

# Orange Peel-impregnated Sodium Montmorillonite as a Sustainable Corrosion Inhibitor for Mild Steel

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**Editor's note:** Chemical corrosion inhibitors are typically toxic and pose significant risks to both the environment and human health. Sheydaei and Edraki proposed the use of sodium montmorillonite modified with orange peel extract as sustainable nanomaterials for creating environmentally friendly inhibitor coatings for mild steel.

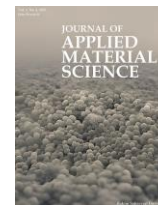
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## Original Research

# Orange Peel-impregnated Sodium Montmorillonite as a Sustainable Corrosion Inhibitor for Mild Steel

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## Abstract

Metal structures are always exposed to corrosion, and this slow but continuous phenomenon causes a decrease in the strength of metals, ultimately causing their destruction and inflicting financial and human losses. Chemical inhibitors have always been used to prevent the corrosion process, but due to their irreparable harm to the environment, the use of green corrosion inhibitors has received much attention. This study investigates the corrosion inhibition properties of sodium montmorillonite nanoparticles (Na<sup>+</sup>-MMT) with orange peel compounds. The prepared nanoparticles (O-MMT) were evaluated using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The evaluation results showed that the orange peel compounds were successfully added to the host (MMT). Then, the nanoparticles were added to the epoxy (EP) matrix and the effect of improving their anti-corrosion resistance was evaluated using electrochemical impedance spectroscopy (EIS) and polarization methods. The results showed that the inhibition efficiency (IE) for O-MMT is around 94%.

Keywords: Anticorrosion; Green chemistry; Environmental pollution; Sustainable inhibitors.

## 1. Introduction

Today, many industries use mild steel in various applications, which can be attributed to its formability, acceptable hardness, and relatively low cost [1]. However, its vulnerability to corrosion can be considered a negative factor in contrast to these advantages [2]. Researchers

have been working on various approaches to improve the corrosion resistance of mild steel for decades, but perhaps the most effective approach is the use of corrosion inhibitors [3,4].

There are many definitions of an inhibitor in the literature, but perhaps the simplest definition for an inhibitor is: a substance that, at low concentrations,

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prevents corrosion (or slows its progress) [5]. Although they have many advantages such as fast reaction and high efficiency, many chemical inhibitors are toxic and are extremely harmful to the environment and humans [6-8]. Therefore, researchers have been looking for alternatives for these materials in recent years, using expired drugs, natural gums, bio-polymers, surfactants, food supplements, and plants [9-12]. Among them, plants are of great interest because they are low-cost and environmentally friendly in nature, due to their non-toxic compounds [13,14].

The peel of many fruits is discarded as waste or used in the preparation of fertilizers [15,16]. Orange peel contains bioactive components such as polyphenolic compounds, flavonoids, and carotenoids, which in addition to antibacterial properties have the ability to provide corrosion resistance [17,18]. One simple method for introducing the compounds of an extract into a host is the cation exchange process, in which the cationic compounds of the host are removed and replaced by the cationic compounds of the extract [19-22].

Na<sup>+</sup>-MMT, a type of nanoclay mineral, can expand in its interlayer spaces when immersed in water or ethanol. This swelling alters its chemical structure and allows it to accept other compounds through cation exchange. In this study, compounds derived from orange peel were incorporated into the interlayer space of sodium montmorillonite (Na<sup>+</sup>-MMT). Then, the modified MMT (O-MMT) was added to an epoxy matrix and applied to a mild steel substrate. The anti-corrosion properties of this coating in a saline solution were then examined using Electrochemical Impedance Spectroscopy (EIS) and polarization techniques.

## 2. Experimental

### 2.1. Materials

The Na<sup>+</sup>-MMT, orange peel powder, sodium chloride, and mild steel were obtained from Rockwood Company (USA), Giyahkala Company (Iran), Ghatran Shimi Tajhiz Company (Iran), and Iranian Mobarakeh Steel Company, respectively.

### 2.2. Preparation of O-MMT and coatings

In this study, O-MMT was prepared using a cation exchange process in an aqueous solution, as reported in the literature [19-22]. For the preparation of nanocomposite

coatings, bisphenol A diglycidyl ether (containing nanoparticles) was first added to xylene and methyl ethyl ketone (ratio 1:1) and stirred for 60 min. Next, Jefamine D230 was used as a hardener and added to the mixture in a ratio of 1:2 (relative to resin) and stirred for 5 min. The substrates were covered with the mixture and kept at ambient temperature for 1 day, and finally placed in an oven at 80°C for 24 h. Also, the content of nanoparticles used in the coatings was 1.5 and 3 wt%.

### 2.3. Measurements

A Tensor II spectrometer was used for FTIR evaluation. SEM VEGA3 was used for images. The dispersion of nanoparticles was investigated by energy dispersive spectroscopy (EDX) coupled with SEM (SEM-EDX) on a Cambridge instrument. An XPert PRO MPD instrument was used for XRD evaluation. A potentiostat-galvanostat instrument (CorrTest CS350) was used to evaluate the corrosion resistance of the samples. For this purpose, two electrolytes (O-MMT in NaCl solution and only 3.5 wt% NaCl solution), three electrodes including a working electrode (MS), a saturated calomel electrode (SCE), and an auxiliary electrode (Pt), were used in the electrochemical cell and the measurements were performed in the open circuit potential (OCP) and the perturbation amplitude of ±10 mV. Also, the polarization test was performed in the solution phase after 24 h of immersing the steel coupon in solutions with a scanning rate of 0.5 mV/s and in the range of ±200 mV of OCP using a similar electrochemical cell device used for the EIS test. The following equation was used to calculate the inhibition efficiency (IE) for the coatings [23]:

$$IE(\%) = \frac{I_{\text{pure coating}} - I_{\text{nanocomposite coating}}}{I_{\text{pure coating}}} \times 100 \quad (1)$$

where,  $I_{\text{pure coating}}$  and  $I_{\text{nanocomposite coatings}}$  are the corrosion current densities of coatings without and with the nanoparticle, respectively.

## 3. Results and discussion

Figures 1 and 2 show the FTIR spectra and the XRD patterns of fabricated nanoclays, respectively. Moreover, Table 1 summarizes the peak assignments for spectra presented in these two Figures. The presence of orange peel peaks in the O-MMT spectrum indicates that the cation exchange process has been completed and that the O-MMT contains orange peel compounds. Also, the

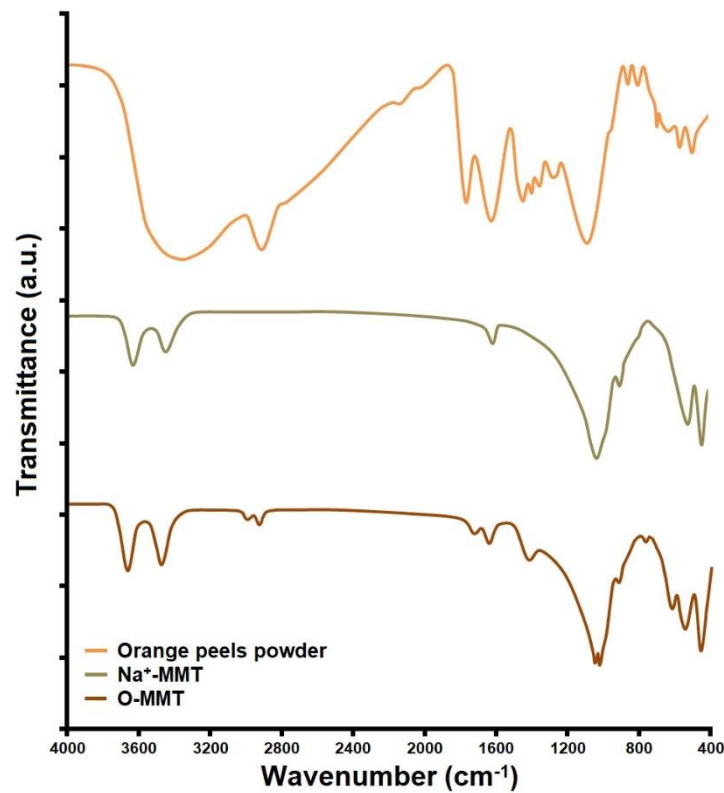


Figure 1. FTIR spectra of orange peel powder, Na<sup>+</sup>-MMT, and O-MMT.

XRD results show a change in  $2\theta$  and  $d$ -spacing due to the absence of Na<sup>+</sup> cation and the presence of orange peel compounds in the final product [19-23].

SEM images of the samples in Figure 3 show that the morphology before and after the cation exchange

process did not change significantly, although this behavior has been reported in the literature [19-23].

SEM-EDX mapping images (see Figure 4) clearly show the presence and distribution of O-MMT (the red dots of Si atoms) in the matrix. The excellent distribution

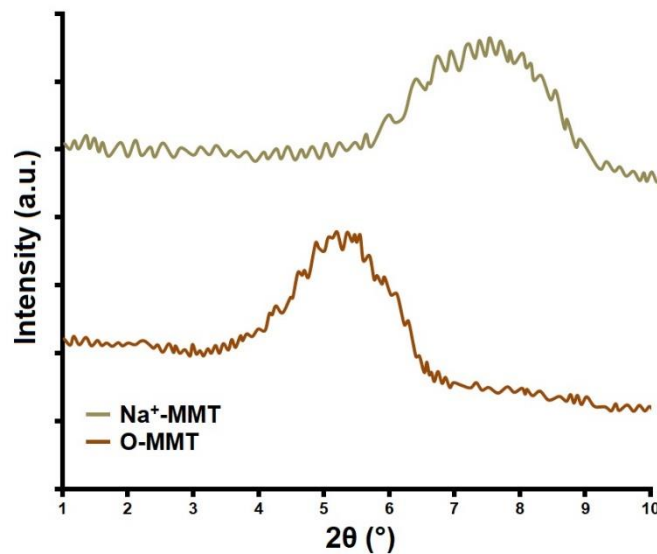
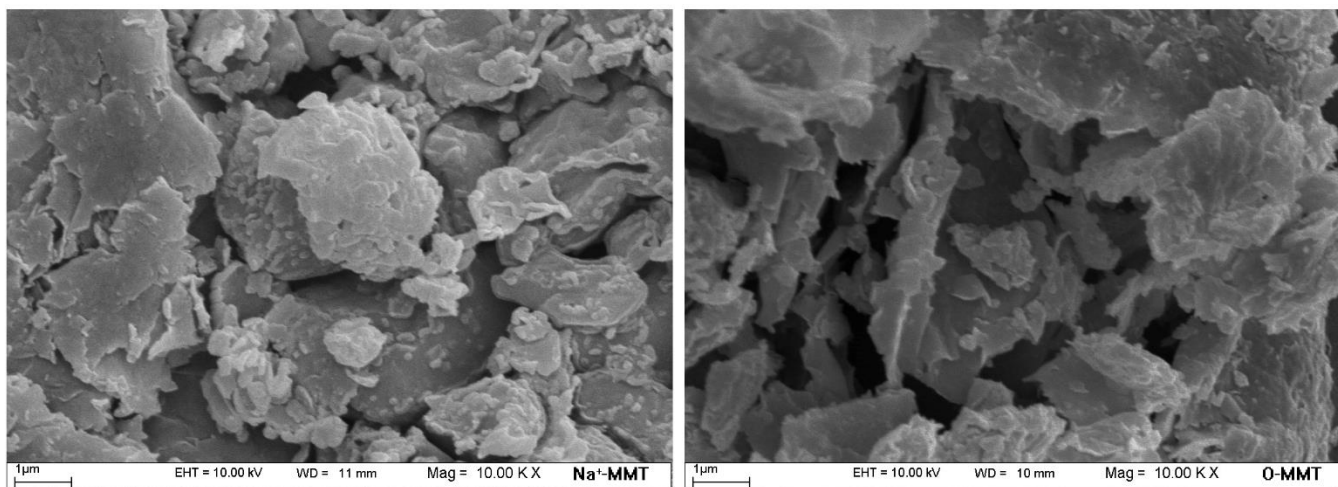


Figure 2. XRD patterns of Na<sup>+</sup>-MMT and O-MMT.

**Table 1.** FTIR absorption peaks and XRD peaks assignments

Sample	Wavenumber (cm <sup>-1</sup> )	Characteristics	Peak 2θ and d-spacing
Na <sup>+</sup> -MMT	455 and 1038	Bending and stretching Si-O vibrations	7.4° and 11.22 Å
	534	Si-O-Al vibration and MgO groups	
	916	Al <sub>2</sub> OH bending groups	
	1616-3405	Scissoring vibrations and symmetric vibrations of OH units	
	3642	Stretching of OH (Si-OH groups)	
Orange peel	3420	OH groups (carbohydrates and lignin groups)	-
	2925	C-H stretching vibration	
	1736	The carbonyl groups (e.g., ester)	
	1617	Aliphatic and/or unsaturated aromatic compounds	
	1428	Aliphatic chains (form the basic structure of lignocellulosic materials)	
	1045	C-O-H or C-O-R (alcohols or esters)	
	3680	Stretching of OH (Si-OH groups)	
O-MMT	3498	Scissoring vibrations and symmetric vibrations of OH units	5.2° and 17.14 Å
	2925 and 3000	C-H stretching vibration	
	1695	The carbonyl groups (like ester)	
	1617	OH units (Na <sup>+</sup> -MMT) or Aliphatic and/or unsaturated aromatic compounds (Orange peel)	
	1418	Aliphatic chains (form the basic structure of lignocellulosic materials)	
	1045	C-O-H or C-O-R (alcohols or esters)	
	1038	Bending and stretching Si-O vibrations	
	916	Al <sub>2</sub> OH bending groups	
	534	Si-O-Al vibration and MgO groups	
	458	Bending and stretching Si-O vibrations	

Notes: References [19-24] were used to assign Na<sup>+</sup>-MMT FTIR peaks, and reference [25] was used to assign orange peel FTIR peaks.

**Figure 3.** SEM images of Na<sup>+</sup>-MMT (left) and O-MMT (right).

in the nanocomposites indicates that the nanoparticles are well-compatible with the matrix and hence do not tend to agglomerate.

The results of the EIS test are reported in Figures 5 and 6 and Table 2. The Nyquist plots in Figure 5 presented that the curve diameter, representing the charge transfer

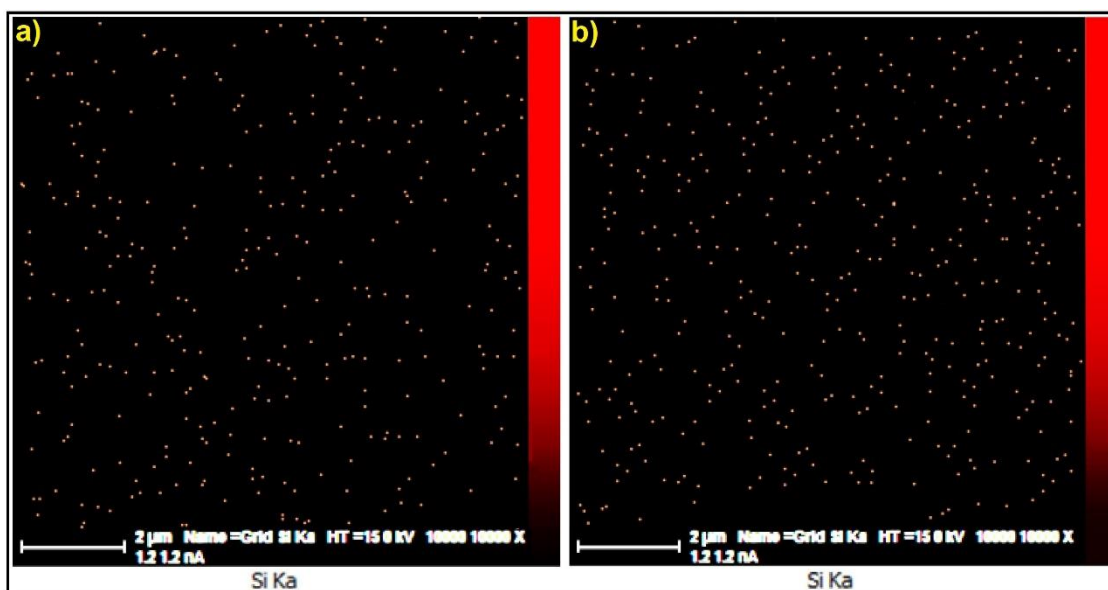


Figure 4. EDX results demonstrate the dispersion of O-MMT in the matrix: (a) EP/1.5% O-MMT and (b) EP/3% O-MMT.

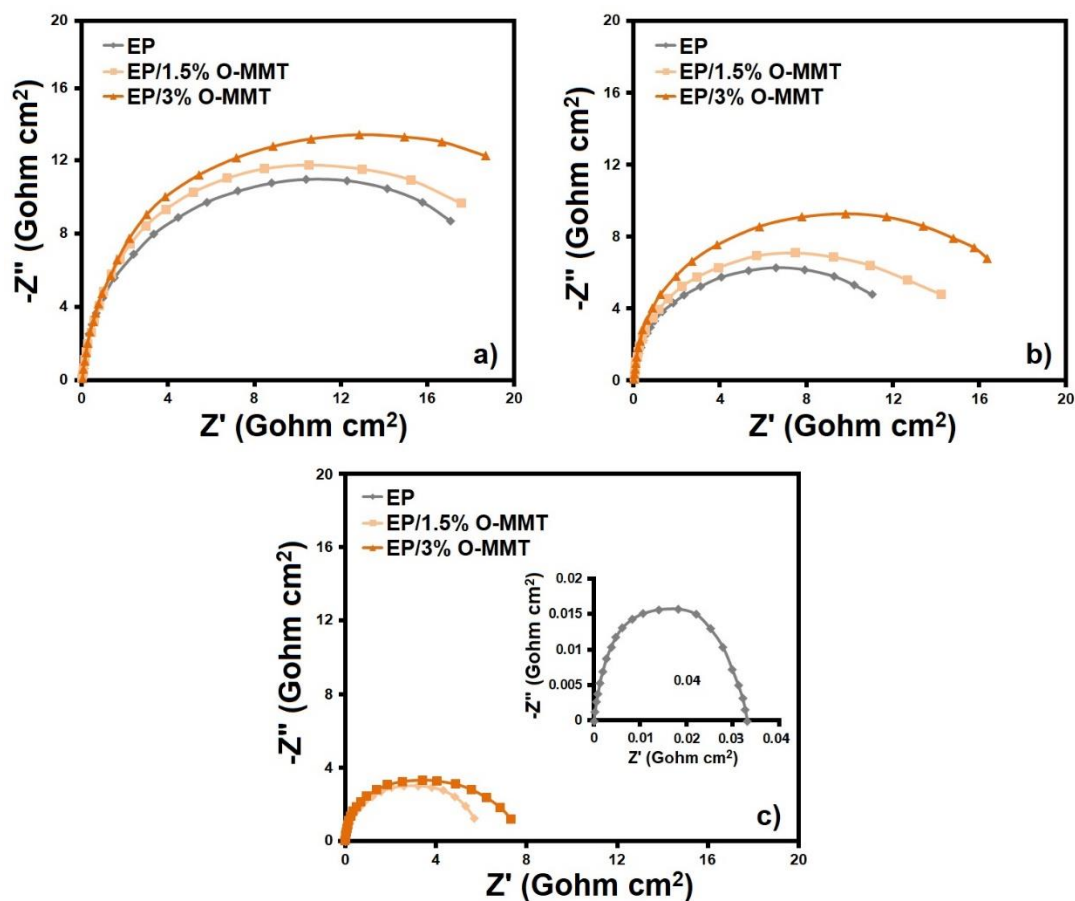
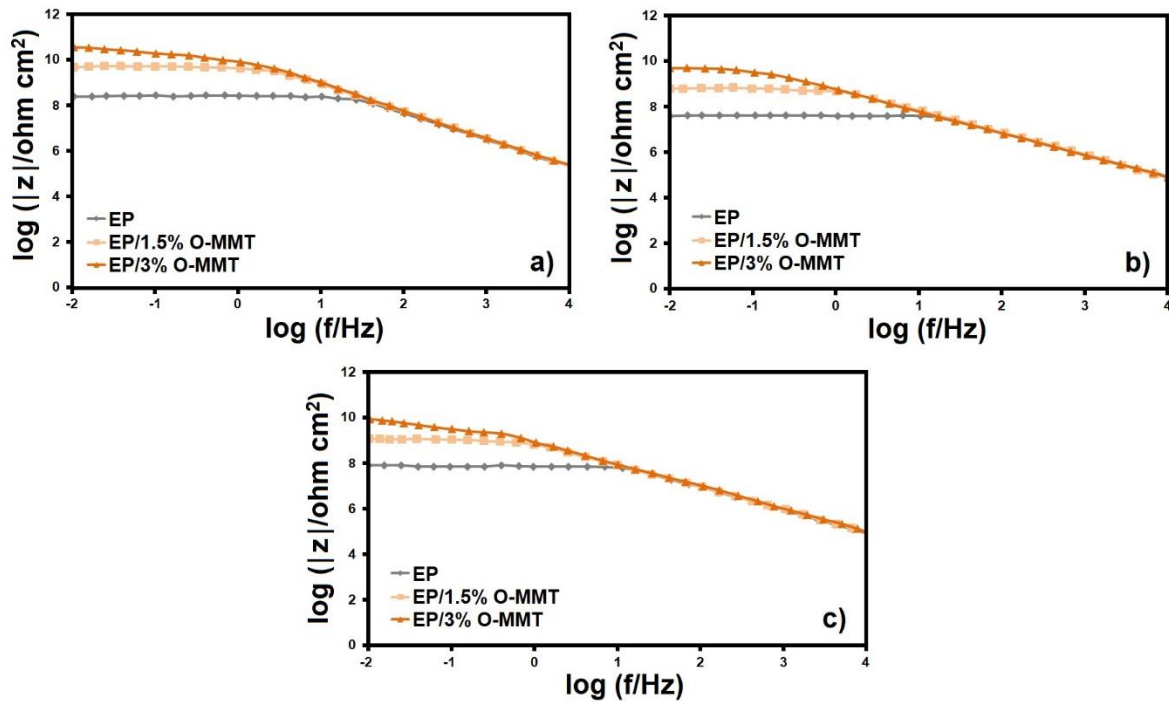


Figure 5. Nyquist diagrams of surfaces coated with EP, EP/1.5%O-MMT, and EP/3%O-MMT after immersion for (a) 9, (b) 16, and (c) 36 days.



**Figure 6.** Bode diagrams of the surfaces coated with EP, EP/1.5 % O-MMT, and EP/3 % O-MMT after immersion for (a) 9 days, (b) 18 days, and (c) 36 days.

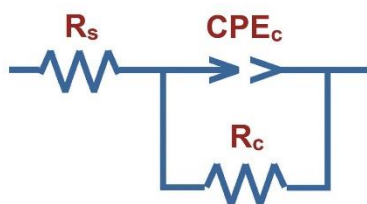
resistance ( $R_{ct}$ ), decreases with increasing immersion time. This trend indicates degradation over time, but this degradation occurs much slower for nanocomposites than for pure matrix, indicating that nanoparticles have anti-corrosion properties. In fact, these anti-corrosion properties are related to orange peel compounds because it has been reported in the literature that  $\text{Na}^+$ -MMT alone cannot improve anti-corrosion resistance [19].

The results show that the pure matrix is very vulnerable over time and water molecules as well as aggressive ions penetrate it very easily. Figure 6 shows the Bode plots that represent the corrosion resistance and impedance. With the passage of time and increasing immersion time, a large change is seen in the frequency region for the pure matrix, which indicates the capacitive behavior of the pure matrix. The results show that nanocomposite coatings are much more resistant to

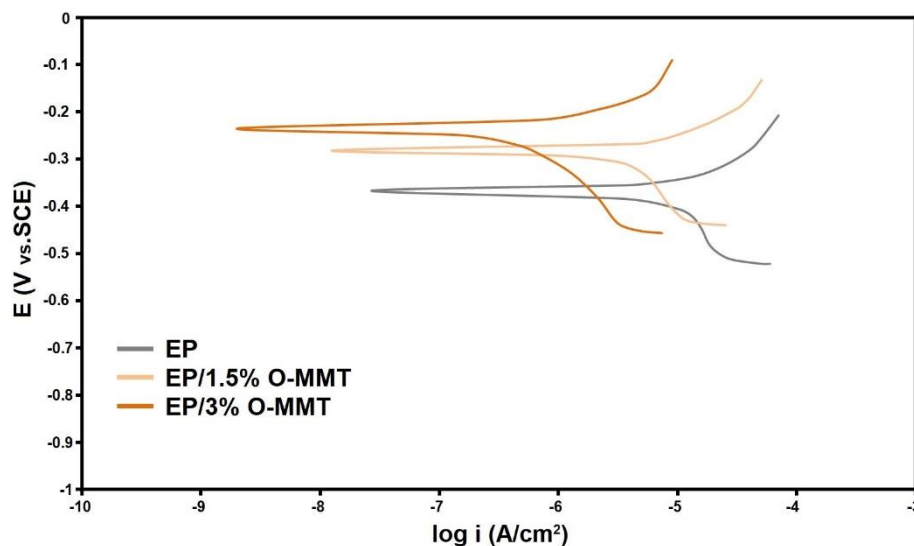
**Table 2.** Electrochemical parameters obtained from EIS results for samples immersed in the 3.5% NaCl solution

Sample	Immersion time (days)	$R_{ct}$ ( $\Omega \cdot \text{cm}^2$ )	$R_c$ ( $\text{M}\Omega \cdot \text{cm}^2$ )	$\text{CPE}_c$		$\text{Log }  z $ ( $\Omega \cdot \text{cm}^2$ )
				$Y_{0,c}$ ( $\text{n}\Omega^{-1} \cdot \text{cm}^2 \cdot \text{s}^n$ )	$n_c$	
EP	9	$17.05 \times 10^9$	13151	3.19	0.82	7.87
	18	$11.04 \times 10^9$	28.9	1.08	0.71	7.50
	36	$0.03 \times 10^9$	7.3	0.46	0.59	7.04
EP/1.5% O-MMT	9	$17.54 \times 10^9$	17924	1.39	0.76	9.02
	18	$14.25 \times 10^9$	6138	1.01	0.68	8.69
	36	$5.69 \times 10^9$	219	0.10	0.54	8.10
EP/3% O-MMT	9	$18.68 \times 10^9$	26413	0.42	0.74	9.98
	18	$16.36 \times 10^9$	10629	0.39	0.72	9.57
	36	$7.31 \times 10^9$	2388	0.32	0.70	8.85

Notes:  $R_c$ : Coating resistance;  $\text{CPE}_c$ : The constant phase element related to the coating;  $n_c$ : The constant related to surface heterogeneity in the coating;  $Y_{0,c}$ : Admittance of the coating;  $\text{Log } |z|$ : The impedance module.



**Figure 7.** Equivalent circuit for the description of coatings (In this circuit,  $R_s$ ,  $R_c$ , and  $CPE_c$  indicate solution resistance, coating resistance, and the constant phase element related to coating, respectively).



**Figure 8.** Results of the polarization test after immersing the samples for 24 days.

corrosion, compared to the pure matrix. According to the results of Table 2, it can be said that the use of nanoparticles has caused an increase in the absolute value of the impedance at all immersion times compared to the pure matrix. This indicates better performance and active inhibition of the nanocomposites.

The destruction of pure epoxy can be attributed to the formation of hydroxyl ions at the coating/metal interface in the cathode areas, which causes an increase in pH below the coating surface [19,23]. This increase in pH ultimately causes hydrolysis of the EP interfacial bonds and reduces its adhesion to the substrate surface

[19]. Also, the equivalent circuit that has the maximum compatibility with the impedance results is shown in Figure 7.

The results of the polarization test are reported in Figure 8 and Table 3. According to the results, the corrosion flow has decreased with the addition of nanoparticles and the corrosion potential has shifted to more positive values. Based on the results, it can be said that nanoparticles can be classified as anodic inhibitors. Also, the nanocomposite with a nanoparticle loading content of 3 wt% has the best performance the lowest corrosion current density, and the lowest corrosion rate.

**Table 3.** Electrochemical parameters obtained from the polarization test on samples immersed in the saline solution

Sample	$i_{corr}$ (A.cm <sup>-2</sup> )	$E_{corr}$ VS.SCE (mV)	$\beta_a$ (V.dec)	$\beta_c$ (V.dec)	IE (%)
EP	$1.009 \times 10^{-5}$	-367	0.245	0.587	-
EP/1.5% O-MMT	$3.27 \times 10^{-6}$	-262	0.101	0.346	67.59
EP/3% O-MMT	$5.96 \times 10^{-7}$	-235	0.114	0.302	94.04

Notes: Corrosion potential:  $E_{corr}$ ; Corrosion current density:  $i_{corr}$ ; The anodic Tafel slope:  $\beta_a$ ; Cathodic Tafel slope:  $\beta_c$ .

**Table 4.** Corrosion inhibition performance of some plants in different corrosion media

Plant	Substrate	Corrosive Medium	Maximum IE (%)	Reference
<i>Garcinia cambogia</i>	Mild steel	NaCl	88.85	[4]
<i>Ganoderma Lucidum</i>	Mild steel	NaCl	98.26	[11]
<i>Clitoria ternatea</i>	Mild steel	NaCl	86	[20]
<b>Pine pollen</b>	Mild steel	NaCl	87.16	[23]
<i>Catharanthus roseus</i>	Mild steel	NaCl	84	[26]
<b>Nettle leaves</b>	Mild steel	NaCl	95	[27]
<b>Orange peel</b>	Mild steel	NaCl	94	This study

The improvement of the corrosion resistance of the coatings can be attributed to the synergistic effect of MMT and orange peel. In fact, MMT with its sheet structure can act as a protective shield against aggressive species, and on the other hand, it has the ability to react with hydroxyl ions in the cathodic region and thereby produce insoluble compounds preventing oxygen from reaching this region [23]. Also, orange peel contains compounds such as polyphenols, flavonoids, carotenoids, and vitamin C [18,25]. These compounds contain benzene rings, heteroatoms, and carbonyl groups that can share their free electron pairs with the empty orbitals of the iron atoms on the metal surface [18,20]. They are adsorbed on the surface in this way [5]. Therefore, they block the anodic regions by forming a layer [18,20]. Table 4 presents a comparison between our results and the IE results of several previous studies.

#### 4. Conclusions

In summary, a new corrosion inhibitor was prepared in this study using orange peel powder and Na<sup>+</sup>-MMT. The results showed that this inhibitor can improve corrosion resistance. The highest inhibition efficiency was related to the nanocomposite containing 3 wt% nanoparticles, which was 94%. This inhibitor is environmentally friendly and is obtained from waste resources. The use of plant compounds can be considered a suitable alternative to chemical inhibitors because they are both inexpensive and highly effective.

#### Conflict of Interest

The authors declare no conflict of interest.

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