



Biomolecules as a sustainable protection against corrosion of reinforced carbon steel in concrete



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ABSTRACT

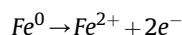
The aim of the present study is to evaluate the biomolecules which can be potentially used as an eco-friendly inhibitor of steel corrosion in concrete. Biomolecules used in this study are a new class of compounds produced from bacteria cells. The inhibition effect in simulated concrete pore solution was demonstrated using classical electrochemical measurements, microscope observations and X-ray Photoelectron Spectroscopy (XPS). The decrease in corrosion current density was pronounced after adding 1 g L⁻¹ of product in the simulated concrete pore solution. Linear Polarization tests and Electrochemical Impedance Spectroscopy showed the relatively good inhibition efficiency properties (≈ 58.6%) of BMs. Moreover, XPS analysis and Scanning Electron Microscopy (SEM) observations shown that this type of biomolecules seems to be a film-forming mixed type inhibitor.

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1. Introduction

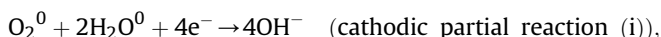
The deterioration of infrastructural installations such as bridges and other concrete constructions becomes very important. In case of collapses due to corrosion, the people safety is in risk. Some examples of such disasters in the history can be detailed, like Highway Mississippi Bridge collapse in Minneapolis, the collapse of a Berlin Congress Hall roof (caused by hydrogen-induced stress corrosion cracking of pre-stressed steel) and the collapse of suspended ceilings in swimming halls in Denmark (due to chloride-induced stress corrosion cracking) (Schmitt et al., 2009). Although corrosion of the reinforcement is not the only one cause of deterioration in civil engineering, but one of the main contributors.

The fundamental meaning of corrosion is the return of metal to its natural state. The authors (Söylev and Richardson, 2008) used a comparison of the corrosion phenomena with the action in flash battery. The body of corroding steel can be represented as a mixed electrode composed for millions of anodes and cathodes and the concrete pore water play the role of electrolyte.

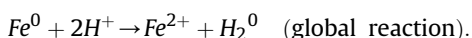
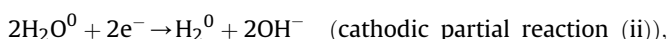


(anodic partial reaction or the reaction of iron dissolution),

The oxygen diffuses into the concrete porous system, dissolves in the pore solution and finally reaches the surface of the steel. On this surface the oxygen will be reduced to hydroxide ion [OH⁻] as in following electron reaction:



This reaction could be associated with an additional cathodic reaction occurring at the steel surface in concrete in relation with the evolution of the chemical composition of the electrolyte at the steel vicinity.



Protection of the steel rebars against the corrosion is ensured by the formation and the stability of the passive layer mainly

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composed of iron oxide based species in the high alkalinity media (pH = 12–13) of concrete (Landolt, 1993). The penetration of carbon dioxide and/or of chloride anions can damage the protective layer formed on the steel surface, leading to local corrosion of steel rebars (Landolt, 1993). Then the corrosion phenomena will slowly progress up to the complete deterioration of steel reinforced concrete.

The protection methods for these systems were widely reported in literature over the last five decades (Cigna et al., 2003). Since 1970, the use of non-corroding fusion bonded epoxy-coating for reinforcement and specially designed low-permeability concrete (low w/c ratio, latex-modified concrete, etc) was observed. Otherwise, the main topic was the development of electrochemical rehabilitation methods, their limits and their effectiveness. The well-known technique is the cathodic protection (by an impressed current using a carbon mesh anode or sacrificial cathodic protection by thermal zinc spraying). Another technique reported in the literature is the use of corrosion inhibitors for reinforced concrete (Baghabra et al., 2003). Their use is more attractive because of their easy-handling (“mixed-in” or “migrate-through”) and because of their low cost comparing with cathodic protection. Recently, there is sufficient variety of inhibitors available on the market, i.e. commonly used, such as nitrite salts, aminoalcohols (AMAs) and sodium monofluorophosphates (MFPs) (Bertolini et al., 2013).

There is always a contradiction in the opinions about the use of inhibitors that were developed, because of their toxicity for humans and the ability to degradation in environment (Patni et al., 2013). Actually, there is a need to develop new so-called “green solutions” to prevent corrosion in concrete.

For instance, in civil engineering the accent is made principally on the use of recycled aggregates (Mefteh et al., 2013) and waste resources, such as copper slag (Thomas and Gupta, 2013) and marble waste (André et al., 2014; Uygunoğlu et al., 2014) in the concrete. These works principally focus on reducing the pollution while recycling waste materials and to economize the natural aggregates (70% by weight of the concrete) and not on the corrosion rate reduction.

Currently, the naturally occurring molecules with ability to prevent corrosion are the focus of studies in different corrosion fields (Raja and Sethuraman, 2008). It is well known that efficiency of these eco-friendly corrosion inhibitors is related to the adsorption on metal surfaces of polar functions with S, O or N atoms in their molecules (Malik et al., 2011). It has been reported that the extracts of *Lannea coromandelica* presents a good inhibitor efficiency in sulfuric solution (0.1 M) for mild steel (Muthukrishnan et al., 2013); the extract of *Salvia officinalis* leaves and *Aloe vera* inhibits the corrosion of 304 stainless steel in 1 M H₂SO₄ (Mehdipour et al., 2015), and 2 M HCl (Soltani et al., 2012). *Azadirachta indica* proves its efficiency in sulfuric acid 1 M for copper (Valek and Martinez, 2007) by chemisorption mechanism; *Jasminum nudiflorum* shows good properties for aluminum in 1 M hydrochloric acid (Deng and Li, 2012).

Regarding to civil engineering, it was found that the extract of *Bambusa arundinacea* in concrete presents a pore blocking effect and leads to a stabilization of silicate hydrates (C–S–H) ability (Asipita et al., 2014). Other study has shown that *Vernonia amygdalina* has a synergetic inhibition effect with calcium nitrite in contaminated concrete exposed to a 0.5 M chlorides media (Loto et al., 2013).

Another class of biodegradable compounds is biomolecules (BMs) derived from yeasts, fungi and bacteria cells. Akcil et al. (2015) report that the biocompatibility of BMs can offer advantages in many applications, but need to be well-studied in long-term because their antibiotic properties can caused the impacts on bacterial communities, i.e. the ecosystem. Despite the criticism,

it has been demonstrated that BMs have the properties to metal removal from marine contaminated sediments (Mulligan et al., 2001).

In view of the fact that today there is a little consideration towards the study of “green inhibitors” dedicated for reinforced concrete; we propose to focus on the use of BMs in order to improve the corrosion resistance of steel rebars in concrete. The aim of our study was to demonstrate that BMs offer the possibility to replace conventional chemical inhibitors for concrete. Their effectiveness against corrosion was validated using accelerated corrosion tests, BMs property of “film-forming” was studied using XPS (X-ray Photoelectron Spectroscopy).

2. Materials and methods

2.1. Samples and solutions

The samples were disks cut from real rebars kindly provided by PLBArmatures (groupe Allians-Snaam, Carquefou, France). The chemical composition of the carbon steel was in accordance with “NF EN 10080” (Carbon Steel for Reinforcement in Concrete) and is presented in Table 1. Fig. 1 presents the ferritic-pearlitic microstructure deduced from nital etching of the low alloy steel, it can be observed that the density of pearlite grains is very low compared to the density of ferritic grains.

The geometrical surface area exposed to the solution was about 0.26 cm². Before electrochemical measurements, samples were mechanically polished with SiC papers up to grade 1200. Then they were degreased in ethanol, and three times in distilled water, and finally dried under an air flow.

The solution used for electrochemical tests was simulated concrete pore solution with addition of chlorides (SCP composition (pH = 12.4) (g/L): Ca(OH)₂ (2.0), NaCl (29.25). This addition of chlorides was 10 times more important than real critical chloride threshold (C_{th}), to initiate the corrosion of steel in concrete (Elshami, 2012). All electrochemical tests were carried out in stagnant conditions at room temperature.

The biomolecules (BMs) of lipopeptide nature extracted from Gram-negative bacteria cells were provided by Thierry Meylheuc (INRA, Massy) and was prepared as described previously in Meylheuc et al. (2001). The 1 g L⁻¹ of BMs was used in the electrochemical tests.

2.2. Electrochemical measurements

The electrochemical measurements were performed with a three-electrode cell with a volume of 0.15 L. The working electrode (WE) was carbon steel samples, the counter-electrode (CE) was a platinum wire with a large surface area, and the reference (Ref) electrode was a saturated calomel electrode (SCE: 0.241 V vs SHE).

Firstly, the corrosion potential (E_{corr}) was measured during 20 h of immersion. The linear polarization method was applied every 30 min, by linear polarization of ±20 mV around the E_{corr} and with a sweep rate of 0.2 mV s⁻¹. Electrochemical impedance diagrams were plotted at E_{corr} after 20 h of immersion, with a frequency domain ranging from 10⁵ Hz to 10⁻³ Hz, 5 points per decade, and amplitude of 10 mV peak-to-peak.

Table 1
Chemical composition of the rebar steel (wt. %).

C	S	P	N	Cu	Fe
0.240	0.055	0.055	0.014	0.850	balance

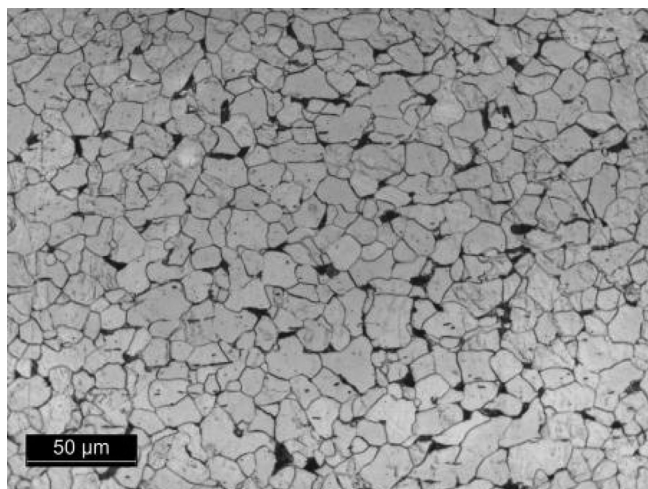


Fig. 1. Microstructure of low carbon steel: the light colored ferrite region and the dark pearlite regions.

All the experiments were performed at room temperature in stagnant conditions. Electrochemical data was obtained from at least three separate experiments. Electrochemical tests and measurements were performed with a VSP potentiostat (Bio-Logic, France) and EC-Lab software v.10.37.

2.3. XPS analysis

XPS spectra were obtained on a Kratos Nova (IMN, Nantes, France) equipped with a monochromated Al $K\alpha$ X-Ray source ($h\nu = 1486.6$ eV). Analysis was carried out using an accelerating voltage of 15 kV and a current of 10 mA. The binding energy was adjusted using a pure silver metal ($Ag\ 3d_{5/2} = 0.55$ eV). All the survey spectra were performed at pass energy of 160 eV to identify all the elements present in the analyzed specimens. Chamber pressure before introduction of X-ray source was kept at 6×10^{-6} Pa and during analysis was 9×10^{-6} Pa. To control charging of the samples, the charge neutralizer filament was used during all experiments. The following sequences of spectra were recording: survey spectra (2 points per specimen), Fe 2p, C 1s, O 2s, N 1s. Binding energies were determined by reference to the C 1s component of C–C, H set at 285 eV.

2.4. Scanning electron microscopy

After immersion in SCP solution without and with biomolecules, carbon steel specimens were coated by a thin film of gold by sputtering, and then micrographs were taken by SEM (Brucker, GmbH). The energy of the acceleration beam employed was 10 kV and a working distance was 10 mm.

3. Results and discussion

3.1. Corrosion inhibition efficiency of biomolecules deduced from electrochemical tests

From Fig. 2, the evolution of E_{corr} as the function of immersion time in corrosive solution can be seen. We can observe the same shape for both curves (with and without biomolecules) with a potential drop from -0.36 V vs SCE to -0.52 V vs SCE. In the absence of biomolecules, the stationary state is reached with the value of -0.55 V after 6000 s. In the presence of biomolecules,

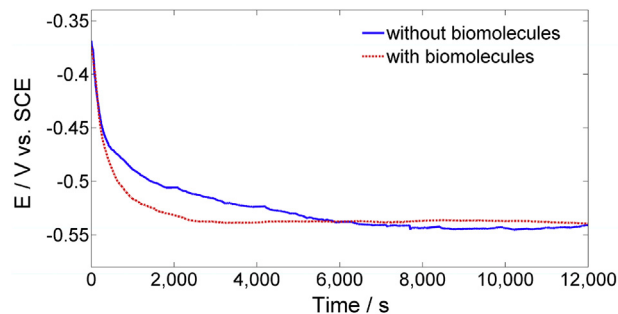


Fig. 2. Corrosion potential of carbon steel (for rebars in concrete) vs. time of immersion in SCP solution without and with addition of biomolecules.

the stationary state value of about -0.54 V is reached after 2000 s. No significant difference was observed between both evolutions of open circuit potential. It is well known that mixed inhibitors reduce the rate of the two partial reactions without modification of the corrosion potential. Linear polarization tests were carried out and polarization curve $i(E)$ were presented on Fig. 3.

From Fig. 3, it can be seen that the cathodic branch of polarization curve as well as the anodic one are reduced by the presence of biomolecules. Thus, the BMs influence the two partial corrosion reactions and can be considered as mixed type inhibitor. Therefore, we can deduce that protection against corrosion occurred by creation of barrier on the carbon steel surface. Visual observations confirm the electrochemical data as the surface seems less attacked during the addition of inhibitor.

Moreover, the measurements of polarization resistance R_p every 1800 s during a total immersion of 240,000 s were an important part for the evaluation of the inhibition efficiency of carbon steel surface against corrosion with time. The evaluation of R_p on carbon steel surface without and with BMs during the immersion tests is presented in Fig. 4. Fig. 4 shows that values of R_p are higher with addition of BMs. In this case, it can be seen a “little hump” at the beginning of the curve and up to 25,000 s, it was also present in the other tests (not shown here). This may be due to the reaction of the BMs with chloride ions in the test solution or to the establishment of stationary state of BMs in solution.

As it can be seen from Fig. 4, corrosion inhibition efficiency (IE) of the BMs can be expressed. This parameter was calculated from the R_p values at the stationary state, using Eq. (1) and is equal to 58.6%.

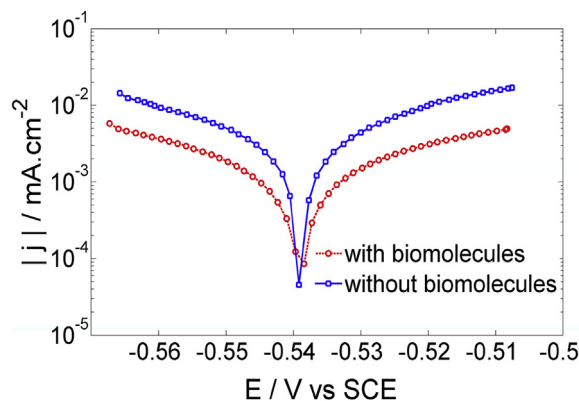


Fig. 3. Polarization curves of carbon steel in aggressive SCP media without and with BMs.

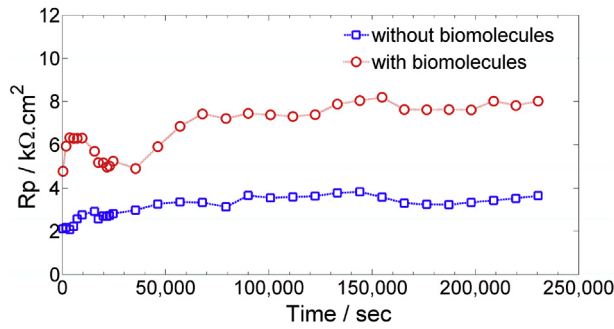


Fig. 4. Evaluation of polarization resistance with time, during the immersion in aggressive solution: without and with biomolecules.

$$IE(\%) = \frac{Rp_{biomolecules} - Rp_{BLANK}}{Rp_{biomolecules}} \cdot 100\%, \quad (1)$$

where $Rp_{biomolecules}$ et Rp_{BLANK} are the values of resistance of polarization with and without biomolecules.

Electrochemical Impedance Spectroscopy (EIS) was also performed in order to validate the inhibition efficiency. The electrochemical impedance Z is a complex number depending of the ac-frequency.

Fig. 5 shows the Nyquist diagrams in the complex plane (opposite of the imaginary part of the impedance $-Z_j$ vs real part of the impedance Z_r) plotted at E_{corr} after 20 h of immersion in corrosive media, without and with biosurfactant BMs. The diagrams present two capacitive loops at middle frequencies (MF) and very low frequencies (LF) as presented in Fig. 5. After 20 h of immersion, we can assume that the first capacitive loop could be associated to the degradation of the low alloyed steel and the low frequency loop would give information of the formation of the corrosion product film on the electrode surface.

The size of the MF loop is significantly increased with the presence of BMs. This result, likewise XPS study (presents below), can declare about the protection against corrosion due a previous BMs adsorption and changes in the composition of oxide layer on the carbon steel surface.

3.2. XPS results

The XPS measurements were carried out after electrochemical test (20 h of immersion) to obtain the information about biomolecules adsorption on the surface. Fig. 6 represents the XPS survey spectrum for the carbon steel material without and with biomolecules. For the spectrum for blank carbon steel, it is observed that the signal of iron (Fe 2p), oxygen (O 1s) and carbon (C 1s) are intensified compared to the remaining elements; and there is no nitrogen (N 1s) signal. For the survey spectrum, which represents protected against corrosion steel surface, the iron (Fe 2p) signal is less significant, and the presence of N 1s is clearly observed.

The decrease of intensity for a core level of iron indicates the adsorbed layer on the surface (Chevalier et al., 2014). Moreover, the important nitrogen signal is a fingerprint of the presence of BMs, as well as, an increase of oxygen and carbon peaks. It must be mentioned that the XPS survey spectra represents only qualitative information and for the further analysis the high resolution peaks must be studied.

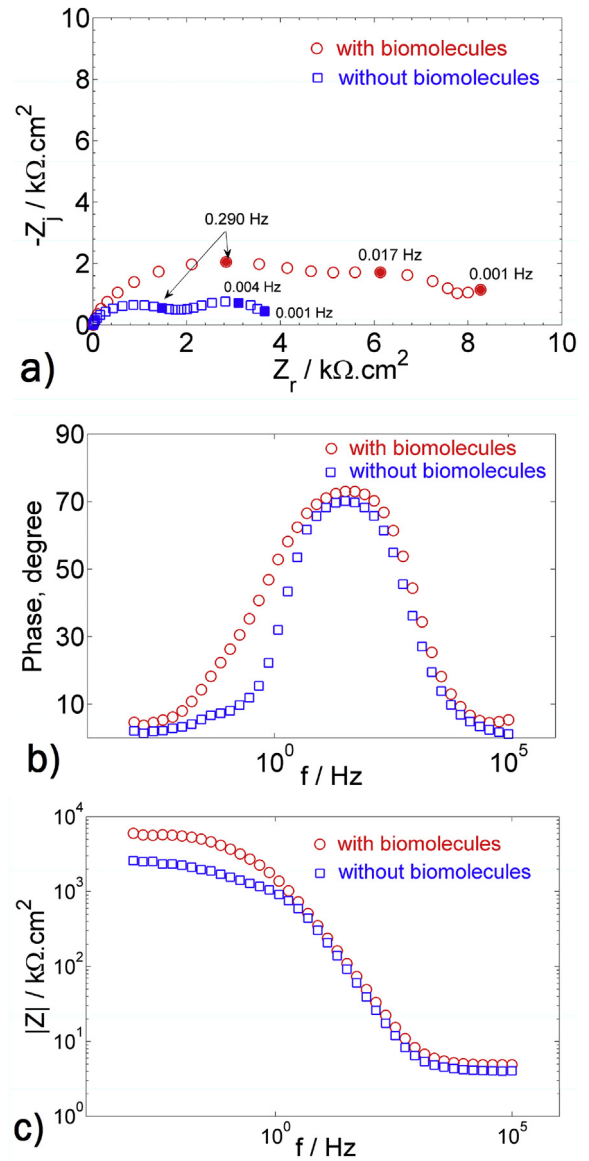


Fig. 5. Experimental Electrochemical Impedance Spectroscopy Diagrams: 5 a) Nyquist diagrams and b), c) Bode representation of carbon steel samples plotted at E_{corr} after 20 h of immersion in simulated contaminated with $[Cl^-]$ concrete pore solutions, (□) without and (○) with BMs.

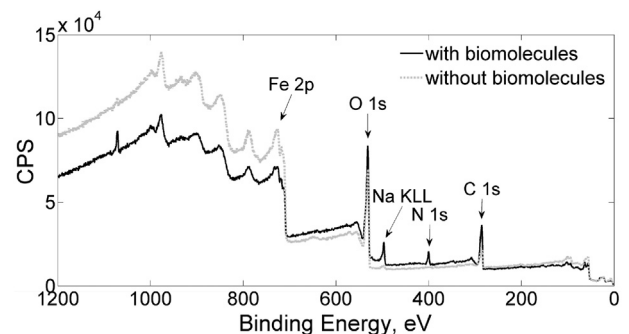


Fig. 6. XPS survey spectra for the carbon steel specimens after corrosion tests: without (dashed line) and with biomolecules (full line).

3.3. SEM study

The SEM images of carbon steel surfaces were carried out to establish a visual aspect of inhibition. Fig. 7 shows the surface before (a) and after 20 h of immersion in solution with an addition of BMs (b). Fig. 7(b) also demonstrates that BMs have a strong tendency to adhere at the carbon steel surface and can be regarded like a good inhibitor against the steel corrosion in the presence of chloride ions.

The BMs particles block both reaction sites: anodic and cathodic, by the creation of the zones of ohmic resistance between the carbon steel surface and electrolyte without changing the chemical conditions leading to the formation of corrosion products. In other words, these zones slow down galvanic reactions and the loss of electrons from the steel surface that leads to development of corrosion.

4. Conclusions

Following conclusions have been drawn from the present study:

- The biomolecules with the concentration of 1 g L^{-1} are demonstrated inhibition efficiency against corrosion of carbon steel in simulated concrete pore solution;
- Linear Polarization tests and Electrochemical Impedance Spectroscopy showed the relatively good inhibition properties ($\approx 58.6\%$) of BMs. The inhibition properties of BMs increase slightly with time. It was shown that inhibitor can be considered as the mixed type inhibitor due to the influence on the two partial corrosion reactions;

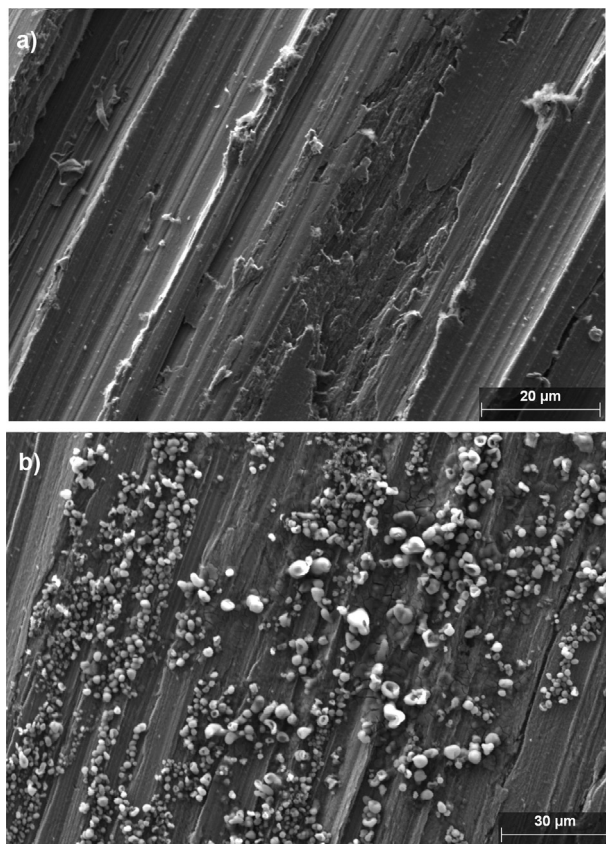


Fig. 7. SEM micrographs of the carbon steel surface: a) before immersion in solution (SE MAG: $\times 600$); b) after immersion ($t = 20 \text{ h}$) in solution with BMs (SE MAG: $\times 1000$).

- The adsorption of BMs on the carbon steel surface was investigated using XPS surface analysis. The presence of N 1s core level for the spectra recorded from carbon steel after the immersion in SCP with BMs is a fingerprint of BMs adsorption;
- SEM analysis also demonstrated the different surface morphology after the immersion in solution containing BMs.

Nevertheless, the validation of inhibition properties of BMs in the real mortar-embedded rebars is needed and will be developed in future study. In parallel, impact on the ecosystems must be performed before the full-scale applications BMs.

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