



Experimental evaluation of new inorganic phosphites as corrosion inhibitors for carbon steel in saline water from oil source wells



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HIGHLIGHTS

- M(HPO₃) compounds are good corrosion inhibitors for carbon steel in saline water.
- M(HPO₃) adsorption is well described by Langmuir isotherm.
- Physisorption is the predominant mode of adsorption.
- Their inhibitive action was studied by weight loss and electrochemical methods.
- Examination of surface morphology by SEM/EDX analysis

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ABSTRACT

Corrosion inhibition potentials of three phosphites namely, M(HPO₃) (where M = Mn, Co and Cu), for carbon steel in saline water from oil source wells were evaluated using weight loss and electrochemical impedance spectroscopy (EIS) methods. Characterization of the surface morphology was performed by SEM/EDX investigations. The corrosion rate of carbon steel in saline water decreased with increasing M(HPO₃) concentration and increased with increasing temperature. M(HPO₃) inhibits the corrosion of carbon steel by an adsorption mechanism, which follows Langmuir isotherm adsorption. The order of the inhibition efficiency of inhibitors is as follows: Mn(HPO₃) < Co(HPO₃) < Cu(HPO₃). The thermodynamic functions of dissolution and adsorption processes were calculated and discussed.

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1. Introduction

Corrosion of carbon steel in the presence of saline water from oil source wells is a common problem across many petroleum industries [1].

Saline water from oil source wells contain accelerative corrosive species such as chlorides and high levels of dissolved solids [2–3].

Corrosion is reduced by inhibitors which are injected continuously or periodically depending on the well corrosivity.

The corrosion inhibitor is one of the best known methods of corrosion protection and one of the most useful in the industry [4–6].

The mechanism of the corrosion inhibitor can occur by (a) adsorption on the surface of the metal and forms a protective thin film; (b) a formation of a film by oxide protection of the base metal; and (c) reacting with a

potential corrosive component present in aqueous media and the product is a complex [7].

Unfortunately, most organic inhibitors are inherently toxic and potential health hazards, such as the carcinogenic effect of aromatic heterocyclic compounds on humans [8]. The use of inorganic inhibitors as an alternative to organic compounds is based on the possibility of degradation of organic compounds with time and temperature [9]. This tempted us to investigate the feasibility of application of new synthetic inorganic compounds (phosphites) as inhibitors in corrosive solution. A phosphite in inorganic chemistry is a salt of phosphorous acid. Historically phosphite has referred to salts containing HPO₃²⁻ [10].

In the present work new corrosion inhibitors, M(HPO₃) (where M = Mn, Co and Cu), have been investigated their inhibition effect on the corrosion of carbon steel in saline water by weight loss and electrochemical impedance spectroscopy (EIS) techniques. Kinetics, isotherm studies and thermodynamic parameters related to the process were also performed. The surface morphology of the corroded surface was also carried out using SEM/EDX analysis.

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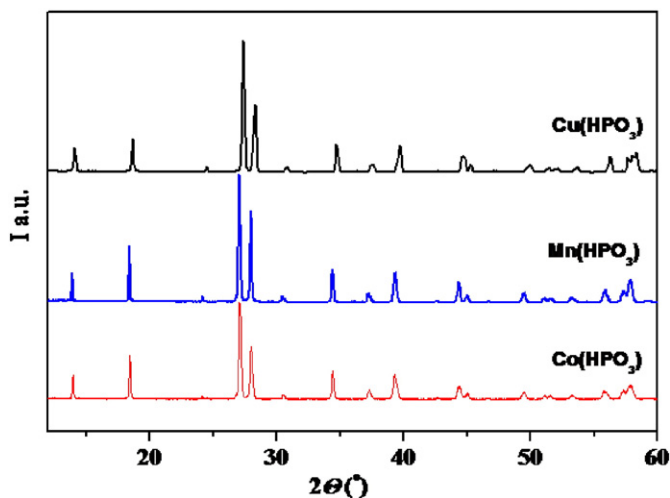


Fig. 1. XRD pattern of $M(\text{HPO}_3)$ (where $M = \text{Mn, Co and Cu}$).

2. Experimental

2.1. Inhibitors synthesis

The inhibitors, namely $M(\text{HPO}_3)$ (where $M = \text{Mn, Co and Cu}$) have been synthesized in laboratory according to the following procedure: H_3PO_3 (12.2 mmol) + $\text{MCl}_2 \cdot 4\text{H}_2\text{O}$ (1.0 mmol) (where $M = \text{Mn, Co and Cu}$) + ethanol (87.4 mmol) were dissolved in distilled water (20 ml). While stirring, tripropylamine (10.5 mmol) was added prior to sealing the mixture in a PTFE-lined stainless steel pressure vessel. The mixture was heated at 443 K for 120 h and then the vessel was slowly cooled to 298 K. $M(\text{HPO}_3)$ crystals were separated by filtration and washed with a water–acetone solution and dried in air. The percent yield is 85% [11]. The structures of the compounds were confirmed by X-ray diffraction (XRD) analysis as shown in Fig. 1. It is clear from Fig. 1 that the XRD patterns of the three inhibitors are identical. This observation may be due to that the three inhibitors are isotopic where they have a similar crystalline phase and the atoms are arranged in similar way.

The percentage purity of $M(\text{HPO}_3)$ was found to be 100%. The obtained compounds are insoluble in cold water, slightly soluble in hot water, and soluble in mineral acids.

2.2. Material and medium

The material used for tests was carbon steel electrode with the following chemical composition (wt.%): 0.06 C; 0.06 Si; 0.7 Mn; 0.005 P; 0.001 S; 0.012 Ni; 0.015 Cr; 0.004 Mo; 0.002 V; 0.02 Cu and Fe (bal.).

The surface preparation of the specimens was carried out using emery paper (grades 300–600–1200) and then washed with distilled water and acetone and dried at room temperature before use.

Saline water was collected from oil source wells in Egypt. Its chemical composition and specifications are given in Tables 1 and 2,

Table 1
Chemical composition of saline water from oil source wells.

Element	(mol/l)
Na^+	0.294.
K^+	0.032.
Ca^+	0.1927.
Mg^+	0.0925.
Cl^-	0.373.
SO_4^{2-}	0.0038.
Br^-	0.0071.
SiO_4^{4-}	0.000128.

Table 2
Specification of saline water from oil source wells.

Property.	Value.
Appearance	Clear, light yellow.
Odor	Mild.
Specific gravity at 25 °C	1.102.
pH	6.7.
TDS (mg l^{-1})	35,825.
Salinity (mg l^{-1})	31,252.

respectively. Microfiltration filters are used to remove solid impurities from the collected water. The collected water is free from crude oil and greases.

The concentrations of the inhibitors employed were varied from 2.0 to 10.0 mM $M(\text{HPO}_3)$. The inhibitor powders are dissolved in 5 ml of dilute nitric acid (10^{-5} M) and saline water was added until a total volume of 100 ml was reached. The pH of the saline water after adding inhibitors was 6.3.

The diluted nitric acid solution was prepared using nitric acid (Merck, 65%) and saline water.

The solution in the absence of $M(\text{HPO}_3)$ was taken as a blank.

The solubility product constant (K_{sp}) for the inhibitors after dissolving in nitric acid solution and added to saline water was measured at 298 K using conductivity method (Conductivity Meter LF 538 WTW). The data clearly reveal that K_{sp} was 5.4×10^{-3} .

All solutions were freshly prepared from analytical grade chemical reagents using doubly distilled water and were used without further purification. For each run, a freshly prepared solution as well as a cleaned set of electrodes was used. Each run was carried out in aerated stagnant solutions at the required temperature (± 1 °C), using a water thermostat.

2.3. Weight loss measurements

For weight loss experiments, clean weighed specimens ($2.3 \times 1.1 \times 0.04$ cm) were dipped in 100 ml of saline water without and with inhibitors for 168 h. The loss in weight was determined after removing the specimens from the electrolyte using an analytical balance (precision ± 0.1 mg). The weight loss was used to calculate the

Table 3
Corrosion rates and inhibition efficiencies η_w values for the corrosion of carbon steel in saline water in the absence and presence of different concentrations of $M(\text{HPO}_3)$ at 298 K.

$M(\text{HPO}_3)$ conc. (mM)	Corrosion rate ($\text{mg cm}^{-2} \text{h}^{-1}$)	η_w %
Blank	0.150	–
<i>Mn(HPO₃)</i>		
2.0	0.113	24.6
4.0	0.096	36.0
6.0	0.080	46.6
8.0	0.069	54.0
10.0	0.062	58.6
<i>Co(HPO₃)</i>		
2.0	0.078	48.0
4.0	0.071	52.6
6.0	0.063	58.0
8.0	0.056	62.6
10.0	0.037	75.3
<i>Cu(HPO₃)</i>		
2.0	0.050	66.6
4.0	0.036	76.0
6.0	0.022	85.3
8.0	0.011	92.6
10.0	0.010	93.3

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