

## Journal Pre-proofs

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PII: S1385-8947(20)31988-4  
DOI: <https://doi.org/10.1016/j.cej.2020.125860>  
Reference: CEJ 125860

To appear in: *Chemical Engineering Journal*

Received Date: 17 February 2020  
Revised Date: 8 April 2020  
Accepted Date: 9 May 2020

Please cite this article as: A. Dehghani, G. Bahlakeh, B. Ramezanzadeh, Designing a novel targeted-release nano-container based on the silanized graphene oxide decorated with cerium acetylacetonate loaded beta-cyclodextrin ( $\beta$ -CD-CeA-MGO) for epoxy anti-corrosion coating, *Chemical Engineering Journal* (2020), doi: <https://doi.org/10.1016/j.cej.2020.125860>

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# Designing a novel targeted-release nano-container based on the silanized graphene oxide decorated with cerium acetylacetonate loaded beta-cyclodextrin ( $\beta$ -CD-CeA-MGO) for epoxy anti-corrosion coating

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## Abstract

For the first time, cerium acetylacetonate (CeA) was encapsulated in a novel controlled-release nano-carrier based on the beta-cyclodextrin ( $\beta$ -CD)/graphene oxide (GO) for effective mitigation of the metal corrosion. The outcomes of the FT-IR, XRD, Raman, and UV-Vis spectroscopies displayed successful interactions of the  $\beta$ -CD-CeA with the surface of GO nano-particles. Tafel curves proved that in the presence of the  $\beta$ -CD-CeA/modified GO (MGO) nano-particles, the corrosion current density of metal was diminished from  $7.62 \mu\text{A}\cdot\text{cm}^{-2}$  (for the uninhibited sample) to  $0.08 \mu\text{A}\cdot\text{cm}^{-2}$ . The EIS results achieved in the solution phase studies demonstrated that the total resistance ( $R_t$ ) increased from  $1469 \Omega\cdot\text{cm}^2$  (for the uninhibited sample) to  $12083 \Omega\cdot\text{cm}^2$  (nearly 88% efficiency) after 48 h of exposure. The observations derived from FE-SEM, EDS, and mapping investigations confirmed the formation of anti-corrosive film over the metallic substrate in the solution phase. After nano-particles incorporation into the epoxy (EP)

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matrix, the EIS evaluations from the scratched EP revealed that the  $R_t$  increased from 19430  $\Omega\cdot\text{cm}^2$  (for neat EP) to 59817  $\Omega\cdot\text{cm}^2$  after 24 h of exposure to the 3.5% NaCl solution, evidencing the effective corrosion inhibition characteristics of the designed composites. Besides, the FE-SEM and EDS/mapping analyses ensured that the defected zone of the epoxy coating was protected with a highly dense inhibitive film. EIS measurements clarified that the corrosion resistance of the intact neat EP coating (92  $\text{M}\Omega\cdot\text{cm}^2$ ) improved significantly after the incorporation of  $\beta$ -CD-CeA-MGO particles ( $\sim 5840 \text{M}\Omega\cdot\text{cm}^2$ ), demonstrating the coating barrier performance enhancement. Furthermore, the DFT modelings strongly affirmed the CeA and  $\beta$ -CD affinity towards the epoxy resin.

**Keywords:** Controlled/targeted release; Self-healing; Smart coating; Beta-cyclodextrin; Mild steel; Epoxy coating; Raman

## 1. Introduction

Recently, due to significant adhesion (to the substrates), high crosslinking density, and excellent thermal and chemical resistances, epoxy (EP) coatings have been introduced as one of the most favorable thermosetting polymers in different industrial applications [1]. However, recent reports displayed that the protection performance of the EP coating can be dramatically diminished in long-term exposure to the corrosive electrolyte, which is related to the electrolyte diffusion into the coating through defects [2, 3]. Besides, most of the epoxy-based materials provide poor fracture and show low resistance against crack propagation [4]. Presently, the inclusion of pigments, e.g., clay [5], ceramic [6], carbon nanotubes [7], and graphene [8] into the EP polymeric matrix is one of the most promising and cost-effective approaches for improving its protection performance in exposure with the aggressive solutions.

Nowadays, graphene particles become a useful and highly popular material in industrial applications due to their high surface area, excellent mechanical properties, high thermal stability, and good electrical conductivity [9]. High Young modulus (1100 GPa) and tensile strength (130 GPa) make the graphene as a sufficient particle for the construction of polymeric composites in a wide range of industrial usages [10, 11]. Earlier studies proved that the graphene layers' existence in the polymeric epoxy matrix provides notable enhancement in corrosion protection performance [12]. Graphene oxide (GO) is a 2D hexagonal structure decorated with hydroxyl, epoxide, carboxylic, and carbonyl functional groups in edges and basal planes [13]. The GO has been mainly employed for the construction of supercapacitors [9], sensors [14], drug delivery systems [15], and solar cells [16]. In recent days, the GO was introduced as high-performance barrier and anti-corrosive nano-pigment against diffusion of water and aggressive ions [17]. However, the strong interactions between the GO layers lead to poor dispersion of particles in the EP matrix, causing reduction in coating barrier properties [18]. It must be considered that the self-healing behavior is not available even after introducing the GO layers in epoxy coating. In order to improve the GO sheets dispersion level in the EP matrix and to provide self-healing ability, different kinds of physical and chemical modifications of GO sheets have been suggested [19, 20].

The modification of GO sheets via pigments is one of the easiest and popular ways of providing self-healing ability in the polymeric-based composites. However, the direct loading of pigments into the polymeric matrix causes destructive effects on the coating structure in long terms [21, 22]. Additionally, hazardous impacts of the commercial chromate and phosphate-based pigments were approved in the recently published papers [23]. A controlled-release strategy is a promising approach, which can be applied for the indirect connection of the pigments with the EP matrix.

For this aim, different types of nano-containers, i.e., carbon nanotubes (CNTs) [24], halloysite nano-tubes (HNTs) [25], layered double hydroxides (LDHs) [26], and organic nano-containers [25, 27] were introduced for pigments encapsulation. The encapsulated anti-corrosive agents can be released from the nano-containers as a function of immersion time that provides desirable protection performance in long terms.

Because of their cyclic geometry, cyclodextrins (CDs) have high potency to emerge as appropriate nano-carriers for a variety of inhibitive compounds. The CD molecules are produced by glucopyranose units with the help of 1,4-glycosidic linkage [28]. Nowadays, three types of CDs have been recognized [29]: (i) alpha-cyclodextrin, which is constructed by six glucopyranose units; (ii) beta-cyclodextrin, which is resulted from the seven glucopyranose units; and (iii) gamma-cyclodextrin which can be produced from the eight glucopyranose units. The beta-cyclodextrin ( $\beta$ -CD) has been employed more than others owing to the larger cavity size. The R-OH and OH functionalities in  $\beta$ -CD give rise to a hydrophilic exterior cavity and hydrophobic interior cavity [30]. Very recent observations illustrated that different molecules can be encapsulated in the  $\beta$ -CD cavity through the host-guest interactions, leading to the formation of inclusion complexes [31]. Scientific reports demonstrated that the inclusion complexes based on the CDs could be employed in drug delivery, wastewater pollutants removal, electromagnetic sensors, and food industries [32-35].

Up to now, the GO layers were utilized as a semi nano-carrier which shows moderate self-healing protection ability in long terms. However, for the first time, the controlled-release strategy was employed alongside the passive (barrier) behavior of the GO layers in the EP composites. In other words, the presence of GO sheets can help passive behavior of EP, and the active protection mechanism in long terms can be provided by a controlled-release mechanism,

which can be resulted by  $\beta$ -CD-CeA inclusion complexes. Moreover, the smart transmission of the corrosion inhibitors is of critical importance in the self-healing mechanism. Therefore, the novelty of the present study is to design and develop a new intelligent self-healable nanocomposite epoxy coatings based on graphene oxide (GO) nano-sheets as smart nano-carriers of inhibitors and targeted manipulation of corrosion inhibition activities on a metallic substrate. More importantly, as a novel approach, the release of the pigment was controlled by introducing the  $\beta$ -CD-based nano-containers.

In the present study, a novel controlled-release nano-carrier based on the graphene oxide was designed and used as an anti-corrosive nano-filler in the EP coating. The synthesized particles were examined by FT-IR, Raman, X-ray diffraction, and UV-Vis techniques. Also, the release degree after 24 h was evaluated by ICP analysis. With the help of FE-SEM micrographs, the steel substrate surface after the extraction process was visualized. The inhibition mechanism and performance of the extracted particles were investigated applying potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods, respectively. After introducing the  $\beta$ -CD-cerium acetylacetonate (CeA)/MGO nano-fillers into the EP, the defected site of the coating was studied by the use of EDS/mapping experiment. Besides, the self-healing mechanism was explored by EIS measurements. The general performance of  $\beta$ -CD-CeA/MGO in an intact EP polymeric matrix was probed with the help of the EIS technique. In addition, detailed-scale (i.e., electronic) DFT modelings were applied to explore the CeA and  $\beta$ -CD propensity for interactions with the coating matrix.

## 2. Methods and materials

### 2.1. Materials

The mild steel (MS) samples (ST12 type) with P=1.2%, Mn=1.1%, Si=1.0%, Mo=1.0%, Ni=1.7%, Cr=0.7% and Fe=balance (wt.%) elemental composition were supplied from Foolad Co. [36-38]. In order to synthesize the GO, the expandable graphite powder (particle size < 50  $\mu\text{m}$ , Kropfmuehl Graphite), sulfuric acid (Aldrich Co.), hydrochloric acid (Merck Co.),  $\text{H}_2\text{O}_2$  (Merck Co.),  $\text{KMnO}_4$  (Merck Co.) and  $\text{NaNO}_3$  (Merck Co.) were purchased. Also, the inclusion complex was constructed using the  $\beta$ -CD (Aldrich Co.) and CeA (Aldrich Co.). The GO modification was done with APTES (Aldrich Co.). For the preparation of EP coating, an Epiran 01-X75 type epoxy resin (75% wt.%, EEW: 434–555 g/eq) and Cray Amid 115-X70 type aromatic polyamide hardener (70% wt.%, amine value: 200–220 mg KOH/g) were acquired from Petro-chemical Co.-Kuzestan and Arkema Co., respectively.

## 2.2. The preparation of $\beta$ -CD and $\beta$ -CD-CeA particles

Initially, a homogenous solution was reached by dissolving 1 gr of  $\beta$ -CD in 50 ml deionized water (30 min). Secondly, 1 gr of the guest molecule (i.e., CeA) was added to 50 ml methanol and mixed for 30 min. The resulting methanolic solution was added to the aqueous solution dropwise during continuous stirring (1:1 wt.%, for 2 h at 75  $^\circ\text{C}$ ). The solution was filtered carefully for the elimination of the unreacted  $\beta$ -CD, and CeA compounds from the solution phase. Finally, the suspension temperature was lowered to 0  $^\circ\text{C}$ . The filtered solid particles were dried in an oven (for 24 h at 70  $^\circ\text{C}$ ), and the obtained white crystals are named as the inclusion complexes. The prepared powder was stored in a desiccator for further characterizations.

## 2.3. GO synthesis

In order to convert the graphite particles to GO nano-sheets, the modified Hammers' method was employed. For this aim, about 0.5 gr of graphite flakes were dispersed in 60 ml strong (99%) H<sub>2</sub>SO<sub>4</sub> solution. After 2 h mechanical stirring, 0.5 gr analytical grade NaNO<sub>3</sub> powder was added gradually. Then, 3 gr KMnO<sub>4</sub> was introduced into the prepared mixture. After 72 h stirring at room temperature, the mixture was diluted by 300 ml distilled water. As the process is exothermic, this procedure was done in an ice bath to control the temperature. Lastly, to terminate the oxidation reactions of the graphene oxide particles, the diluted H<sub>2</sub>O<sub>2</sub> (20 wt.%) was added dropwise. The produced graphite oxide particles were then centrifuged two times and washed by 1 M HCl solution for three times and deionized water for two times. The particles were then exfoliated in water medium applying ultrasonication (at 150 W for 20 min).

#### **2.4. MGO synthesis**

After the synthesis of GO nano-particles, the GO was dispersed (0.12 gr) in DMF via a solvent exchange approach. For this aim, the GO was centrifuged to separate the water from the GO sheets. The GO was then washed by 20 ml DMF and centrifuged five times (at 4000 rpm for 2 min). Subsequently, the prepared GO sheets (0.12 gr) were mixed with APTES (0.12 gr, 1:1 wt%) in a round bottom flask (for 2 h at 85 °C). The final black solution was cleaned by DMF twice. The resulting solid black compound was named as MGO.

#### **2.5. $\beta$ -CD/MGO and $\beta$ -CD-CeA/MGO synthesis**

After preparing the MGO nano-particles, about 0.12 gr of MGO was mixed with 0.12 gr of pure  $\beta$ -CD (1:1 molar ratio) in 50 ml deionized water (at room temperature for 2 h). Also, 0.12 gr of  $\beta$ -CD-CeA and 0.12 gr of MGO particles were separately dissolved in aqueous baths. In order to



modify the GO sheets with the  $\beta$ -CD and  $\beta$ -CD-CeA complexes, the solution pH was adjusted in about 8 using 20 wt.% NaOH solution. Finally, the obtained nano-particles were centrifuged (at 4000 rpm during 5 min) (**Figure 1**). The resulting semi-solid black products are called  $\beta$ -CD-MGO and  $\beta$ -CD-CeA-MGO.

**Figure 1**

## **2.6. Coating fabrication**

About 0.1 wt% of the prepared MGO,  $\beta$ -CD/MGO, and  $\beta$ -CD-CeA/MGO nano-particles was centrifuged and washed by DMF (twice, at 4000 rpm for 5 min) and toluene (once, at 4000 rpm for 5 min). The solid product was dispersed in 30 gr epoxy resin and then sonicated. Before sonication, about 3 ml toluene was added to the mixture. After sonication, about 23 gr polyamide hardener was added to the epoxy composite. The obtained mixtures were applied to the pre-cleaned steel samples through a film applicator for an average thickness of  $120 \pm 5$   $\mu\text{m}$ . The coated samples were stored in a clean room for 5 days and cured in an oven for 2 hr at 100 °C. For better comparison, the neat EP was applied to the MS substance by the same procedure.

## **2.7. Characterizations**

### **2.7.1. Particles characterization**

Different techniques such as FT-IR (Perkin Elmer), Raman (Almega Thermo Nicolet equipped with a Leica microscope (Buffalo Grove, IL), 1200 L/mm grating and a CCD camera and 532 nm light used for excitation), XRD (PW1730 model, X' Pert Pro Panalytical diffractometer instruments, Cu K $\alpha$  radiation, wavelength=1.54 Å), and UV-Vis (Cecil Ce9200 double beam) spectroscopies were utilized for identifying the structure of the synthesized nano-particles, i.e., GO, MGO,  $\beta$ -CD/MGO, and  $\beta$ -CD-CeA/MGO. To this purpose, the suspensions containing 0.12

gr of GO, MGO,  $\beta$ -CD/MGO, and  $\beta$ -CD-CeA/MGO were centrifuged (during 5 min and at a rotation speed of 4000 rpm). The resulting semi-solid product was heated in an oven for 5 h at 80 °C. The FT-IR spectra were recorded in the wavenumber range of 400  $\text{cm}^{-1}$  and 4000  $\text{cm}^{-1}$  (with scanning speed of 2 mm/s) using KBr tablets of the nano-powders. Additionally, the Raman technique was performed in the wavenumber range of 500-3500  $\text{cm}^{-1}$  to prove the structure of the particles. For displaying the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transitions, about 1 ml of GO, MGO,  $\beta$ -CD/MGO, and  $\beta$ -CD-CeA/MGO powders was dispersed in 10 ml distilled water. After significant dispersion, the interactions were analyzed in the wavelength range of 200-800 nm. The particle's thermal stability (from 30 °C to 600 °C with 10 °C step rate under nitrogen environment) was examined by TGA/DTG (Pyris Diamond instrument) technique. The morphology of the nano-particles was assessed by FE-SEM (Tescan Mira3 LMU) analysis. The stability of 0.1 gr of GO, MGO,  $\beta$ -CD/MGO, and  $\beta$ -CD-CeA/MGO particles in polar (deionized water), semi-polar (DMF) and non-polar (Toluene) solvents was studied.

### 2.7.2. Characterizations in solution phase

Before performing the electrochemical and morphological experiments, the surface of all steel samples (3 cm  $\times$  12 cm) was abraded by 200-1000 grits carbide papers to reach a shiny/clean surface. The organic impurities were then removed by acetone solution [39, 40]. To evaluate the protection behavior and inhibition performance of the synthesized particles, Tafel and EIS measurements were conducted (1 cm  $\times$  1 cm exposed area). All electrochemical studies were executed in an electrochemical cell, including platinum (as counter), Ag/AgCl (as reference), and mild steel (as working) electrodes. The frequency range during the EIS measurement was 0.01 Hz-10000 Hz [41], with a potential amplitude of  $\pm 10$  mV. Also, the Tafel plots were provided in

a potential range of -250 mV to +250 mV with a  $1 \text{ mV}\cdot\text{s}^{-1}$  interval [42, 43]. All measurements were carried out on three identical samples, and the mean values of three measurements were reported. The impedance data were fitted by proper electrical models using Zsimp win v.2 demo version software. To prepare the electrolytes for solution-phase investigations, about 3.5 gr NaCl powder was dissolved in 100 ml deionized water. Then, the chloride-containing solutions were protected by GO, MGO,  $\beta$ -CD/MGO, and  $\beta$ -CD-CeA/MGO extracts. For this purpose, 1000 ppm of these particles was introduced into separate bathes. After 1 h stirring, the protected solutions were centrifuged (at 4000 rpm for 5 min) for separating the particles. The obtained supernatant solution was employed for electrochemical evaluations. The effects of pigments on the steel substrate morphology were examined by FE-SEM micrograph (Mira 3) and contact angle (OCA plus) test. The surface structure was inspected using EDS-Mapping (LEO 1455VP) and GIXRD (PW1730 model) experiments. To this purpose, the steel coupons ( $1 \text{ cm} \times 1 \text{ cm}$ ) were dipped in the protected and un-protected solutions. After 24 h exposure, the samples were dried carefully, and different elemental and morphological analyses were performed. The release degree of  $\beta$ -CD in a 3.5% NaCl solution was investigated by ICP-OES (Arcos EOP) experiment. The 1000 ppm of  $\beta$ -CD-CeA/MGO powder was dispersed in the NaCl solution. After 24 h, the  $\beta$ -CD release degree was measured and reported.

### **2.7.3. Coating characterizations**

To prepare the steel samples, the same preparation procedure was conducted on  $10 \text{ cm} \times 15 \text{ cm}$  samples. After coating fabrication, different electrochemical/morphological techniques were employed. The self-healing mechanism was proved by the EIS test. For this purpose,  $1 \text{ mm} \times 1.5 \text{ cm}$  artificial scratch was produced on the EP coatings. Subsequently, the samples were subjected

to 3.5% NaCl solution, and EIS measurement was applied after different immersion times (1, 5, 24, 48, and 96 h). Furthermore, the morphology and composition of the film deposited in the scratched regions (after 24 h exposure) were investigated by FE-SEM, and EDS/Mapping analyses. The effect of the synthesized nano-fillers on the intact (without defect) EP coating was evaluated using EIS analysis executed during 2, 7, 14, and 24 days of exposure to a 3.5% NaCl solution. The accelerated salt spray corrosion test (up to 900 h exposure) was done by SHT-2140 cabine test (at ambient temperature and pH~7). Three samples were prepared for each composite coatings to ensure the repeatability of the measurements.

## 2.8. Electronic-scale theoretical studies

The affinity of CeA and  $\beta$ -CD molecules towards the epoxy resin coating molecule was assessed applying the DFT approach in DMol<sup>3</sup> code [44]. The interactions relevant for the exchange-correlation term were manipulated with GGA/PBE algorithm connected with the DNP basis set. As shown in **Figure 2**, two model structures (designated as model-1 and model-2) were taken into account for organic/inorganic CeA complex [45]. A previously chosen structure was utilized herein for epoxy resin [46]. To explore the CeA and  $\beta$ -CD affinity against epoxy resin, hybrid clusters were prepared by placing two models of CeA complexes and  $\beta$ -CD near the epoxy resin. Subsequently, the geometries of CeA,  $\beta$ -CD, epoxy resin, and constructed clusters (i.e., CeA/epoxy resin and  $\beta$ -CD/epoxy resin) were submitted to structural optimization. The optimized CeA complexes and  $\beta$ -CD molecule (side and top view) were provided in **Figure 2**.

**Figure 2**

### 3. Results and discussion

#### 3.1. Nano-particles characterization

##### 3.1.1. FT-IR spectroscopy

The presence of C-O-C ( $1063\text{ cm}^{-1}$ ), O-H ( $1382\text{ cm}^{-1}$ ), C-O ( $1633\text{ cm}^{-1}$ ), symmetric ( $1736\text{ cm}^{-1}$ ), and asymmetric ( $1633\text{ cm}^{-1}$ )  $\text{CH}_2$  and O-H ( $3430\text{ cm}^{-1}$ ) absorption bands in the FT-IR spectrum of GO represents the successful synthesis of GO (**Figure 3-a**). The  $\text{CO}_2$  vibration at  $2362\text{ cm}^{-1}$  is associated with the adsorbed air pollution [47-49]. Upon GO modification (MGO), the new peaks in  $1622\text{ cm}^{-1}$ ,  $1588\text{ cm}^{-1}$ ,  $1258\text{ cm}^{-1}$ ,  $1122\text{ cm}^{-1}$ ,  $1024\text{ cm}^{-1}$ ,  $885\text{ cm}^{-1}$ ,  $860\text{ cm}^{-1}$ ,  $2923\text{ cm}^{-1}$ , and  $2854\text{ cm}^{-1}$  are respectively relevant for the primary amines (N-H) vibration, C-N in-plane stretching and/or C-H-N deformation, C-N vibrations of the primary and secondary amines, Si-O-C anti-symmetric vibration, Si-O-Si anti-symmetric vibration, N-H (primary and secondary amines) vibration, Si-O-C vibration,  $\text{CH}_2$  (symmetric stretching) vibration and  $\text{CH}_3$  (symmetric/asymmetric) stretching vibration [50, 51]. According to the FT-IR plot of the  $\beta$ -CD, the characteristic peaks located in  $3397\text{ cm}^{-1}$ ,  $2927\text{ cm}^{-1}$ ,  $1645\text{ cm}^{-1}$ ,  $1158\text{ cm}^{-1}$ , and  $1026\text{ cm}^{-1}$  reveal the presence of the O-H, C-H, H-O-H, C-O and C-O-C bonds in  $\beta$ -CD structure (**Figure S1**) [34, 52]. Obviously, a slight difference is noted in the FT-IR diagram of the  $\beta$ -CD/MGO. The H-O-H bending vibration in  $\beta$ -CD resulted in the peak overlap at  $1653\text{ cm}^{-1}$ . Additionally, observation of a new peak in  $1152\text{ cm}^{-1}$  (C-O bonds vibration in  $\beta$ -CD) evidenced the interactions of  $\beta$ -CD molecules with the MGO nano-particles. By introducing the inclusion complexes on the MGO nano-sheets, various peaks were overlapped. It should be considered that the energy level of the guest molecule (CeA) lowered considerably after inclusion, and for this reason, the characteristic peaks are not too sharp in FT-IR diagrams [53]. In low wavenumbers ( $800\text{ cm}^{-1}$ - $500\text{ cm}^{-1}$ ), overlapping is apparent which is attributed to the Ce-O presence in CeA

structure. Moreover, a slight overlapping in  $1100\text{ cm}^{-1}$ - $1000\text{ cm}^{-1}$  originated from the acetate fragments (C=CH and C-H vibrations). The displacements are seen in the presence of the  $\beta$ -CD-CeA complex on MGO, an observation assigning to the successful interactions between these particles.

### 3.1.2. XRD spectroscopy

The XRD patterns of pure GO contain one heightened characteristic peak (001) in  $2\theta$  of  $11^\circ$ , representing the GO interlayer spacing (**Figure 3-b**). Generally, the GO interlayer d-spacing is dependent on the oxygen containing moieties in GO basal planes (i.e., epoxide) and GO edges (i.e., carboxyl). The displacements towards the lower degrees for MGO particles revealed the presence of APTES on the GO surface, causing the GO interlayer spacing [54]. Additionally, the presence of relatively intense characteristic peaks occurred in high degrees indicates the ring-opening interactions over the GO layers. After introducing the  $\beta$ -CD nano-carrier, the (001) peak shifted slightly, conveying the fact that  $\beta$ -CD could have an impact on the MGO interlayer space. However, the characteristic peak displaced to lower positions evidencing the  $\beta$ -CD/APTES interactions with the MGO sheets [55]. After CeA encapsulation, the peak in low angles did not shift clearly. In high degrees, a slight shift happened as compared with  $\beta$ -CD/MGO, explaining the CeA complexes encapsulation by the  $\beta$ -CD cavity [56]. It is noteworthy to notice that after inclusion, the crystallinity degree was changed considerably due to the CeA amorphous structure [57].

### 3.1.3. Raman spectroscopy

Final Raman deconvoluted diagrams illustrated two pronounced peaks in middle wavenumbers because of the G-band ( $1609\text{ cm}^{-1}$ ,  $\text{sp}^2$  carbon) and D-band ( $1362\text{ cm}^{-1}$ ,  $\text{sp}^3$ ) (**Figure 3-c**). Also,

the 2D region is observed in high wavenumbers. Recent investigations indicated that the D-band intensity is related to the GO defects and/or  $sp^2 \rightarrow sp^3$  carbon conversion. In other words,  $sp^2$ -hybridized carbon conversion to  $sp^3$  leads to the generation of many defects on the GO basal plane, affecting the D-band strength [58]. On the other side, the G-band intensity depends on the  $sp^2$  carbon atoms in GO sheets (**Figure S2**) [59]. The  $I_D/I_G$  value is one of the most reliable parameters for evaluating the GO surface structure. In the present work, the  $I_D/I_G$  value was about 0.87, pointing to the high existence of the characteristic oxygenated groups on the GO basal planes [60]. The slight displacements of the G-band and D-band after GO modification with APTES reflect the increment of C=C bond and ring-opening interactions, respectively. These results can be approved by  $I_D/I_G$  values. Visibly, this parameter diminished to 0.83 after GO modification, which is likely caused by ring-opening reactions and high aggregation of the GO sheets. In the presence of  $\beta$ -CD nano-carriers, the amount of  $I_D/I_G$  parameter was enhanced suitably ( $\sim 1$ ), demonstrating that the G-band was influenced slightly but the D-band was improved substantially. This is possibly due to the  $\beta$ -CD interactions with APTES molecules, resulting in sufficient defects on the basal planes of GO. Besides, the low G-band intensity variation clarified that the interactions between  $\beta$ -CD and MGO sheets were not in a chemical state. It is clearly noticed that the inclusion complex ( $\beta$ -CD-CeA) affected both D-band and G-band intensities. The increment of D-band strength relies on the released Ce ions and acetate molecules from  $\beta$ -CD, which instead influenced the GO sheets structure.

Based on the literature, the 2D band intensity peak is a signification of the stacked graphene oxide sheets. The decline of  $2D_{MGO}/2D_{GO}$  displayed that the  $2D_{MGO}$  increased slightly owing to the charge density neutralization of GO layers after APTES modification, which can affect the stacked GO layers. The presence of  $\beta$ -CD molecules provided higher 2D magnitudes, reflecting

that more GO sheets are attached [61]. Such an observation can be rationalized by limiting the electrostatic/electromagnetic repulsion forces between the GO layers and/or APTES molecules, which reduces the GO interlayer space. However, after CeA encapsulation, the high value of the 2D parameter is available. This increment was caused by the release of CeA from the  $\beta$ -CD, producing strong electrostatic repulsions between the GO layers. This behavior leads to the higher interlayer space and lower GO layers stacking [62]. The  $\beta$ -CD/MGO and  $\beta$ -CD-CeA/MGO normalized plots were reported in **Figure S2**. Evidently, the G-band and D-band intensities varied negligibly, disclosing that the CeA did not affect the MGO defects,  $sp^3$ , and  $sp^2$  carbon atoms. However, the 2D band zone intensity was improved dramatically after CeA encapsulation proving the higher MGO interlayer distance.

#### 3.1.4. FE-SEM

FE-SEM micrographs related to the unmodified GO sheets represented accumulated GO layers (**Figures 3-d**). The GO aggregation mainly depends on the oxygenated characteristic groups that exist in the GO edges, causing electrostatic interactions between the GO layers. For the APTES modified GO, the crystallinity changed substantially. However, the layered structure was preserved affirming the GO interactions with APTES molecules. After  $\beta$ -CD nano-containers loading into GO sheets, a small cone-like structure was grown probably due to the  $\beta$ -CD interactions with the MGO basal planes. As proved in XRD and Raman tests, with encapsulation of the CeA inclusion complexes inside the  $\beta$ -CD cavity, the crystallinity degree experienced significant change. These achievements were confirmed by FE-SEM images of  $\beta$ -CD-CeA/MGO.

**Figure 3**



### 3.1.5. UV-Vis spectroscopy and ICP

The GO UV-Vis spectrum evidently indicated two characteristic peaks corresponding to the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transitions, resulted from the conjugated C=C and carbonyl (C=O) groups of the GO sheets (**Figure 4-a**) [63]. After modification with APTES, the  $\pi$ - $\pi^*$  transition-related peak was altered because of the APTES molecules coverage over the GO sheets. Upon  $\beta$ -CD/APTES molecules interactions, the shape of the UV-Vis diagram did not vary significantly. Such an outcome directly arises from the C=C and C=O bonds absence in the  $\beta$ -CD structure. In other words, no characteristic peak in the UV-Vis polt of the pure  $\beta$ -CD declares that  $\beta$ -CD could not affect the UV-Vis spectrum of the MGO [64]. The localization of CeA complexes inside the  $\beta$ -CD cavity slightly displaced the  $\pi$ - $\pi^*$  transitions, describing the C=C bondings in the CeA complexes. Additionally, because of the C=O bonds of CeA, the  $n$ - $\pi^*$  characteristic peak was noted to raise and shift. After introducing the  $\beta$ -CD-CeA/MGO extract into the 3.5% NaCl, the ICP measurements were conducted. Achievements proved the presence of 25 ppm  $Zn^{2+}$  ions in the extract solution.

### 3.1.6. Zeta potential (ZP)

The surface charge density of the synthesized particles was assessed by Zeta potential technique (**Figure 4-b**). Generally, the variation of ZP values  $>+30$  mV and/or  $<-30$  mV implies the stability of the dispersion. Clearly, a descending trend was observed for pure GO as a function of pH. The ascending trend under alkaline conditions is ascribed to the double-layer compression and GO ionization [65]. Recent studies have illustrated that in low pHs ( $\sim 4$ ), the carboxylic groups, and in high pHs ( $\sim 10$ ), the phenolic groups' ionization happens. For MGO particles, the

Zeta potential moved to the higher values. This improvement is attributed to the ring-opening interaction (epoxide groups) in the presence of APTES [66]. The  $\beta$ -CD existence clearly affected the MGO charge density. In the low pHs, the  $\beta$ -CD ionization is unavailable, and only the electrostatic repulsion between the MGO layers can be neutralized. However, by increasing the solution pH, the OH groups, existed on the  $\beta$ -CD exterior cavity, can be ionized which influence the particle charge density. Moreover, the Zeta potential varied slightly in alkaline pHs, an observation caused by complete ionization of the OH groups in lower pHs [67]. After the CeA encapsulation, the potential increased drastically, reflecting that the encapsulated CeA affected the electrostatic/electromagnetic repulsions. The declined Zeta potential values in neutral pHs were resulted from the OH groups ionization and/or small CeA release from the  $\beta$ -CD cavities. However, in alkaline situations, strong repulsion between the  $\beta$ -CD and encapsulated CeA complexes brings about the great release, which again leads to the potential variation [68].

### 3.1.7. TGA/DTG

Observations from the TGA diagram of pure GO demonstrated the weight loss happening in three specific stages (**Figures 4-c,d**). (i) Until 120 °C, the GO weight reduction originates from the evaporation of the physically absorbed H<sub>2</sub>O molecules from the GO interlayers. (ii) The weight loss from 120 °C to 375 °C points to the disappearance of the hydroxyl, carboxylic, and epoxide groups from GO layers. (iii) Eventually, at high temperatures, the main destruction of the GO skeleton is evident [69]. After GO modification, the thermal stability decreased, corresponding to the physically adsorbed silane groups (in low temperatures) and the grafted silane groups decomposition over the GO layers [70]. After introducing  $\beta$ -CD, the thermal stability of the nano-particle was enhanced intensely, relating to the high thermal stability of  $\beta$ -CD. The particle weight decreased slightly in 180-300 °C due to the OH groups' destruction in  $\beta$ -

CD. Additionally, the  $\beta$ -CD damage at higher temperatures caused weight reduction. On the other hand, the particle behaved very sensitive against temperature after CeA encapsulation, which can be attributed to different reasons. (i) The CeA destruction occurred at very low temperatures can notably reduce the particles weight. (ii) After increasing the temperature over 300 °C, the destruction of oxygen containing groups can affect the  $\beta$ -CD-CeA/MGO particles weight. (iii) By enhancing the temperature, the  $\beta$ -CD destruction can help the weight reduction. The weight reduction values occurred in different stages are reported in **Table 1**.

**Figure 4**

**Table 1**

### 3.1.8. Particles stability test

Recent studies evidenced that the presence of many oxygen containing groups over the GO layers can assist the GO dispersion improvement in water media. On the other side, the GO layers are entirely stable in polar/non-polar (e.g., DMF) solvents. These observations may correspond to the presence of the oxygenated groups over the GO layer, which can help the hydrogen bonding formation between the solvent and GO sheets. This instead gives rise to the improved GO dispersion in polar and semi-polar solvents. However, the GO layers aggregate noticeably in non-polar solvents (e.g., toluene). For this reason, the GO provides insufficient interactions with the semi-polar EP matrix. Obviously, the proper dispersion of MGO particles in polar solvents at initial times was observed, attributing to the existence of the oxygen-containing groups at the MGO edges. However, in long terms, the stability of the particles diminished dramatically. Clearly, after GO modification, the dispersibility was improved in non-polar (toluene) solvent, which is associated with the fact that the MGO can interact with the EP coating matrix (**Figure S3**). For  $\beta$ -CD-CeA/MGO nano-particles, the same trend is obvious. The

$\beta$ -CD-CeA/MGO particles showed desirable dispersion in the initial immersion times, but in long terms, the stability of the particles diminished significantly. In a non-polar solvent, a high distribution was noted, reflecting desirable interactions between the non-polar EP groups and  $\beta$ -CD-CeA/MGO particles. The improvements in dispersion of  $\beta$ -CD-CeA/MGO particles (in comparison with MGO and  $\beta$ -CD-MGO) corresponds to the existence of CeA complexes, which can improve the hydrogen bonding formation between the solution and synthesized particles.

### 3.1.9. Open circuit potential analysis

The open circuit potential (OCP) measurements during 800 min of iron exposure clarified that the potential relevant for the un-protected sample lowered severely in primitive times, disclosing the galvanic cell generation and aggression occurrence on the steel substrate (**Figure 5-a**) [71]. After introducing the  $\beta$ -CD/MGO extract, the metal potential maintained the same trend, exhibiting that the  $\beta$ -CD molecules covered the steel active cathodic sites (that is cathodic protection). With the release of the encapsulated CeA complexes, the potential variation becomes slower, revealing that a dense protective layer limited the electrolyte/steel direct access [72]. The slight variations during the iron exposure are associated with the iron oxide and/or protective compounds adsorption/detachment.

### 3.1.10. Potentiodynamic polarization

The protection mechanism of the particles in solution phase was explored by Tafel studies (**Figure 5-b**). Simply, the Tafel curves for the protected steel were slightly affected. The displacements toward cathodic zones illustrated the steel substrate cathodic inhibition in the presence of  $\beta$ -CD molecules. However, by the release of the encapsulated CeA complexes, the

Tafel curves shifted to the anodic zones. This displacement arises from the anodic inhibition effect of the actonate molecules. It should be noted that the Ce ions result in  $\text{CeO}_2/\text{Ce}(\text{OH})_3$  components creation on the steel active cathodic sites [73]. In other words, the CeA compounds are able to protect the cathodic and anodic sites simultaneously. The Tafel curve displacement for the  $\beta$ -CD-CeA/MGO is higher than +85 mV, emphasizing the inhibition via anodic mechanism (**Table 2**) [61, 74]. The small reduction of the corrosion current density ( $i_{\text{corr}}$ ) for the  $\beta$ -CD sample proposed the inability of the protective layer in significant retardation of the corrosion activities. But after introducing the  $\beta$ -CD-CeA inclusion complexes, the  $i_{\text{corr}}$  diminished intensely due to the strong protective film emergence over the substrate. The slight difference of the  $\beta$ -CD cathodic ( $\beta_c$ ) slope verified the coverage of the iron active cathodic sites with the inhibitive molecules [75]. However, after  $\beta$ -CD-CeA addition, the slope related to the anodic branch ( $\beta_a$ ) lowered noticeably, declaring the CeA complexes (acetate molecules) adsorption on the active anodic regions [76, 77].

**Table 2**

### 3.1.11. EIS measurements in solution phase

Evidence from **Figure 5** indicated the low resistance of the bare sample in the chloride solution. The negligible corrosion resistance enhancement of the blank sample corresponds to the iron oxide particle coverage over the metal surface [78]. The presence of a one-time constant loop in Nyquist diagrams proved that the corrosion reactions occurred under control of the charge transfer mechanism. The single-time constant in Bode diagrams further supported this outcome [79]. Clearly, the presence of the MGO nano-sheets in the electrolyte could not improve the steel surface resistance, suggesting the poor corrosion inhibition effect of MGO. With the use of  $\beta$ -CD-MGO extracts in 3.5% NaCl media, the steel resistance was enhanced slightly, deducing the

undesirable protection behavior of  $\beta$ -CD molecules. The highest resistance was reached after 5 h subjection to the chloride environment, exhibiting that the maximum  $\beta$ -CD protective layer performance was achieved after 5 h of immersion. Thereafter, the metal resistance diminished due to the diffusion of the ions into the inhibitive film [80]. A slight corrosion resistance enhancement after 48 h of immersion is ascribed to the generation of the iron oxide products, causing a small improvement in the metal corrosion resistance. The inspection of the Bode diagram of  $\beta$ -CD/MGO displayed that the  $\log |Z|$  (Bode-plots, 10 mHz) values in the low frequency raised slightly, signifying the low  $\beta$ -CD inhibition (**Figure S4**). Additionally, the absence of film time-constant affirmed the low effectiveness of the  $\beta$ -CD protective layer. By introducing the CeA complexes into the chloride media, the resistance increased intensely, suggesting a high inhibition behavior. In addition, the increment trend is evident for  $\log |Z|$  values after  $\beta$ -CD-CeA/MGO extraction. The presence of a new time constant at high frequencies showed satisfactory protective layer performance against aggression [81]. However, after 48 h, the film time-constant disappeared, implying the electrolyte penetration. Analysis of the solution resistance ( $R_s$ ), as listed in **Table 3**, illustrated that the pure  $\beta$ -CD increased the solution conductivity, but after releasing the CeA complexes, the solution conductivity lowered approximately. The film resistance related to the  $\beta$ -CD/MGO was not adequate. The increment of  $R_f$  in the initial immersion times verified the adsorption of the  $\beta$ -CD molecules over the metal substrate [82, 83]. On the other side, the higher film resistance of the  $\beta$ -CD-CeA/MGO extract ensured sufficient protection ability in chloride environments. Evidently, by enhancing the immersion time, the  $R_f$  values declined dramatically, disclosing the electrolyte diffusion into the constructed protective layer. The sinusoidal variations of this parameter are related to the CeA and/or  $\beta$ -CD adsorption/desorption over the formed anti-corrosive layer. The  $Y_{0,f}$  quantities

diminished profoundly after  $\beta$ -CD-CeA/MGO extraction, which explains that a denser protective film covered the substrate surface compared to the pure  $\beta$ -CD [84]. Additionally, the reducing tendency of  $Y_{0,dl}$  after enhancement of the  $\beta$ -CD-CeA/MGO component highlights the water/inhibitive molecules displacement on the active metal zones [85, 86]. The inhibitive film and the double layer heterogeneity index can be explained by “ $n_f$ ” and “ $n_{dl}$ ” values, respectively. Observations proved that in the presence of  $\beta$ -CD-CeA/MGO nano-particles a higher “ $n_f$ ” is available, clarifying that a homogeneous protective film covered the metal substrate. In other words, in comparison with the  $\beta$ -CD/MGO, the  $\beta$ -CD-CeA/MGO particles could provide a high compact/smooth inhibitive layer against corrosive attacks. Also, the “ $n_{dl}$ ” values were enhanced drastically after introducing  $\beta$ -CD-CeA/MGO extract in a 3.5% NaCl solution. The lowest “ $n_{dl}$ ” amounts reached from the bare sample, which is assigned to a deep corrosion occurrence resulting in the double layer heterogeneity and lowered metal surface smoothness. After enhancing the  $\beta$ -CD/MGO nano-particle, the “ $n_{dl}$ ” shifted toward the higher magnitudes, attributing to the constructed inhibitive layer over the metal active sites. Visibly, the highest “ $n_{dl}$ ” values were achieved after introducing the  $\beta$ -CD-CeA/MGO extract, confirming that the electrolyte connection with the steel substance could be controlled significantly. The corrosion inhibition efficiency ( $\eta\%$ ) in 3.5% NaCl solution on mild steel surface was calculated using total resistance ( $R_t=R_s+R_{ct}$ ) values as expressed by the following equation [80, 87]:

$$\eta\% = \left[ \left( R_t^i - \frac{R_t^0}{R_t^i} \right) \right] \times 100 \quad (1)$$

Where  $R_t^i$  and  $R_t^0$  are the total resistance for the protected and un-protected samples, respectively. Inspections revealed that after 48 h of immersion, nearly 88% of corrosion inhibition was achieved.

**Table 3**

### 3.1.12. EDS/Mapping of extract

Elemental analysis of the substrate showed the high value of the O element because of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  particles formation (**Figure S4**). After introducing the  $\beta$ -CD nano-containers, the content of the Fe element significantly decreased, ascertaining the surface coverage with  $\beta$ -CD molecules (**Figure 5**). The percentage of O element diminished noticeably, inferring that the iron oxidation was retarded after  $\beta$ -CD adsorption. Detection of cerium cations on the steel adsorbent approved the CeA release and adsorption. Final Mapping micrographs proposed the significant coverage of the active sites of steel with cerium ions, describing the emergence of the inhibitive film.

**Figure 5**

### 3.1.13. FE-SEM micrographs of extract

The FE-SEM images presented in **Figure 6** clarified the high aggression of the bare sample immersed in a chloride environment. The steel substrate was obviously covered by iron oxide particles, which resulted in accelerated metal corrosion activities. After extracting the pure  $\beta$ -CD, a uniform layer emerged on the steel substrate controlling its direct connection with the corrosive ions. However, the porosities are completely evident, giving rise to the electrolyte/ion diffusion and subsequent metal aggression. It is also seen that upon CeA encapsulation and extraction, a highly dense and uniform protective film was generated on the substrate, leading to the vanishing of micro-porosities and the constrained penetration of electrolyte.

### 3.1.14. The contact angle of extract

Evidence from literature proved that the presence of insoluble iron oxide particles on the steel affects the contact angle notably (**Figure 6**). These features are owing to the hydrogen bondings



between the electrolyte and  $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ . Additionally, the surface heterogeneities caused by severe aggression lowered the droplet angle sharply [88]. The  $\beta$ -CD adsorption slightly influenced the contact angle, relating to more hydroxyl groups on the  $\beta$ -CD exterior cavity, which causes hydrogen bonding between the  $\beta$ -CD and electrolyte (droplet spread) [89]. The CeA encapsulation partly enhanced the angle droplet. This increment is rationalized by the hydrophobic chemical nature of the adsorbed acetate molecules [90].

### 3.1.15. GXR D of extract

The GIXRD pattern of the bare sample resulted in different peaks related to the iron and iron oxide particles (**Figure 6**). Detection of  $\alpha$ - $\text{Fe}_2\text{O}_3$  ( $28^\circ$ ),  $\text{Fe}_2\text{O}_3$  ( $36^\circ$ ), and other types of iron oxides ( $14$ - $26^\circ$ ) on the corroded metal evidenced significant metal surface degradation. In the presence of  $\beta$ -CD, the intensity relevant for the iron oxide peaks was noted to lower significantly, proving the protective film appearance on the sample surface. The existence of the Ce ions on the metallic substrate is not entirely distinct. However, the pure Fe characteristic peaks were intense in higher degrees compared with the bare sample, declaring that an active layer inhibited the substrate corrosion.

**Figure 6**

### 3.1.16. Inhibition mechanism and film formation in solution phase

After releasing CeA species in the 3.5% NaCl media, the complexes can interact with the steel substrate as follows (**Figure S5**): (I) The presence of heteroatoms in acetate molecules can provide a condition for chemical bonding of the Fe atoms with CeA molecules on the active sites of steel. (II) After MS subsection, a cation exchange process may occur. In other words, the  $\text{Fe}^{2+}$  ions can interact with acetate molecules causing a protective layer formation on the active

cathodic sites. (III) The released Ce ions (in the cation exchange process) can make the Ce oxide/hydroxide particles generation over the metal cathodic sites. (IV) The acetate molecules can interact with the Fe oxide/hydroxide particles through H-bonding leading to cathodic site coverage by acetate molecules. (V) The presence of Ce oxide/hydroxide results in the H-bonding formation between the acetate molecules and  $\text{Ce}_2\text{O}_3/\text{Ce}(\text{OH})_3$  particles.

## 3.2. Epoxy coating characterization

### 3.2.1. Self-healing investigation

The self-healing mechanism was explored by the EIS technique (**Figure 7**). To this aim, the resistance of the defected EP was measured in different exposure times. The dramatical reduction in corrosion resistance was observed in the initial immersion times caused by electrolyte/ions diffusion into the coating [91]. A small improvement after 48 h of immersion evidences the corrosion particle aggregation in the defected zone of EP, leading to the slight improvement in the corrosion resistance of the coated sample. However, by progressing the immersion time, the inhibitive capacity of the iron oxide products decreased due to their structure damage, which brings about the resistance decrement [92]. According to the Bode diagrams, during 24 h of metal subjection, the corrosion was restricted based on a charge transfer reaction (**Figure S6**). However, after 24 h and 48 h of metal exposure, the resistive layer time constant is apparent in high frequencies, an observation resulted from the iron oxide compounds. The film time constant vanished after 96 h of immersion, exhibiting the electrolyte/ion diffusion into the semi-protective iron oxide layer. The changes of  $\log |Z|$  values in low frequencies provide helpful information concerning the layer efficiency. The low values from the neat scratched EP reflected its reduced corrosion protection effectiveness. By introducing the  $\beta$ -CD/MGO nano-particles into the EP

matrix, the resistance increased in the initial times, which is attributed to the adsorption of  $\beta$ -CD in the defected region [7]. However, after 5 h of exposure, the protection activity diminished remarkably due to the  $\beta$ -CD hydrophilicity, causing the diffusion of electrolyte/ion. In other words, the  $\beta$ -CD adsorption on the metal surface in the scratched part of the EP affects its protection capacity. The layer time constant (5 h iron immersion) corresponds to the existence of the  $\beta$ -CD molecules in the EP defect. However, the disappearance of the layer time constant (after 24 h) ensures the undesirable protection [93]. The release of the encapsulated CeA complexes from the  $\beta$ -CD enhanced the steel resistance markedly, evidencing the scratched site's coverage with the CeA complexes. Also, the performance is still high in long periods of exposure because of the significant protection. The existence of layer time constant even after 96 h and the increment of  $\log |Z|$  values manifested the promising protection performance [94]. Further explorations disclosed the high film resistance ( $R_f$ ) after the release of CeA from the  $\beta$ -CD. On the other side, the low quantities of  $R_f$  for neat EP and  $\beta$ -CD-MGO/EP samples exhibited the low inhibition impact of the iron oxides and  $\beta$ -CD against corrosion. Little shift of the  $n_f$  for the neat EP indicated the little smoothness of the semi-inhibitive iron oxide product (**Table 4**). Also, the  $n_f$  reduction points to the separation of iron oxide particles from the substrate. For the  $\beta$ -CD-introduced samples, the  $n_f$  magnitudes were improved in the initial times, which is reflective of  $\beta$ -CD adsorption on the steel sites. However, the decreasing trend of  $n_f$  presented the electrolyte diffusion in long terms. After introducing the  $\beta$ -CD-CeA/MGO nano-particles, the high  $n_f$  amounts are available, demonstrating that a high smooth protective film could fill the defected zone of EP. Visibly, the  $n_f$  values are high enough even after 24 h, confirming that the electrolyte penetration was controlled significantly. Furthermore, a small  $n_{dl}$  shift is associated with the neat EP and  $\beta$ -CD-MGO/EP, indicating the direct electrolyte contact with the

metallic substance, influencing the interface smoothness. By covering the iron sites with CeA complexes, the access was retarded, and for this reason, the high  $n_{dl}$  values were derived. The enhancement of  $Y_{0,f}$  magnitudes displayed that the corrosive electrolyte/ions could diffuse into the constructed inhibitive layer, affecting the layer capacitance. In comparison with other samples, the  $Y_{0,f}$  values diminished significantly, reflecting that a high compact/protective film covered the steel active sites. On the other side, the  $Y_{0,dl}$  varied notably for neat EP and  $\beta$ -CD-MGO/EP samples, indicating that the corrosive media could diffuse into the inhibitive layer and the solution was connected to the metal interface. However, the  $Y_{0,dl}$  values varied slightly for  $\beta$ -CD-CeA-MGO/EP sample, evidencing that the solution/metal connections were controlled considerably after the protective layer construction.

#### Table 4

### 3.2.2. Non-defected EP coating anti-corrosion performance analysis

The Nyquist and Bode plots belonging to the coated and uncoated samples were illustrated in **Figure 7**. Based on the Bode diagrams related to the neat EP sample, the low impedance values (recorded at 0.01 Hz) depicted inefficient protection. Also, the impedance parameter lessened severely in long exposure times, describing the water/ion migration from the EP micro-porosities, an outcome varying the EP structure and disbondment [95]. The charge-transfer time constant (after 14 days) evidently existed in low frequencies, explaining the electrolyte access to the interface. Moreover, the second constant (charge transfer) is clear from the Nyquist diagram after 24 days of immersion. Generally, the Bode diagrams can be divided into two specific parts: (i) capacitive region with -1 slope value, and (ii) resistive part with a slope of  $\sim 0$  (**Figure S6**) [11]. The capacitive/resistive behaviors of the components give useful information regarding the adhesion loss and the coating damage degree. Based on recent researches, the resistive domains

point to the coating delamination, and the capacitive region illustrates the coating delamination index [96]. The coating delamination index ( $D_1\%$ ) was achieved from the formulation defined below [97]:

$$D_1(\%) = \left( \frac{Z_1 - Z_2}{Z_1} \right)_{0.01\text{HZ}} \times 100 \quad (2)$$

Where the  $Z_1$  and  $Z_2$  are respectively related to the impedance values in the initial (2 days) and final (7, 14, and 24 days) immersion times. The substantial reduction of impedance in the case of the neat EP reflected the diffusion of corrosive ions into the EP matrix, which is accompanied by profound damage (**Table 5**). The damage index of the coating containing the  $\beta$ -CD-MGO nano-filler was limited slightly due to the slight active inhibition capacity of  $\beta$ -CD-MGO in the EP matrix. However, a slight impedance reduction after enhancing the  $\beta$ -CD-CeA-MGO particles declares the fact that the electrolyte movement was restrained, and the pathways were reduced significantly.

Generally, the coating delamination relies on the  $\text{OH}^-$  ions in cathodic sites and iron oxides. The  $\text{OH}^-$  fragments could shift the pH values toward the alkaline condition, leading to the hydrolysis and destruction of the polymer-metal interfacial bondings [98]. On the other hand, the iron oxides affect the adhesion by reducing the connections between the EP and substrate. The coating damage index ( $D_2$ ) was expressed as [97]:

$$D_2(\%) = \left( \frac{A_1 - A_2}{A_1} \right) \times 100 \quad (3)$$

The  $A_1$  and  $A_2$  parameters denote the capacitive and resistive regions, respectively. Observations from Bode plots proved that the resistive part covered a wide frequency range in final immersion times compared with the  $\beta$ -CD-CeA-MGO/EP sample. Also, the resistive domain is entirely apparent in  $\beta$ -CD-MGO/EP sample, representing a high coating damage index. An undesirable corrosion inhibition effectiveness of  $\beta$ -CD-MGO nano-filler is ascribed to the hydrophilic nature

of the  $\beta$ -CD exterior cavity assisting the electrode diffusion. Evidence from the reported EIS parameters displayed the significant  $R_f$  values enhancement after introducing  $\beta$ -CD-CeA-MGO nano-particles into the EP matrix, demonstrating that the EP pathways were successfully filled with the inhibitive compounds, which result in a lower electrolyte diffusion and higher corrosion resistance. Apparently, for the neat EP and  $\beta$ -CD-MGO/EP samples, the  $R_f$  decreased dramatically after 7 days of exposure, disclosing the diffusion of chloride solution into the EP matrix. However, for the  $\beta$ -CD-CeA-MGO/EP sample, a notable reduction in  $R_f$  value was identified after 24 days of immersion, proposing that the electrolyte penetration was retarded after 24 days. The same trend is obvious from the  $R_{ct}$  parameter. Clearly, for the EP and  $\beta$ -CD-MGO/EP samples, the  $R_{ct}$  values are not available in the initial immersion times. However, after 7 days of exposure, the  $R_{ct}$  increased to the higher amounts, declaring the electrolyte diffusion into the metal interface. On the other hand, after introducing the  $\beta$ -CD-CeA-MGO pigment, the  $R_{ct}$  values are not available even after 24 days, which illustrates that the solution could not reach the metal surface and the coating drastically inhibited the electrolyte diffusion. Significant values of  $n_f$  parameter from the  $\beta$ -CD-CeA-MGO/EP composite evidenced that the composite body did not destruct even in long terms. Furthermore, the  $n_{dl}$  magnitudes are high enough for this composite, depicting that the corrosion attacks slightly affected the steel double layer zone.

**Figure 7**

**Table 5**

### 3.2.3. EDS/Mapping

The EDS/Mapping elemental analysis of the EP defected zone disclosed high magnitudes of O element in the scratch part arising from  $Fe_2O_3$  and  $Fe_3O_4$  compounds (**Figure S7**). Also, the high concentration of the C element belongs to the EP structure according to the Mapping

micrographs. By the addition of  $\beta$ -CD-MGO particles to the EP matrix, a higher level of O element was detected over the iron surface that corresponded to the C-O-C and O-H characteristic groups present in the  $\beta$ -CD structure (**Figure 8**). It should be noticed that the high O element concentration emphasizes the presence of iron oxide particles in the scratched part. Clearly, the cerium ions adsorbed on the metal surface within the EP defect site, indicating that the CeA complexes could retard the metal corrosion. An adequate reduction of O element signified the disappearance of the iron oxide particles.

#### 3.2.4. FE-SEM

The FE-SEM micrographs obtained from the defected zone of the coating after 24 h immersion manifested a remarkable aggregation of the oxidized Fe particles (**Figure 8**). High amounts of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  particles reflected the severe aggression in the scratched region. After incorporating the  $\beta$ -CD-MGO nano-particles into the EP matrix, the  $\beta$ -CD molecules released and covered the metal surface at the artificial defect. However, the  $\beta$ -CD coverage was not suitable enough, and the corrosive ions diffused into the inhibitive layer easily. By the partial dissolution of the CeA complexes, the inhibitive species could cover the steel substance adequately, resulting in the retardation of the electrolyte accessibility in long terms.

#### Figure 8

#### 3.2.5. Salt spray test

The images obtained from the scratched EP depicted that during 200 h salt spray test, the red rusts covered the defected zone clearly (**Figure S8**). This outcome may be related to the  $\beta$ -CD hydrophilic nature. However, in long terms, the corrosive ions entered under EP, bringing about a high disbondment. Also, after 900 h salt spray, blistering is completely evident from the neat

EP sample. The same tendency is evident after  $\beta$ -CD/MGO nano-particles loading into the EP coating. Corrosion products were developed over the metal surface under the EP coating. However, the aggression was lowered sufficiently after the EP defect protection by CeA complexes. Such an improvement is ascribed to the CeA hydrophobic nature, which retards the diffusion of corrosive agents into the EP matrix.

### 3.2.6. Self-healing and corrosion inhibition mechanisms

The electrolyte and corrosive ions (i.e.,  $\text{Na}^+$  and  $\text{Cl}^-$ ) can be entered into the defected sites of neat EP, resulting in the occurrence of the cathodic and anodic reactions. The iron cations can be produced on the anodic site ( $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$ ), and simultaneously, the cathodic reactions cause the hydroxyl ions generation on the cathodic regions ( $\text{O}_2 + 2\text{H}_2\text{O} + 2e^- \rightarrow 4\text{OH}^-$ ). The generated  $\text{OH}^-$  ions can interact with the  $\text{Na}^+$  ions, leading to the local pH increment and destruction of the physical/chemical interactions between the EP and steel surface. As proved, the existence of MGO nano-sheets cannot control the electrolyte/ions penetration. Because of the  $\beta$ -CD hydrophilicity, the electrolyte penetration was intensified after  $\beta$ -CD molecules coverage. A repulsion force existed between the  $\beta$ -CD cavity and encapsulated CeA complexes (in high pHs) results in the CeA release from the  $\beta$ -CD interior cavity [99]. After the CeA release, the complex can adsorb on the metal surface via different methods (**Figure 9**). (I) The CeA complexes interact with the steel substrate through electrostatic interactions (i.e., physical adsorption). (II) The acetate molecules can cover the anodic and cathodic sites by electron donation mechanisms simultaneously. (III) After the cation exchange process, the Ce ions can be detached from the CeA complex. After oxidation, the cathodic zones can be protected by Ce



oxide/hydroxide particles. (IV) The detached acetate molecules interact with the Ce oxide/hydroxide particles and thereby adsorb on the metal cathodic sites [100, 101].

In detail, after CeA release from  $\beta$ -CD, the anodic and cathodic interactions can occur as follows (**Figure 10**): (I) In the presence of mild steel, the Fe (II) ions can be generated over the cathodic sites of the defected zone. Then, the interactions of acetate molecules with these ions lead to the coverage of cathodic sites by acetate:Fe complexes (cathodic protection). (III) On the other hand, the OH groups present over the anodic sites of metal can interact with the released Ce ions (from CeA complexes) giving rise to the cathodic site's coverage with Ce oxide/hydroxide particles.

**Figure 9**

**Figure 10**

### 3.3. DFT analysis of epoxy interactions with CeA and $\beta$ -CD

The possible interactions of CeA complexes and  $\beta$ -CD molecule with epoxy resin molecule were inspected at microscopic level by DFT method. The lowest energy configurations related to CeA/epoxy and  $\beta$ -CD/epoxy clusters were given in **Figure 11**. This figure illustrates that the selected cerium acetylacetonate models and also the  $\beta$ -CD molecule were able to stabilize in the vicinity of the epoxy resin coating molecule. This graphical outcome highlighted the affinity of CeA and  $\beta$ -CD towards the epoxy resin. Such affinity was more ensured by the estimation of the binding energy [102]. The model-1 and model-2 of CeA interacted with epoxy resin with -41.94 and -38.62 kcal/mol energy, respectively. Also, epoxy resin interactions with bottom and exterior parts of  $\beta$ -CD happened with -46.85 and -39.29 energies. The negative energies are supplemental evidence for CeA and  $\beta$ -CD affinities relative to the coating molecule [102].

**Figure 11**

### 3.4. $\beta$ -CD-CeA/MGO industrial application advantages

Nowadays, conventional zinc phosphate and zinc chromate pigments are the most practical compounds for corrosion protective coatings formulation in the industrial scale. However, the hazardous impacts of these types of pigments have been reported in different documents. Additionally, as discussed in the introduction, the direct connection of pigments with the polymeric epoxy matrix provides destructive effects on the mechanical properties of the epoxy coating. For this reason, the modified graphene oxide-based pigments were introduced in recent days. Although these pigments are almost expensive (3-6\$ per gr) compared with other types of pigments, the high effectiveness at very low loadings (below 0.2%) in the EP formulation makes the system completely economical. Our investigations proved that about 0.1 wt.% of graphene-based pigments could provide significant protection. However, in order to reach desirable protection performance, about 15-20 wt.% of commercial pigments must be used in the EP matrix. Using the high loading of these pigments causes the coating mechanical properties to decline. Besides, it should be noted that the costs of zinc phosphate and zinc chromate pigments are nearly 5-8\$ and 20-30\$ per Kg, respectively. By a simple calculation, it can be realized that the cost of the graphene-based pigment is proper for industrial applications.

### 4. Conclusion

In the present study, the self-healing mechanism of the  $\beta$ -CD-CeA-MGO/EP nanocomposite was explored by electrochemical and morphological approaches. The self-healing behavior of the  $\beta$ -CD-CeA-MGO/EP was studied using the EIS approach. Evidences proved that the presence of  $\beta$ -CD-CeA-MGO provides promising self-healing ability in EP matrix (about 40387  $\Omega$ .cm<sup>2</sup> resistance enhancement after 5 h of steel exposure to saline media). The EIS measurements from

the un-defected EP reflected the lowered electrolyte pathways following  $\beta$ -CD-CeA-MGO nanoparticles loading in the polymeric matrix. Observations clarified that after 24 days of iron exposure to the chloride media, the total resistance increased from 92  $M\Omega.cm^2$  to 5840  $M\Omega.cm^2$ . FE-SEM micrographs associated with the EP defected zone exhibited sufficient coverage of the scratched regions with CeA complexes. Severe adsorption of the Ce ions on the metal surface in the defected parts derived from EDS/Mapping analysis ensured the smart corrosion inhibition occurrence in the action of the fabricated nanocomposite. Furthermore, the long-term corrosion inhibition effects were observed by the salt spray test. The results displayed the corrosion retardation propensity of the  $\beta$ -CD-CeA-MGO over the steel substrate. The detailed-level DFT studies strongly ensured the interactions of CeA complex and  $\beta$ -CD molecules with the organic coating molecules. Despite the good corrosion inhibition impact of the constructed nano-carriers based on  $\beta$ -CD-CeA-MGO, this system is not intelligent enough to show inhibition action only in the case of pH changes. Therefore, applying a pH-sensitive polymeric shell over the  $\beta$ -CD-CeA-MGO particles may cause the system completely intelligent. In this case, the constructed system will act more efficiently for longer exposure times and release the inhibitors on-demand. This can be the topic for future researches.

### **Acknowledgment**

The present study was supported by Golestan University, Gorgan, Iran.

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### Highlights:

- $\beta$ -CD was used as novel nano-container for corrosion inhibitor encapsulation.

- Modified graphene oxide assisted the smart-transmission of inclusion complexes.
- Designed nano-filler significantly improved the self-healing feature of coating.

**Table 1-** Particles weight reduction percentage between 30 °C and 600 °C temperatures.

<b>Nano-particle</b>	<b>30-120 °C</b>	<b>120-200 °C</b>	<b>220-320 °C</b>	<b>450-600 °C</b>
<b>GO</b>	10%	3%	6%	14%
<b>MGO</b>	8%	13%	40%	0%
<b><math>\beta</math>-CD-MGO</b>	8%	8%	12%	14%
<b><math>\beta</math>-CD-CeA-MGO</b>	8%	18%	40%	0%

**Table 2-** Potentiodynamic polarization parameters for the mild steel sample after 24 h immersion in 3.5% NaCl solution.

Sample	$E_{\text{corr}}^1$ (V/Ag/AgCl)	$i_{\text{corr}}^2$ ( $\mu\text{A.cm}^{-2}$ )	$\beta_a^3$ (mV.dec <sup>-1</sup> )	$-\beta_c^4$ (mV.dec <sup>-1</sup> )
Blank	-0.70	7.62	112	152
$\beta$ -CD/MGO	-0.83	0.88	260	172
$\beta$ -CD-CeA/MGO	-0.64	0.06	245	102

<sup>1</sup> The standard deviation varied between 3% and 8%

<sup>2</sup> The standard deviation varied between 5% and 9%.

<sup>3</sup> The standard deviation varied between 4% and 8%.

<sup>4</sup> The standard deviation varied between 5% and 9%.

**Table 3-** Electrochemical impedance spectroscopy parameters for the mild steel sample after 48 h immersion in 3.5% NaCl solution.

Sample	Time (h)	$R_s^1$ ( $\Omega \cdot \text{cm}^2$ )	$R_f^2$ ( $\Omega \cdot \text{cm}^2$ )	CPE <sub>f</sub>			CPE <sub>dl</sub>			$\eta$ (%)
				$Y_0^3$ ( $\mu\Omega^{-1} \text{cm}^{-2} \text{s}^n$ )	$n^4$	$R_{ct}^5$ ( $\Omega \cdot \text{cm}^2$ )	$Y_0^6$ ( $\mu\Omega^{-1} \text{cm}^{-2} \text{s}^n$ )	$n^7$	$\log  Z $ ( $\Omega \text{ cm}^2$ )	
Blank	1	15	-	-	-	784	394	0.83	2.8	-
	5	21	-	-	-	1214	314	0.82	3.1	-
	24	19	-	-	-	1452	953	0.70	3.1	-
	48	20	-	-	-	1469	321	0.74	3.1	-
MGO	1	13	-	-	-	1107	565	0.77	3.0	-
	5	11	-	-	-	1136	534	0.77	3.1	-
	24	12	-	-	-	1265	520	0.73	3.1	-
	48	10	-	-	-	800	550	0.71	2.9	-
$\beta$ -CD/MGO	1	10	25	287	0.84	2640	279	0.84	2.4	70
	5	10	45	352	0.79	5112	193	0.91	2.9	76
	24	11	15	249	0.80	2080	241	0.82	2.3	31
	48	10	11	611	0.70	3226	531	0.80	2.5	54
$\beta$ -CD-CeA/MGO	1	27	11064	117	0.91	3325	131	0.95	4.1	94
	5	29	8707	130	0.85	7184	147	0.95	4.1	92
	24	29	4051	113	0.85	8673	177	0.89	4.0	88
	48	26	6644	115	0.83	5439	230	0.92	4.0	88

<sup>1</sup> The standard deviation varied between 4% and 6%<sup>2</sup> The standard deviation varied between 3% and 8%.<sup>3</sup> The standard deviation varied between 5% and 9%.<sup>4</sup> The standard deviation varied between 7% and 10%.<sup>5</sup> The standard deviation varied between 6% and 12%.<sup>6</sup> The standard deviation varied between 5% and 7%.<sup>7</sup> The standard deviation varied between 5% and 8%.

**Table 4-** Electrochemical impedance spectroscopy parameters for scratched EP after 96 h immersion in 3.5% NaCl solution.

Sample	Time (h)	$R_f^1$ ( $\Omega.cm^2$ )	CPE <sub>r</sub>		$R_{ct}^4$ ( $\Omega.cm^2$ )	CPE <sub>dl</sub>		$R_t$ ( $\Omega.cm^2$ )
			$Y_0^2$ ( $\mu\Omega^{-1}cm^{-2}s^n$ )	$n^3$		$Y_0^5$ ( $\mu\Omega^{-1}cm^{-2}s^n$ )	$n^6$	
EP	1	194	54	0.87	23850	6	0.86	24044
	5	367	64	0.80	19063	12	0.82	19430
	24	678	55	0.74	11813	11	0.80	12491
	48	745	76	0.70	14865	62	0.68	15610
	96	412	98	0.65	10946	89	0.60	11358
$\beta$ -CD-MGO/EP	1	64	11	0.86	16532	5	0.89	16596
	5	149	21	0.79	19345	6	0.94	19494
	24	524	9	0.81	7645	10	0.88	8169
	48	359	51	0.80	11845	46	0.82	12204
	96	298	61	0.75	10115	52	0.79	10413
$\beta$ -CD-CeA-MGO/EP	1	377	12	0.81	26531	15	0.85	26908
	5	525	16	0.82	59292	14	0.91	59817
	24	1003	23	0.80	43563	17	0.90	44566
	48	2011	26	0.70	28275	10	0.97	30286
	96	1069	28	0.72	11739	24	0.89	12808

<sup>1</sup> The standard deviation varied between 4% and 9%

<sup>2</sup> The standard deviation varied between 5% and 8%.

<sup>3</sup> The standard deviation varied between 6% and 11%.

<sup>4</sup> The standard deviation varied between 5% and 9%.

<sup>5</sup> The standard deviation varied between 6% and 10%.

<sup>6</sup> The standard deviation varied between 3% and 6%.

**Table 5-** Electrochemical impedance spectroscopy parameters for un-scratched SC after 24 days immersion in 3.5% NaCl solution.

Sample	Time (day)	$R_f^1$ ( $M\Omega.cm^2$ )	$CPE_f$		$R_{ct}^4$ ( $\Omega.cm^2$ )	$CPE_{dl}$		$D_1$ (%)	$D_2$ (%)
			$Y_0^2$ ( $\mu\Omega^{-1}cm^{-2}s^n$ )	$n^3$		$Y_0^5$ ( $\mu\Omega^{-1}cm^{-2}s^n$ )	$n^6$		
EP	2	1300	0.00016	0.88	-	-	-	-	-
	7	814	0.00026	0.85	12	0.0026	0.91	50	10
	14	310	0.00065	0.79	36	0.0032	0.88	80	29
	24	92	0.00142	0.71	82	0.0053	0.81	94	43
$\beta$ -CD-MGO/EP	2	5312	0.00013	0.89	-	-	-	-	-
	7	1743	0.00021	0.91	5	0.0018	0.93	63	48
	14	1125	0.00028	0.85	11	0.0021	0.90	84	73
	24	600	0.00052	0.76	21	0.0026	0.88	95	89
$\beta$ -CD-CeA-MGO/EP	2	36841	0.00006	0.95	-	-	-	-	-
	7	23806	0.00011	0.95	-	-	-	31	-
	14	18620	0.00019	0.91	-	-	-	51	-
	24	5842	0.00031	0.85	10	0.0009	0.95	72	78

<sup>1</sup> The standard deviation varied between 4% and 8%

<sup>2</sup> The standard deviation varied between 7% and 12%.

<sup>3</sup> The standard deviation varied between 5% and 8%.

<sup>4</sup> The standard deviation varied between 6% and 11%.

<sup>5</sup> The standard deviation varied between 8% and 10%.

<sup>6</sup> The standard deviation varied between 4% and 7%.