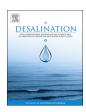


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# Corrosion inhibition of heat exchanger tubing material (titanium) in MSF desalination plants in acid cleaning solution using aromatic nitro compounds



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ARTICLE INFO

Keywords: Heat exchanger Titanium MSF desalination plants Corrosion

#### ABSTRACT

The inhibition impact of aromatic nitro compounds on the corrosion of heat exchanger tubing material (titanium tubes) in MSF desalination plants in acid cleaning solution ( $1.0\,\mathrm{M}$  sulfuric acid) was explored. Corroborative results between chemical and electrochemical (EIS) methods have been reported. FTIR and SEM analysis were further used to characterize the morphology and the nature of the film adsorbed on the titanium surface. The study informed that the maximum corrosion rate of titanium ( $0.260\,\mathrm{mg\,cm^{-2}\,h^{-1}}$ ) was obtained in  $1.0\,\mathrm{M}$  sulfuric acid at 298 K. Aromatic nitro compounds act as effective corrosion inhibitors for titanium in acid cleaning solution. The efficiency of these compounds boosts with concentration and diminishes with temperature. The aromatic nitro compounds exhibit a maximum inhibition efficiency of 73.0% (NI), 82.6% (NII) and 94.6% (NIII) at 600 ppm. They form a good protective layer on titanium surface through their adsorption. The adsorption of aromatic nitro compounds on titanium surface obeys Langmuir model. The performance of these compounds decreases in sequence: (NI) < (NIII) < (NIII).

#### 1. Introduction

Titanium tubes have used considerably for the construction of heat exchangers of MSF desalination plants due to the high resistance of titanium towards corrosion [1].

Excessive scale formation during desalination operations leads to the growth of scale layers inside the titanium tubes and this causes blockage in MSF desalination system [2].

The cleaning of titanium tubes to remove the scale ( $GaCO_3$  and Mg ( $OH)_2$ ) using  $H_2SO_4$  solutions is an effective method for maintenance operation [3].

The main problem here, the descaling using corrosive acids like  $\rm H_2SO_4$  causes severe corrosion for titanium tubes. The best way to protect titanium tubes from corrosion in acids is adding corrosion inhibitors [3]. The greater numbers of the famous inhibitors are organic materials [4–9].

Anticorrosive mechanisms by organic materials involve formation barrier on metal surface, depending on the chemical structures of inhibitors [10,11]. Aromatic nitro compounds have been inspected for their strength to reduce corrosion reactions, taking advantage of their non-toxicity and low price.

The main goal of this work is to test the hypothesis that aromatic nitro compounds (4-nitro-o-phenylenediamine (NI), 3-Nitro-p-

hydroxyethylaminophenol (NII) and N, N'-bis(2-hydroxyethyl)-2-nitrop-phenylenediamine (NIII)) inhibit the corrosion of titanium tubes when added to acid cleaning solution (1.0 M  $H_2SO_4$ ).

#### 2. Experimental

The material used for tests was titanium metal (Grade 3) with chemical composition (wt%): Fe (0.15%), O (0.28%), C (0.015%), H (0.001%), N (0.019%), and Ti (Bal.).

The weight loss experiments were carried out using titanium strips  $(2.0\,\text{cm}\times 1.75\,\text{cm}\times 0.6\,\text{cm})$  in  $100\,\text{ml}$  of  $1.0\,\text{M}$   $H_2SO_4$  solution (Sigma-Aldrich Co.) for 6 h. Short immersion time (6 h) can yield representative corrosion rates. This because that the accumulation of corrosion products on the titanium metal for long time can adversely influence the results. The value of corrosion rate ( $\nu$ ) was obtained from relation:

$$v = [(\text{weight loss mg})/(\text{area cm}^2 \times \text{time } \text{sec})]$$
 (1)

Gill AC instruments (Serial no. 947) was used to perform the electrochemical experiments (EIS measurements). In this system, titanium metal (Grade 3), saturated calomel electrode (SCE) and Pt electrodes were utilized as reference, counter and working electrodes, respectively. The EIS experiments were performed from 1.0 Hz to 30 kHz

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Table 1
The chemical, name, structures and abbreviation of the tested aromatic nitro compounds.

Chemical name	Chemical structure	Abbreviation
4-nitro-o-phenylenediamine	NH <sub>2</sub> NH <sub>2</sub>	(NI)
3-Nitro-p-hydroxyethylaminophenol	NO₂ O	(NII)
	HO NO OH	
N,N'-bis(2-hydroxyethyl)-2-nitro- $p$ -phenylenediamine	" Н ООН	(NIII)
	HO N N N O	

using small amplitude of (5 mV) at  $E_{OCP}$ .

The number of replicates for each test is three times to produce adequate reproducible data.

The titanium surface characterizations were recoded using SEM instrument (JEOL-JEM 1200) and FTIR spectrophotometer (Shimadzu).

The tested aromatic nitro compounds (Table 1) were supplied from JAMES ROBINSON Company.

The electrolyte solution  $(1.0 \text{ M} \text{ H}_2\text{SO}_4)$  was prepared using 98%  $\text{H}_2\text{SO}_4$  (SIGMA–ALDRICH) and distilled water. The concentration range of aromatic nitro compounds was 100–600 ppm (by weight). These concentrations were chosen depending on the price of aromatic nitro compounds and the inhibition efficiency.

#### 3. Results and discussion

#### 3.1. Chemical studies

The performance of aromatic nitro compounds to protect titanium from corrosion in  $1.0\,\mathrm{M}$  H<sub>2</sub>SO<sub>4</sub> solution at room temperature (298 K) is shown in Table 2.

The inhibition efficiency ( $\eta_w$ %) was extracted from the relation:

 $\begin{tabular}{ll} \textbf{Table 2} \\ \textbf{Corrosion rates ($\nu$) and inhibition efficiencies ($\eta_w$\%) values for the corrosion of titanium in 1.0 M $H_2$SO$_4 solution in absence and presence of different concentrations of aromatic nitro compounds at 298 K.$ 

Inhibitors conc. (ppm)	$\nu  (\mathrm{mg}\mathrm{cm}^{-2}\mathrm{h}^{-1})$	$\eta_{ m w}\%$
Blank	$0.260 \pm 0.04$	
(NI)		
100	$0.174 \pm 0.03$	33.0
200	$0.138 \pm 0.03$	46.9
300	$0.126 \pm 0.02$	51.5
400	$0.102 \pm 0.02$	60.7
500	$0.079 \pm 0.01$	69.6
600	$0.070 \pm 0.01$	73.0
(NII)		
100	$0.147 \pm 0.04$	43.4
200	$0.124 \pm 0.03$	52.3
300	$0.107 \pm 0.02$	58.8
400	$0.087 \pm 0.01$	66.5
500	$0.064 \pm 0.01$	75.3
600	$0.045 \pm 0.01$	82.6
(NIII)		
100	$0.126 \pm 0.04$	51.5
200	$0.102 \pm 0.02$	60.7
300	$0.079 \pm 0.02$	69.6
400	$0.048 \pm 0.02$	81.5
500	$0.026 \pm 0.01$	90.0
600	$0.014 \pm 0.01$	94.6

$$\eta_{\rm w}\% = \frac{\nu_0 - \nu}{\nu_0} \times 100 \tag{2}$$

where  $\nu_0$  and  $\nu$  represent the corrosion rate of titanium without and with aromatic nitro compounds, respectively.

It is found that the performance of aromatic nitro compounds  $\eta_w$ % increases with increasing their concentrations, while corrosion rate decreases with aromatic nitro compounds concentrations. The adsorption of the aromatic nitro compounds between titanium surface and acid solution is the main reason of their good performance [12].

From Table 2, it is clear that the performance of these compounds decreases in sequence: (NI) < (NII) < (NIII).

The effects of temperature rising from 298 K to 338 K on the performance of aromatic nitro compounds are shown in Fig. 1. It is evident from Fig. 2 that the temperature rising has negative effects on the performance on inhibitors which lowering the  $\eta_{\rm w}\%$  values. Where the temperature rising leads to the acceleration of titanium dissolution process and partial desorption of aromatic nitro compounds from titanium surface [13].

The activation energy ( $E_a$ ) for the corrosion of titanium in tested solutions is determined from Arrhenius relation [14,15].

$$v = \lambda e^{\frac{-E_a}{RT}} \tag{3}$$

Here *R* equals  $8.314 \,\mathrm{J}\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1}$ , *T* represents solution temperature (K) and  $\lambda$  is equation constant factor.

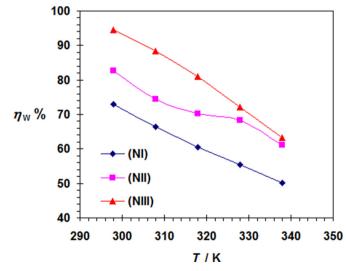


Fig. 1. Variation of inhibition efficiency with temperature for the corrosion of titanium in  $1.0~M~H_2SO_4$  solution in absence and presence of 600 ppm of aromatic nitro compounds.

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