



Chitosan biopolymer as a green corrosion inhibitor for 304 stainless steel

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ABSTRACT

Chitosan (CTS) is a widely bio-available polymer with a structure rich in oxygenated and nitrogenous functional groups that promotes its interaction with the metallic surface of steels. The efficiency of CTS as an environmentally friendly corrosion inhibitor for 304 stainless steels (304SS) in hydrochloric acid (HCl) medium was investigated using open circuit potential, potentiodynamic polarization, and electrochemical impedance spectroscopy. The electrochemical tests were carried out in HCl 0,5 mol. L⁻¹ in the absence and presence of CTS at different concentrations, and it was also tested the synergy between CTS and potassium iodide (KI). The inhibition percentage achieved was 77.1% and 89.4% for 200 ppm CTS and 200 ppm CTS/100 ppm KI. Scanning electron microscopy and Raman spectroscopy characterizations of the 304SS surface before and after contact with the different corrosive media proved the adsorption of CTS/KI with the formation of protective layer on the metal surface.

Keywords: Natural polymers, corrosion, green inhibitors, 304 austenitic stainless steel.

Introdução

Industrial processing of stainless steel, including chemical cleaning and pickling, is conducted under acidic conditions (1) an aggressive environment for steel due to the susceptibility to corrosion (2) leading to the dissolution of the metal. Chitosan (CTS), a linear polysaccharide (3), is an environmentally friendly inhibitor that offers corrosion protection while minimizing environmental impact (4) in acidic environments (5,6), due to the presence of functional groups with oxygen and nitrogen heteroatoms in its structure, which facilitate the inhibitor adsorption on the surface of metal (7).

This study investigates the efficiency of chitosan as a corrosion inhibitor for 304 stainless steels in an HCl medium. To enhance its performance without altering the biopolymer's structure, the effect of addition of iodide ions was evaluated.

Experimental

Chemicals and Reagents

A CTS stock solution (10,000 ppm) was prepared in 1.0% (v/v) acetic acid, while a KI stock solution (5,000 ppm) was prepared in 0.5 mol L⁻¹ HCl. All aqueous solutions were prepared using ultrapure water ($\rho > 18.2 \text{ M}\Omega \cdot \text{cm}$) obtained by a Milli-Q® purification system.

Corrosion Assay

304 stainless steel (304SS) coupons were polished using metallographic fabric with a 1.0 μm alumina suspension, then washed with ultrapure water, followed by an ultrasonic bath with anhydrous ethanol. The corrosive medium was prepared with 20 mL of 0.5 mol L⁻¹ HCl solution with varying concentrations of CTS (50, 100, 200, 500 ppm), and also with 200 ppm of CTS and KI (50 and 100 ppm). Electrochemical evaluations, included open-circuit potential (OCP), potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS), were conducted in a three-electrode cell setup with 304SS, with a delimited area of 0,44 cm² as the working electrode, Pt as the counter electrode, and Ag/AgCl (3.0 mol. L⁻¹ KCl) as the reference. Measurements were performed using a PGSTAT 128 N potentiostat (Metrohm), following a 1-hour stabilization at OCP. Potentiodynamic scans ranged from -0.55 V to 0.0 V at 1.0 mV s⁻¹, while EIS was conducted from 100 mHz to 10 kHz with a 10 mV perturbation.

Morphological Characterisation.

Surface and structural characterizations were conducted via scanning electron microscopy (SEM) (JEOL JSM-6010LA), Fourier-transform infrared spectroscopy (FT-IR) (Varian 660-IR), and Raman spectroscopy (Renishaw InVia Micro-Raman), using respective high-resolution instruments.



Results and Discussions

The open circuit potential (OCP) measurements for the 304SS coupons exhibited similar trends, as shown in Figure 1. The presence of the inhibitor resulted in a shift of the potential toward less negative values, indicating a reduced tendency for oxidation, due to the presence of inhibitor.

From the polarization curves the corrosion parameters were obtained, as shown in Table 1. The inhibitor efficiencies were calculated based on corrosion current densities (j_{corr}), where the CTS exhibited maximum inhibition at a concentration of 200.0 ppm with 77.1 %. And the addition of 100 ppm KI to the corrosive medium resulted in an inhibition efficiency of 89.4%, demonstrating a synergy between CTS and KI.

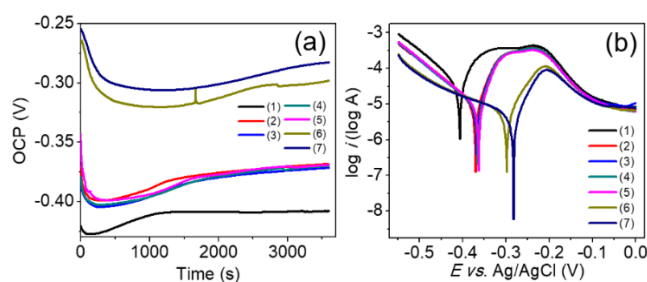


Figure 1. (a) OCP and (b) potentiodynamic polarization curves obtained for 304SS in 0.5 mol L⁻¹ HCl medium containing different concentrations of CTS and KI: (1) 0.0 ppm, (2) 50.0 ppm CTS, (3) 100.0 ppm CTS, (4) 200.0 ppm CTS, (5) 500.0 ppm CTS, (6) 200.0 ppm CTS/50.0 ppm KI and (7) 200.0 ppm CTS/100.0 ppm KI.

Table 1. Parameters recorded from the OCP and polarization curves for 304SS at 0.5 mol L⁻¹ HCl medium in the absence and presence of CTS/KI.

C (CTS) (ppm)	C(KI) (ppm)	OCP (mV)	E _{corr} (mV)	j _{corr} (μA cm ⁻²)	I (%)*	R _p (Ω)
0.0	0.0	-408	-406	78	---	423
50.0	0.0	-372	-370.3	26	67	1108
100.0	0.0	-373	-368	21	72	1268
200.0	0.0	-371	-363	17.9	77.1	1437
500.0	0.0	-363	-358	19.6	74.9	1373
200.0	50.0	-298	-298	13.9	82.2	3388
200.0	100.0	-283	-282	8.3	89.4	4068

* $I(\%) = \left(\frac{j_{corr}^0 - j_{corr}^i}{j_{corr}^0} \right) \times 100\%$, where j_{corr}^0 and j_{corr}^i are the corrosion current densities in the absence and presence of inhibitor.

Electrochemical impedance spectroscopy (EIS) measurements were performed at the optimal inhibitor concentrations to assess their effect on charge transfer resistance (R_{ct}). The R_{ct} increased from 505 Ω in the uninhibited medium to 1360 Ω with the addition of CTS, and further to 2740 Ω when CTS was combined with KI. These results confirm the effectiveness of CTS and KI in inhibiting corrosion by forming a protective layer on the 304SS surface.

Morphological and chemical aspects

The morphological and chemical characteristics of 304SS corrosion were evaluated by SEM and Raman spectroscopy in the absence and presence of 200 ppm chitosan (CTS) and 200 ppm CTS combined with 100 ppm KI. SEM analysis revealed severe surface degradation after 24 h in HCl, while the presence of CTS reduced the extent of corrosion and promoted the formation of a protective layer. The addition of KI further improved surface coverage and corrosion resistance. The formation of a well-adherent layer is attributed to interactions between oxygen- and nitrogen-containing groups in CTS and the metal surface, as supported by FT-IR data. Iodide ions enhanced these interactions through chemical and electrostatic effects (8). The Raman spectra exhibit a broad band between 1000 and 2000 cm⁻¹ and a sharp peak around 685 cm⁻¹, indicative of chitosan (9) and KI adsorption on the 304SS surface.

Conclusion

This study presents, for the first time, the application of chitosan as a corrosion inhibitor for 304 stainless steel in a hydrochloric acid medium. An inhibition efficiency of 77.1% was achieved with 200 ppm CTS, which increased to 89.4% upon the addition of KI. EIS, SEM, and Raman analyses confirmed the formation of a protective adsorptive layer on the 304SS surface.

Acknowledgments

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References

- 1.S. Santos, R. G.; S. Barbosa, T. A.; A. Mafra, M. P.; Ribeiro, A. F.; Sousa, F. F.; Andrade-Filho, T. *Mater. Lett.* **2022**, 308,
- 2.Asfia, M. P.; Rezaei, M.; Bahlakeh, G. *J. Mol. Liq.* **2020**, 315, 113679.
- 3.Verma, C.; Quraishi, M. A.; Alfantazi, A.; Rhee, K. Y. *Int. J. Biol. Macromol.* **2021**, 184, 135–143.
- 4.Wei, H.; Heidarshenas, B.; Zhou, L.; Hussain, G.; Li, Q.; Ostrikov, K. (Ken). *Mater. Today Sustain.* **2020**, 10, 100044.
- 5.Ashassi-Sorkhabi, H.; Kazempour, A. *Carbohydr. Polym.* **2020**, 237, 116110.
- 6.Rabizadeh, T.; Asl, S. K. *Mater. Corros.* **2018**, 70, 738–748.
- 7.Mouaden, K. El.; Chauhan, D. S.; Quraishi, M. A.; Bazzi, L.. *Sustain. Chem. Pharm.* **2020**, 15, 100213.
- 8.N.K. Gupta, P.G. Joshi, V. Srivastava, M.A. Quraishi, *Int. J. Biol. Macromol.* 106 (2018) 704–711.
- 9.G. Blanda, V. Brucato, F. Carfi, G. Conoscenti, V. La Carrubba, S. Piazza, C. Sunseri, R. Inguanta, *ACS Biomater. Sci. Eng.* 5 (2019) 1715–1724.