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Transformation of rust in the presence of mangrove (*Rhizophora apiculata*) tannins and phosphoric acid

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Abstract

The known hazardous effects of most synthetic corrosion inhibitors are reasons to search for safer and environmentally friendly natural products. The role of mangrove (*Rhizophora apiculata*) tannins and phosphoric acid as rust converters by phase transformation studies is evaluated. With the addition of 0.5 % mangrove tannins and 15 % and 30 % phosphoric acid, phosphates in the form of vivianite were evident from the XRD experiments. The formation of ferric-tannates and phosphates was confirmed from the FTIR and SEM micrographs. To support the results obtained, the rate of rust transformation of the individual rust component namely lepidocrocite, magnetite, maghemite and goethite was studied and varying degree of rust transformation was observed from the FTIR analysis depending on the type of rust component employed. The FTIR analysis demonstrated that in the presence of phosphoric acid and a mixture of mangrove tannins and phosphoric acid, the transformation rate was in the following order:

lepidocrocite > magnetite > maghemite > goethite.

The protective capacity of the deposits against corrosion was accomplished by the humidity chamber and salt spray tests. It was found that corrosion protection was best provided by mangrove tannins alone with the present solution compositions employed, indicating its potential in corrosion protection of iron and steel.

Introduction

The known hazardous effects of most synthetic corrosion inhibitors are reasons to search for safer and environmentally friendly natural products. Naturally occurring substances such as vanillin [1], *Opuntia* extracts [2], lawsonia extract [3], natural honey [4] and extracts of chamomile, halfabar, black cumin and kidney bean [5] are plant compounds recently evaluated as corrosion inhibitors for different metals in various environments while other studies of plant extracts included the various tannin extracts [6-13]. The transformation of rusty iron into a blue-black coating layer has been attributed to the interaction of polyphenolic moieties from the tannins with iron oxides and oxyhydroxides, thereby forming ferric-tannate complexes as the major product. The view that ferric-tannates of dark blue colour are highly insoluble and acts as a barrier layer are shared by several authors [11, 13-14]. However the ability of the ferric-tannates to protect against further corrosion has not been resolved. Tannins are thought to be more effective when used in conjunction with phosphoric acid [11, 15], but some investigators think that even the efficiency of this type of pre-treatment is inadequate [13, 16]. Our previous electrochemical studies have shown that the inhibition efficiency of pre-rusted steel in 3.5% NaCl solution containing 3 g L⁻¹ mangrove tannins depended on the concentration of phosphoric acid and the pH of solution [17]. In this study, the phase transformations of pre-rusted steels in the presence of tannins extracted from the barks of mangrove of the Matang forest, Malaysia and phosphoric acid are evaluated and are correlated to the corrosion efficiency.

Materials and methods

Phase transformation of rust in the presence of tannins and phosphoric acid

Pre-rusted samples (2.5 cm x 4.0 cm) were prepared according to the following procedures :

- i. Immersion in 3.5 % (w/v) NaCl solution for 35 days at room temperature (20 °C) (Sample A)
- ii. Alternating Immersion Tests (8 hours immersion in 3.5 % (w/v) NaCl solution and 16 hours drying in an oven at 40 °C) for two weeks (Sample B)

The pre-rusted samples were immersed in solutions containing 15 % (w/v) and 30 % (w/v) phosphoric acid, 0.5 % (w/v) mangrove tannin and 15 % (w/v) phosphoric acid and 0.5 % (w/v) mangrove tannin and 30 % (w/v) phosphoric acid. The pH of the solution was adjusted to pH 4.0. The phase transformation was evaluated via X-ray, FTIR and SEM analyses. Mangrove tannins extracts were obtained by total immersion in 70% aqueous acetone as described elsewhere [17].

Phase transformation of individual rust components in the presence of mangrove tannins and phosphoric acid

Standard powders (10 mg) of goethite (α -FeOOH), lepidocrocite (γ -FeOOH), magnetite (Fe_3O_4) and maghemite (γ - Fe_2O_3) (Alfa Aeser) were mixed with 10 mL of test solutions consisting of :

- i) 15 % (w/v) phosphoric acid
- ii) 0.5 % (w/v) mangrove tannin and 15 % (w/v) phosphoric acid

The resultant solution was adjusted to pH 4.0. Samples were collected at intervals of 1 day, 1 week, 2 weeks and 1 month. Collected samples were filtered using filter paper, dried at 40 °C for 2-3 hours before being analysed. The FTIR spectrums of the collected samples were then taken using Perkin Elmer System 2000 Spectrometer while a Goniometre C diffractometer, incorporating a cobalt radiation ($\lambda=1.78892 \text{ \AA}$) was used to obtain the X-ray diffraction pattern of the samples.

Corrosion protection via humidity chamber tests and salt spray tests

The pre-rusted plates (2.5 x 7.0 cm for humidity chamber and 4.0 cm x 4.0 cm for salt spray) were immersed in 15 % (w/v) phosphoric acid, 0.5 % (w/v) mangrove tannin, 0.5 % (w/v) mangrove tannin + 15 % (w/v) phosphoric acid. The pH of the solution was adjusted to pH 4.0. The plates were then subjected to the humidity chamber (Liebisch KBEA 300) tests [8 hours at 100 % humidity and 40 °C and 16 hours of drying at ambient conditions (standard method DIN 50017)] for 45 days. The salt spray tests of the plates were carried out according to the ASTM B 117 standard procedure for 6 hours.

Results and discussion

Phase transformation of rust in the presence of tannins and phosphoric acid

Both sample preparations produced lepidocrocite and magnetite as the main rust components. The transformation of rust in the presence of phosphoric acid and a mixture of mangrove tannins and phosphoric acid are summarised in Table 1 as observed from XRD, FTIR and SEM analyses. The SEM micrographs of both pre-rusted samples immersed in phosphoric acid portrayed mainly tiny flakes of phosphates with irregular shaped cracks. When phosphoric acid was added to mangrove tannins, the flakes were replaced by a blend of tannate and phosphate structures with cracks still visible (Fig. 1). The formation of phosphates was also confirmed from the FTIR spectrums which exhibited a broad

characteristic peak of phosphate at 1042-1051 cm^{-1} , superimposing the tannate and lepidocrocite peaks. Upon treatment of 15 % and 30 % phosphoric acid, the pre-rusted surfaces were found to be dominated by white-bluish vivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ as confirmed by XRD (Fig. 2). Nevertheless it was quite difficult to distinguish the extent of transformation between the addition of 15 % and 30 % phosphoric acid from the XRD patterns. Ferric phosphates and ferric-tannates are amorphous [19] and thus could not be detected via XRD.

Table 1 Transformation of rust after immersion in phosphoric acid and a mixture of mangrove tannins and phosphoric acid on samples A and B.

Sample reference	Components present		
	Before tannin + phosphoric acid immersion	After phosphoric acid immersion	After tannin + phosphoric acid immersion
Sample A	$\gamma\text{-FeOOH}$, Fe_3O_4 NaCl	FePO_4 , $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ $\gamma\text{-FeOOH}$, Fe_3O_4	Fe-tannate, FePO_4 , $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ $\gamma\text{-FeOOH}$, Fe_3O_4
Sample B	$\gamma\text{-FeOOH}$, Fe_3O_4 , $\alpha\text{-FeOOH}$	FePO_4 , $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ $\gamma\text{-FeOOH}$, Fe_3O_4	Fe-tannate, FePO_4 , $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ $\gamma\text{-FeOOH}$, Fe_3O_4

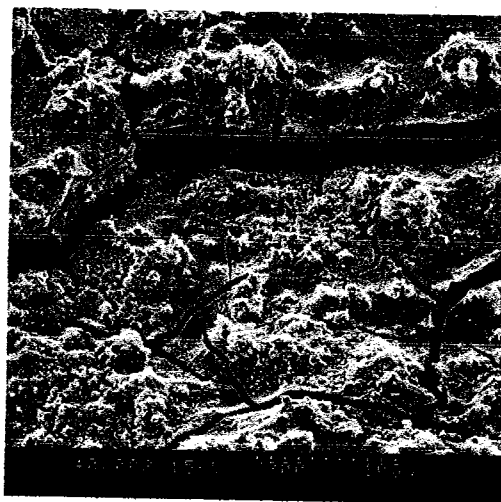


Fig. 1 SEM micrographs of pre-rusted plates for sample A containing 15 % H_3PO_4 and 0.5 % mangrove tannins

Phase transformation of individual rust components in the presence of mangrove tannins and phosphoric acid

The transformation of rust components with immersion time in the presence of 15 % phosphoric acid as viewed by FTIR spectroscopy showed that phosphate peak was present with lepidocrocite, magnetite and maghemite treated powders. However a slower transformation was displayed by maghemite and magnetite. Conversely, no reaction occurred between phosphoric acid and goethite. The transformation kinetics was slower to that of mangrove tannins.

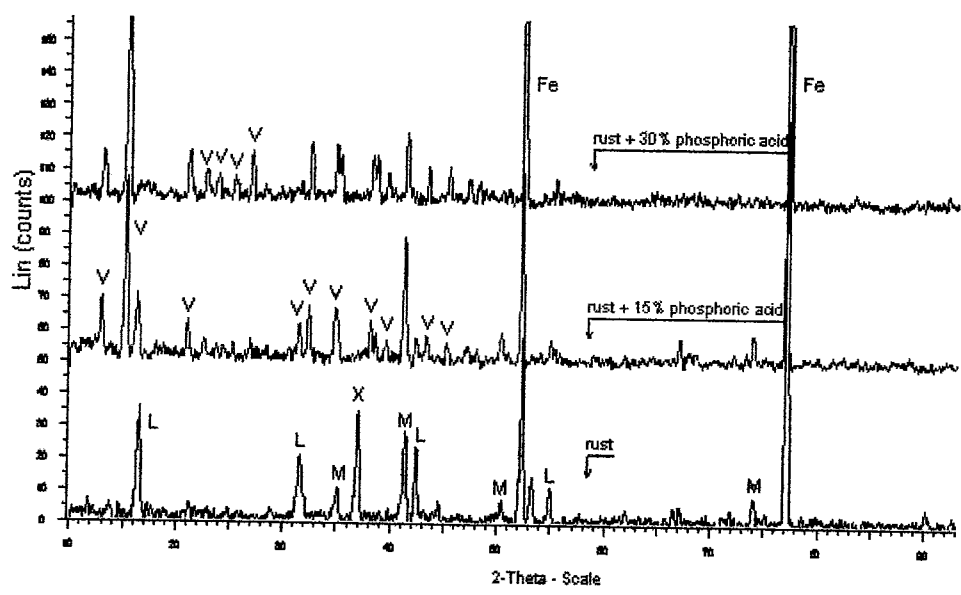


Fig. 2 XRD pattern of a bare rust surface immersed in phosphoric acid

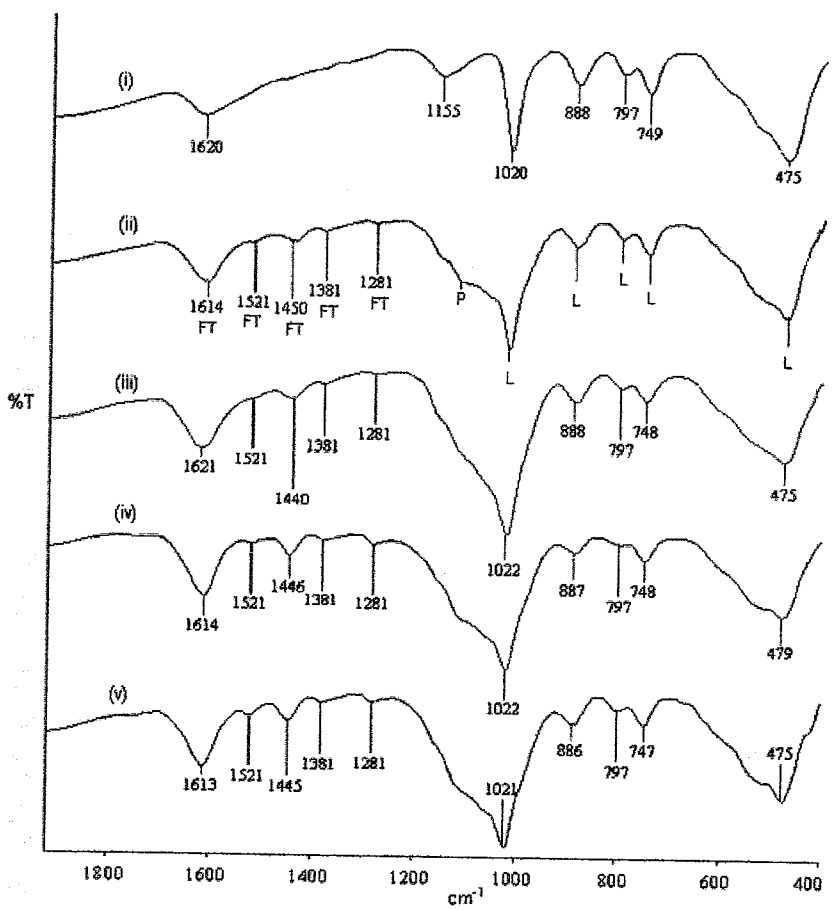


Fig 3 Spectrum of (i) untreated lepidocrocite and lepidocrocite treated with 0.5 % mangrove tannins and 15 % phosphoric acid after (ii) 1 day, (iii) 1 week, (iv) 2 weeks and (v) 1 month immersion : FT-ferric-tannate, L-lepidocrocite, P-phosphates.

Gust [10] reported that the reaction kinetics of tannins was slower to that of phosphoric acid while Barrero *et al.* [16] Almeida *et al.* [18] and Nasrazadani [19], agreed that the rust transformation by phosphoric acid depended on the surface condition, solution concentrations and exposure time. In this study, the addition of 0.5 % mangrove tannin to 15 % phosphoric acid relatively improved the rate of rust transformation as compared to 15% phosphoric acid alone. Transformation of lepidocrocite treated samples was most rapid when both phosphate and tannate peaks were present after one day immersion and the lepidocrocite peak decreased slightly after one month immersion (Fig. 3). A competing reaction between mangrove tannins and phosphoric acid was demonstrated by magnetite. The phosphates were initially formed after one day to two weeks immersion followed by tannates and phosphates after a month immersion. Transformation of maghemite to phosphates and tannates were evident after one day immersion, after which the rate of transformation increased gradually with time. The conversion was slowest with goethite, indicated by the appearance of both phosphates and tannates after a week of immersion which nonetheless intensified with time. It could therefore be deduced that the addition of 0.5 % mangrove to 15 % phosphoric acid was sufficient to exert an effect on the degree of transformation of rust. In summary the transformation rate was in the following order :

lepidocrocite > magnetite > maghemite > goethite.

Corrosion protection via humidity chamber tests and salt spray tests

It was then necessary to evaluate the protective capacity of these deposits against corrosion and this was accomplished by the humidity chamber and salt spray tests. It was found that re-rusting of treated samples was the slowest with the application of mangrove tannins and the fastest with the application of phosphoric acid when exposed to the humidity chamber. According to the humidity chamber tests, the application of mangrove tannins and phosphoric acid resulted in the formation of rust amidst black deposits after 35 days of exposure. This observation could infer that the region occupied by the less adhered phosphates was replaced by newly formed rust, leaving the tannates intact. Since it has been shown that phosphoric acid has comparatively low protection efficiency, the application of phosphoric acid to mangrove tannins resulted in reduced corrosion protection as compared to the application of mangrove tannins alone. This study indicated that the protective efficiency is dependent on the adherence of phosphates and tannates deposited.

For samples exposed to the salt spray chamber, all treated samples exhibited some degree of resistance to corrosion as compared to the standard sample (Fig. 4) for the same exposure time. The slowest rust conversion was again shown by mangrove tannins and the fastest by phosphoric acid alone. A lower corrosion protection was also shown by the addition of both mangrove tannins and phosphoric acid as compared to the addition of mangrove tannins alone. It has been shown that solution composition and exposure conditions are contributing factors to the contradictory reported results by Gust and Bobrowicz [11], Matamala *et al.* [15], Barrero *et al.* [16] and Pardini *et al.* [13] pertaining to the protective capacity of tannins and phosphoric acid.

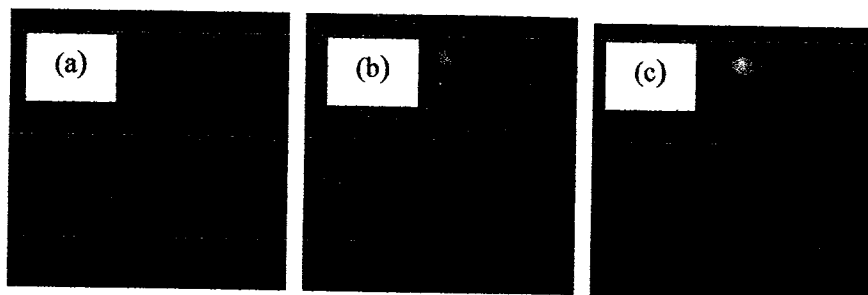


Fig. 4 Evolution of rust formation of (a) bare steel plate and pre-rusted plates immersed in (b) 0.5 % mangrove tannins (c) 15 % phosphoric acid after exposure to the salt spray chamber for 6 hours

Temporary corrosion protection was shown by all treated samples regardless of the type of evaluation employed. The outer layer, predominantly lepidocrocite was easily transformed and the inner more impermeable layer remained unchanged as shown from the XRD and FTIR experiments and SEM micrographs. The initial transformation of lepidocrocite increased the outer layer impermeability, adding a new barrier, hence protection against corrosion. However, the varying degree of rust transformation by tannins and phosphoric acid as shown from the FTIR analysis led to the various degrees of tannates and phosphates deposited. In addition, the lack of adhesion of tannates and phosphates as shown from the SEM micrographs inferred a physical absorption of deposits of which is in agreement with the report by Martinez and Stern [6]. On top of that, the cracked morphology of deposits provided easy penetration of moisture into the cracks leading to the formation of new rust. All of these factors contributed to the observed protective efficiency.

Conclusion

1. Partial transformations of rust into phosphates and ferric-tannates were observed in all samples evaluated.
2. The degree of transformation of rust in the presence of mangrove tannins and phosphoric acid was in the following order : lepidocrocite > magnetite > maghemite > goethite.
3. Temporary corrosion protection was shown by all treated samples regardless of the type of evaluation employed.

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