Cresol red as corrosion inhibitor in chitosan thin layers on zinc

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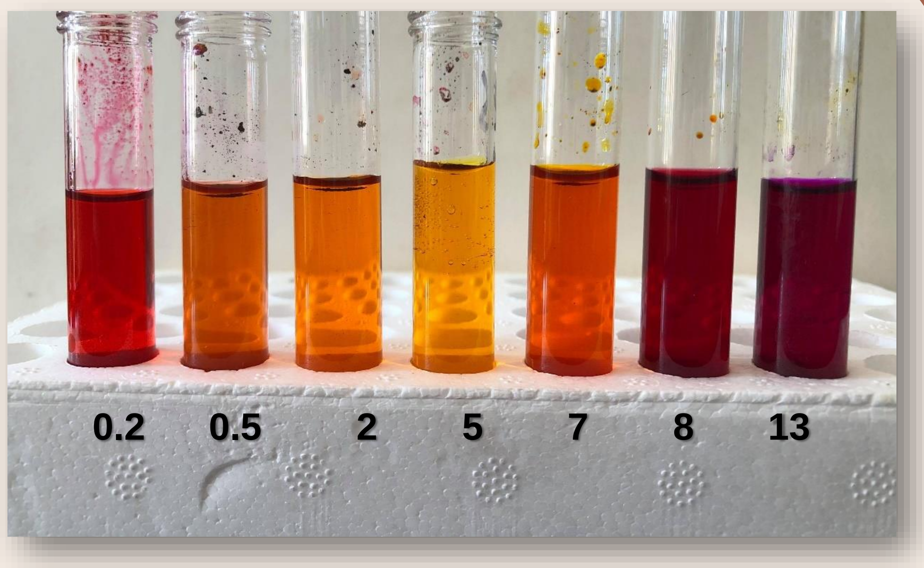
Introduction

Chitosan (Chit) is a biopolymer which is synthesized by the deacetylation of chitin extracted from the shells of crustaceans. In the past few years, chitosan was widely used in physical and electrochemical research due to its cost- efficiency, low toxicity and eco- friendly nature [1]. The corrosion inhibition potential of chitosan is due to the amino and hydroxyl groups present in the polymer structure. Chitosan can provide a possible temporary coating on several metal layers [2-3] and the anti-corrosive properties can improve by adding different inhibitors in the chitosan system. Cresol red (CR) is a widely used pH indicator, red below 1 pH, yellow/orange at pH below 7.2 and purple color at pH higher than 8.8. In the pH range between 7.2 and 8.8 is red [4].

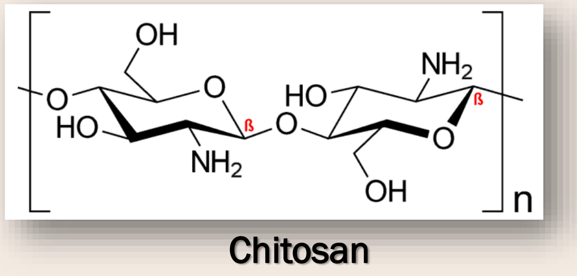
This study focuses on the influence of cresol red as a possible corrosion inhibitor for chitosan thin layers on zinc substrates and at the same time a possible indicator of corrosion process starting by color change of the coating.

Experimental section

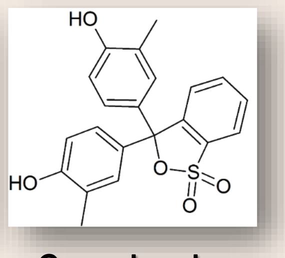


Cresol red (10^{-3} M) color change at different pH values

- **Reagents**:
  - Medium molecular weight chitosan from Aldrich
  - Cresol red (CR)
  - 99.8% acetic acid from Lachner



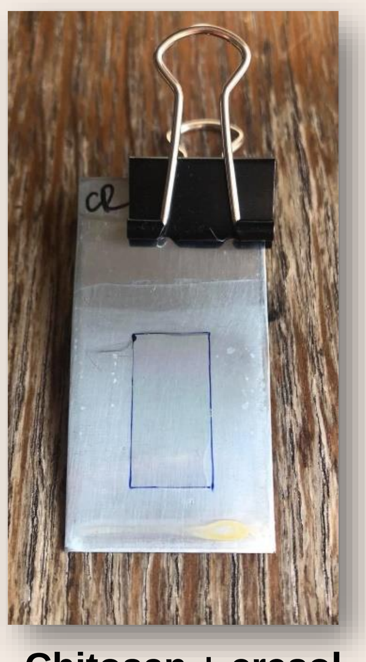
Chitosan



Cresol red

- **Sample preparation:**
  - Zinc samples were polished, ultrasonicated and cleaned with 0,1 N HCl/isopropanol
  - 1 w/w% medium viscosity chitosan solution was prepared in 1w/w% acetic acid solution was used then CR was added to the mixture in three different concentrations (10^{-2}, 10^{-3}, 10^{-4} M)
  - The coatings were prepared by dip-coating method with a withdrawal speed of 5 cm/min and were left to dry 24h at room temperature.

- **Electrochemical study:**
  - The electrochemical measurements were made in 0.2 g/L Na_2SO_4 solution at pH=7.
  - Polarization curves were recorded at OCP ± 20 and OCP ± 200 mV vs. Ag/AgCl, KCl_{sat} ; impedance spectra were recorded between 10mHz- 100kHz. The measurements were monitored in cycling wet-dry conditions.
  - The samples were kept in 0.2g/L Na_2SO_4 solution during the measurements then the solution was wiped off and left at room temperature, in laboratory conditions.



Chitosan + cresol red coating on zinc

Results

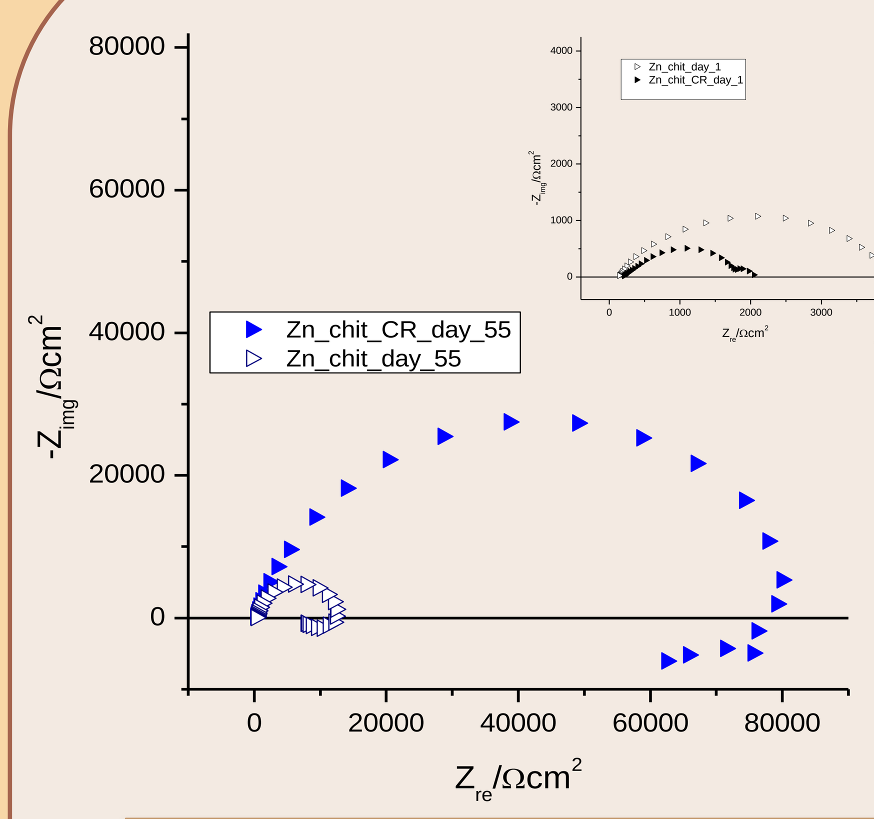


Figure 1. Nyquist impedance curves obtained for chitosan and Chit + CR_10^{-3} M coatings at the first day (▼) and after fifty five days (▲) recorded in 0.2g/L Na_2SO_4 at pH=7.

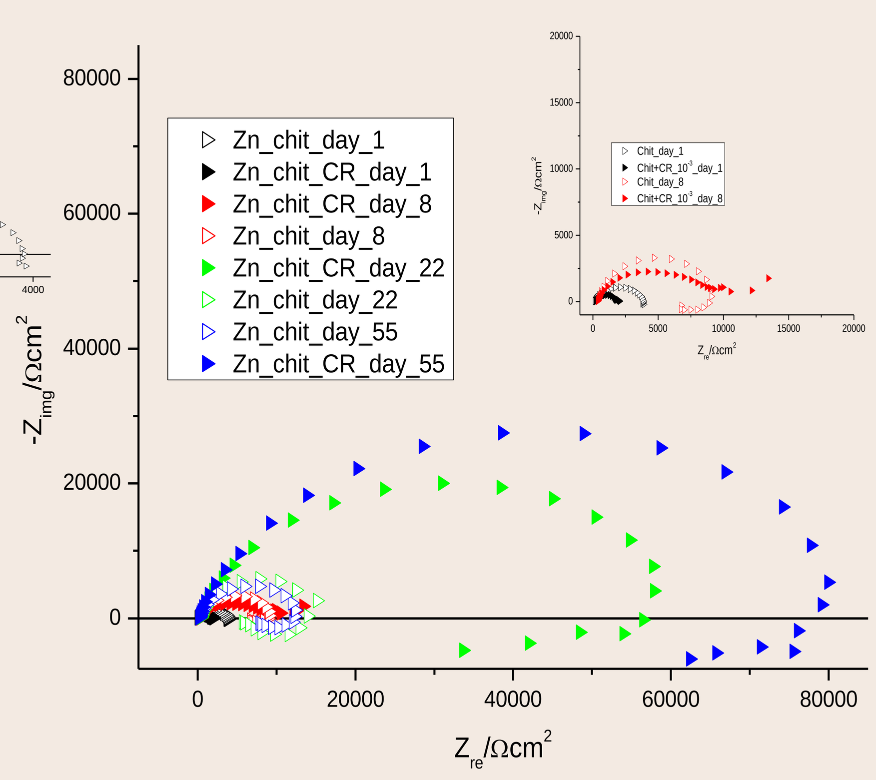


Figure 2. Time dependence of EIS diagrams for Chit and Chit + CR_10^{-3} M coatings recorded in 0.2g/l Na_2SO_4 at pH=7.

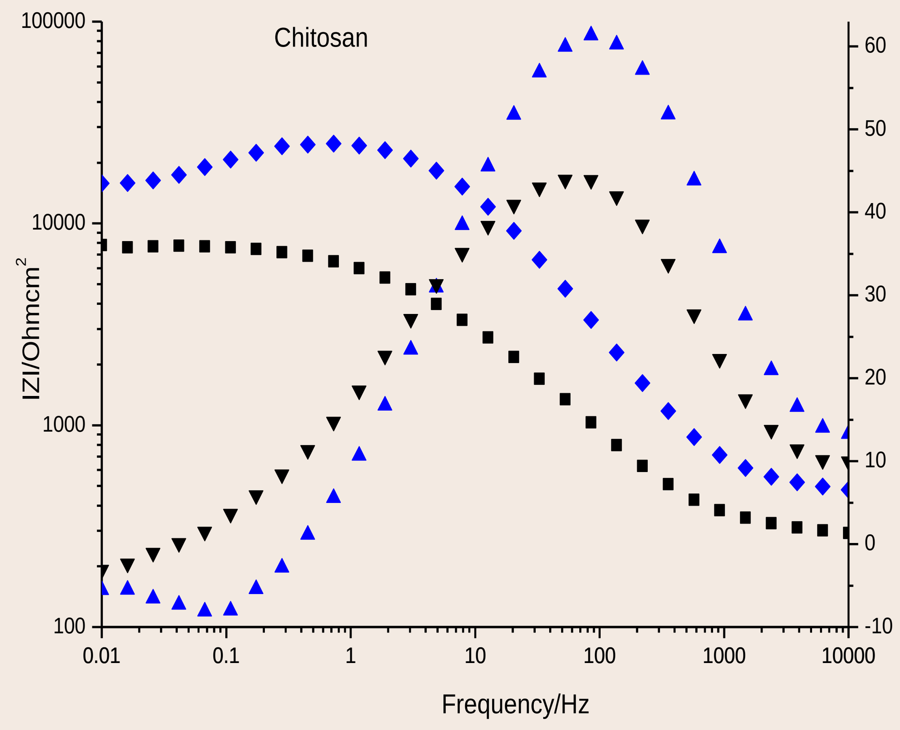


Figure 3. Bode plot of chitosan coatings at first day and after fifty five days of dry wet cycles.
Symbols: IZI ◆ Phase angle ▲ -day 55
IZI ▬ , Phase angle ▼ -day 1

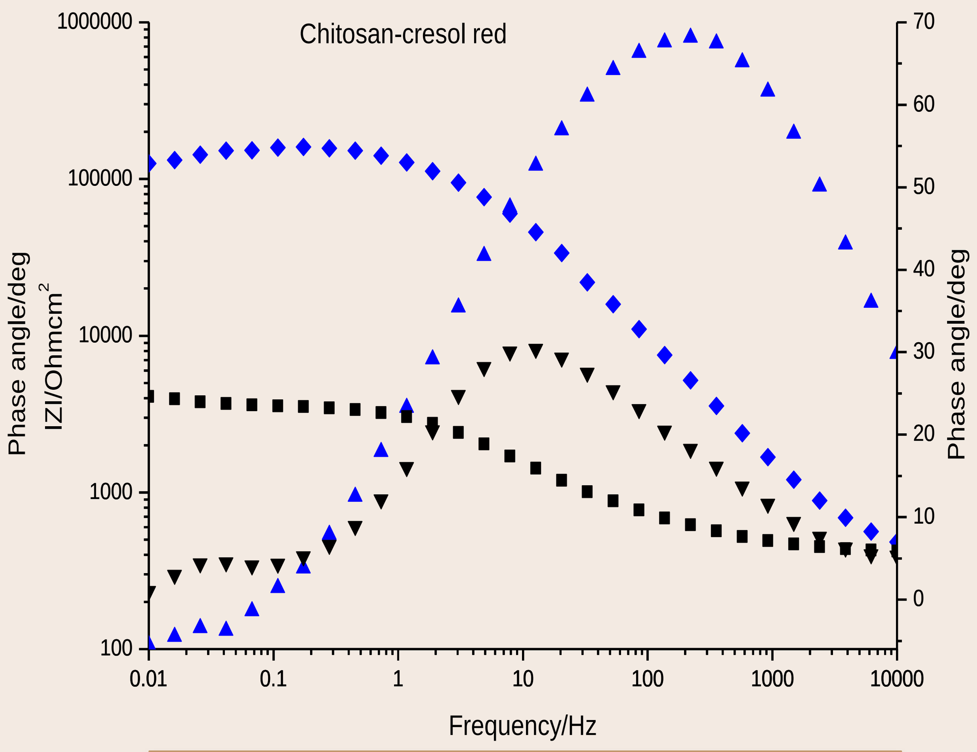


Figure 4. Bode plot of Chit + CR_10^{-3} M coatings at first day and after fifty five days of wet dry cycles.
Symbols: IZI ◆ , Phase angle ▲ - day 55
IZI ▬ , Phase angle ▼- day 1

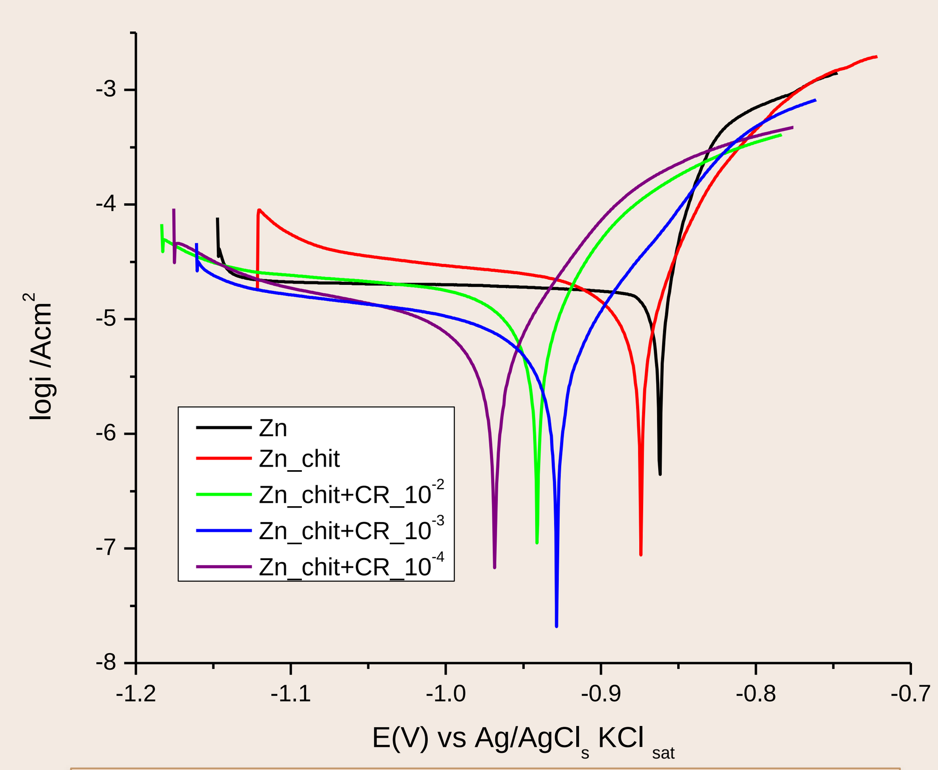


Figure 5.: Influence of CR concentration on the polarization curves of Chit + CR coatings recorded in 0.2g/L Na_2SO_4 at pH=7.

Sample	E_{corr} V vs. RE	b_c V/dec	b_a V/dec	I_{corr} μAcm^{-2}	IE (%)
Zn	-0.861	-	0.025	1.918	-
Zn_chit	-0.874	0.357	0.045	1.562	18.56
Zn_chit_CR_10^{-2}	-0.941	0.001	0.102	2.497	59.85
Zn_chit_CR_10^{-3}	-0.928	0.556	0.077	0.838	46.35
Zn_chit_CR_10^{-4}	-0.968	0.344	0.071	0.833	46.67

Table 1. Kinetic parameters of the corrosion process of chitosan and Chit + CR coatings of different CR concentrations on zinc, in 0.2g/L Na_2SO_4, pH=7.

Conclusions

- In this study were successfully produced anti-corrosive coatings containing chitosan and cresol red in different concentrations; the optimal cresol red concentration was proven to be 10^{-3} M.
- The Bode impedance diagrams suggest a change of the corrosion mechanism is the presence of cresol red, possibly due to the ionic crosslinking of chitosan with cresol red.
- IZI $_{0.01\ Hz}$ is slightly increasing in time indicating a good polarization resistance of the chitosan + cresol red coatings (one order of magnitude larger than in CR absence).
- The chitosan+ cresol red coatings were monitored in dry-wet cycles during 55 days and the plots present large capacitive loops indicating a good corrosion resistance even after this period of time.

References

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[3] F. Szoke et al.,Carbohydrate Polymers Volume 215, (2019) 63-72

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