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# Controlled delivery of multi-substituted triazole by metal-organic framework for efficient inhibition of mild steel corrosion in neutral chloride solution

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## ABSTRACT

A triazole-based compound containing multiple active groups and promising strategy of controlled delivery by metal-organic framework were developed for corrosion inhibition of mild steel in 0.5 M NaCl solution. Electrochemical analysis showed the inhibitor effectively suppressed both the anodic and cathodic reactions by forming a protective film, achieving the efficiency around 98% at an optimal concentration of  $5.5 \times 10^{-4}$  M. Impressively, the inhibitor loading onto MOF particles leads to a reduction of optimal dosage by a factor of 4. The equivalent concentration of the loaded inhibitor is less than  $1.3 \times 10^{-4}$  M. The results of electrochemical quartz crystal microbalance measurement and surface characterization indicated the controlled delivery largely enhances the inhibition ability by giving rise to densification of protective film. Combined spectroscopic analysis provided direct evidences for the inhibitor-MOF interaction and film formation mechanism.

## 1. Introduction

Steel-based facility of marine engineering is susceptible to general, localized and galvanic corrosion, which has become a great concern in terms of economic losses, potential environmental impacts, and safety [1]. Although the corrosiveness of marine environment depends on variable factors, the chloride media is known to play the dominant role [2]. Hence NaCl solutions (0.35–0.85 M) are frequently used for saline condition simulation in laboratory, which in many cases are even more aggressive toward carbon steel than natural seawaters [3].

Application of various organic compounds, usually those rich in nitrogen, sulphur, and oxygen heteroatoms, as corrosion inhibitors has been proven experimentally and theoretically to be an excellent method for protection of carbon steel in a wide range of acidic media containing aggressive chloride ions [4–7]. The positively charged steel surface in the acidic solution facilitates either the direct coordination with electronegative functional groups of organic inhibitor or the indirect adsorption of inhibitor cations through synergistic effect with chloride ions to form self-assembled films that enhance the corrosion resistance [8–10]. By contrast, the inhibitive power of the same organic compounds for steel corrosion in near neutral NaCl solutions is relatively

limited [11,12]. In most cases, the increase in adding amount or assistance by synergistic agents is necessary to overcome this issue, despite giving rise to extra costs and complexity in the application [13,14]. This is also the reason why most of the existing studies only focused on the corrosion inhibition of copper in marine environment, which is more favourable for the adsorption of organic inhibitors [15,16]. In the previous work [17,18], we have found that the integration of selected functional groups such as triazole, thiazole, thiol, furan, or acylhydrazone into a single inhibitor molecule structure often provide superior adsorption ability on steel surface to that with the individual groups. Therefore, it is conceivable that the development of new compounds with multiple active sites could be a novel way to resolve the main problem concerning the inhibitive property for steel corrosion in seawater media.

Additionally, the enhancement in inhibition effectiveness are now mainly carried out by means of modification in molecule structure [19], synergistic effect [20], and increase in concentration [21], conventionally confined to the perspective of thermodynamics. However, it has been reported that adsorption kinetics of a given inhibitor might also have significant influences on the inhibition effectiveness of the formed film [22,23]. Different adsorption mechanisms can be

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characterized by specific film formation kinetics, respectively. For example, slower growth usually claims complete, tight, and polymerised inhibitor film that has more protectiveness [24], while the kinetics in conformity with a linear law is attributable to the formation of chemisorbed layer [25]. To date, there has been limited effort to deal with the matter of adsorption kinetics, in turn attempting to improve and maximize the inhibitor performance.

The controlled delivery can be considered as an advanced route to regulate the growth kinetics of inhibitor film [26]. Typically, the sustained release based on the loading of inhibitors into nanocarrier systems is able to provide long-term corrosion protection by extending the film growth period [27,28]. The metal-organic frameworks (MOFs), composed of metal ions connected by organic linkers, have received considerable attentions to serve as drug-delivery nanocarriers [29], due to their important loading capability, biocompatibility, and convenient synthesis under mild conditions. Zeolitic imidazolate framework-8 (ZIF-8,  $\text{Zn}(\text{2-methylimidazole})_2$ , sodalite-related zeolite type structure) is a flagship of MOFs with exceptional thermal and chemical stabilities [30]. The unique surface chemistry, owing to the presence of additional vacant coordination sites, exposed defects, and the binding of functional groups, offers unprecedented opportunities for its application in sustained drug release [31]. Therefore, ZIF-8 as an attractive candidate for controlled inhibitor delivery, are expected to enhance the inhibition effectiveness by regulating growth kinetics of adsorption film.

In this vein, we firstly designed a novel inhibitor by the combination of functional groups including triazole, thiol, and amino. Each group has been reported to be efficient inhibition centre for steel corrosion in acidic salt solutions [5,17,18]. Then, a facile method simply by soaking the ball-milled MOF particles in methanol solution of the inhibitor was employed to obtain an inhibitor-loaded MOF complex. The inhibition performance was evaluated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves. The inhibitor uptake and release by loading system were followed by UV–vis adsorption spectra and high performance liquid chromatography (HPLC). The film formation behaviour of adsorbed inhibitor was investigated by rotating electrochemical quartz crystal microbalance (REQCM) and scanning electron microscope (SEM). The in-depth understanding into effects of controlled inhibitor delivery on inhibition effectiveness is expected to open a new window of inhibitor research by the consideration of ample possibility to minimize the optimal dosage and administration frequency.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Inhibitor, steel specimen, solution, and general testing condition

The studied inhibitor was designed and prepared in our laboratory, which was purified and characterized by  $^1\text{H}$  NMR, IR or MS to confirm the proposed molecular structure. The flowchart of synthesized process is demonstrated in Fig. 1, where the formula of the inhibitor, named as ATT, is also included.

The material of testing specimens is mild steel with a chemical composition (wt%): 0.16C, 0.53 Mn, 0.30 Si, < 0.045 P, < 0.055 S, 0.3 Ni, 0.3 Cu, and Fe balance.

The solution used for corrosion testing and inhibitor evaluation is 0.5 M NaCl (about 3% in mass percentage, pH = 7.0, 25 °C), which was prepared by the analytical grade chemical with double-distilled water. The concentration of the inhibitor tested is ranged from  $5 \times 10^{-5}$  to  $5.5 \times 10^{-4}$  M (pH  $\approx$  7.5, 25 °C).

Unless specified otherwise, all tests were conducted at room temperature of 25 °C, and open to the air. Furthermore, to ensure the reproducibility of testing results, each test was performed at least 3 times under the same experimental condition.

### 2.1.2. ZIF-8

The pristine ZIF-8 was purchased from Sigma-Aldrich (Shanghai, China). ZIF-8 particles were placed inside a stainless container alongside three 8 mm stainless milling balls. The container was then oscillated at 20 Hz for 2 min using a Retsch MM200 mixer mill resulting in surface defected ZIF-8. This short time treatment was applied in order to marginally modify the external surface of ZIF-8 by controlling the mechanical force.

### 2.1.3. Inhibitor-loaded ZIF-8

The inhibitor loading was performed by introducing, under stirring during 12 h, 85 mg of the ball-milled ZIF-8 (previously dehydrated overnight at 150 °C in order to avoid the presence of water which renders more difficult the uptake of the inhibitor molecules) in a 100 mL solution of methanol containing 60 mg of ATT. The ATT-loaded ZIF-8 was then collected by centrifugation at 5500 rpm for 20 min and dried under vacuum at 100 °C to remove remaining solvents. The uptake amount of inhibitor was quantified by using a UV–vis spectrophotometer at 265 nm measuring the concentration of ATT presents in the supernatant after the centrifugation step. The loading efficiency was calculated as the percentage of inhibitor effectively loaded onto ZIF-8 with regard to the total amount of inhibitor used in the preparation procedure. The loading capacity is determined by the following equation:

$$\text{Capacity (wt\%)} = \frac{\text{ATT}_{\text{loaded}}}{\text{ATT}_{\text{loaded}} + \text{ZIF-8}} \times 100 \quad (1)$$

The inhibitor release was carried out by soaking 100 mg of the ATT-loaded ZIF-8 in 100 mL 0.5 M NaCl solution under bi-dimensional continuous stirring. At different incubation times, an aliquot of supernatant was recovered by filtration using 0.22  $\mu\text{m}$  Millipore cellulose membranes and replaced with the same volume of fresh medium. The amount of released inhibitor was determined by HPLC.

## 2.2. Measurements

### 2.2.1. EIS and potentiodynamic polarization curve

The electrochemical experiments were performed on an Autolab PGSTAT302N system (Metrohm AG). A three-electrode cell was used, with a platinum plate as counter electrode, a saturated calomel electrode (SCE) as reference electrode and the mild steel as working electrode. The working electrodes were cut into a cylinder and embedded into epoxy resin with an exposed surface area of about 1  $\text{cm}^2$ , which were ground up to 1500 grit silicon carbide paper, rinsed with deionized water and degreased in acetone. Prior to electrochemical tests, the open circuit potential of the steel electrode was monitored as a function of time for 12 h to ensure that a steady state condition was attained. EIS was measured at a sinusoidal excitation potential of 10 mV in the frequency ranging from 100 kHz to 10 mHz while the specimen was kept at the corrosion potential. The inhibition efficiency obtained from EIS measurement was calculated as following:

$$\eta_{\text{eR}} \% = \frac{R_{\text{ct}} - R_{\text{ct}}^0}{R_{\text{ct}}} \times 100 \quad (2)$$

Here  $R_{\text{ct}}$  and  $R_{\text{ct}}^0$  represent the resistance of charge transfer in the presence and absence of the inhibitor, respectively. Potentiodynamic polarization curves were measured at a potential sweep rate of 1 mV/s. The obtained inhibition efficiency was calculated as following:

$$\eta_{\text{ei}} \% = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \times 100 \quad (3)$$

Here  $i_{\text{corr}}$  and  $i_{\text{corr}}^0$  are the corrosion current density of the electrode with and without inhibitor in the solution, respectively. To ensure the reproducibility of the testing results, each test was repeated at least three times. The mean value and the standard deviation were included for each data point, which was given in the tables listing the measured and

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