocks the iron molecules leaching from the steel to the solution. The same effect is observed for HCA, where the complex is formed after the first day, which also obstructs the remove of iron ions from the steel to the phenolic solution. However, the complex formation in the PCA-based experiment is slower, takes 2 days to start forming the complex and consequently, the protective layer in the surface takes longer to be formed, what leads to higher iron content in

the solution. All these results are quantified by ICP/MS technique, and summarized in **Table S5**.

Table S5. Concentration values of the remaining Iron in the supernatant solutions calculated by ICP/MS).

Sample	Fe ppm	error
Blank immersion	281ppm	2ppm
PCA immersion	450ppm	2ppm
HCA immersion	358ppm	2ppm
TA immersion	347ppm	2ppm