INFLUENCE OF HUMIC ACID ON CORROSION OF LOW CARBON STEEL IN NEUTRAL AQUEOUS SOLUTION CONTAINING CHLORIDES

Leoš DOSKOČIL, Pavlína ŠOMANOVÁ, Martin BUCHTÍK, Tomáš HORÁK,
Jaromír WASSERBAUER

Brno University of Technology, Faculty of Chemistry, Brno, Czech Republic, EU,
doskocil@fch.vut.cz

Abstract

The effect of lignitic humic acid in 0.1 M NaCl at pH 7 on low carbon steel was investigated using potentiodynamic polarization and immersion test. The morphology and elemental composition of the corrosion products were characterized using scanning electron microscopy with energy dispersive spectroscopy. The results showed that humic acid accelerated the corrosion of low carbon steel in 0.1 M NaCl. The negative effect of humic acid was attributed to the complexation of the molecules with iron ions. After seven days, immersion tests revealed that steel in 0.1 M NaCl was covered with the discontinuous black corrosion products, whereas humic acid in 0,1 M NaCl induced the formation of a continuous layer of brown corrosion products with low adhesion to the surface. The elemental composition of the black and brown corrosion products corresponded to Fe_3O_4 and $FeOOH$, respectively.

Keywords: Humic acid, low carbon steel, corrosion, corrosion product

1.   INTRODUCTION

Low carbon steel is a conventional engineering material widely used for a large range of applications including pipes for transport of gas or oil, sheet and strip products, plates, ship sides, wires and many others. The disadvantage of the low carbon steel materials is their susceptibility to corrosion, which can lead to dramatic degradation of mechanical properties [1]. Many of the low carbon steel components are in contact with water and/or soil where they may be subject to corrosion. The failure of the components results in economic costs, and even more serious problem is, it can present particularly serious risks to human health and the environment [1,2]. It is well known that aggressive ions such as chlorides and sulphates present in water and soil cause corrosion of metallic materials. In addition to the inorganic components, water and soil environments also contain various naturally occurring organic molecules such humic acids, which can have a significant effect on the corrosion behaviour of the metallic material and the properties of the surrounding environment [3].

Humic acids are the heterogeneous mixture of organic molecules and colloids that are insoluble at pH lower than 2. They are characterized by high molecular weight and a high content of oxygen-functional groups such as carboxylic and hydroxyl groups. Humic acid occurs not only in water and soil but also in peat, coal and leonardite, whereas their chemical-physical properties may differ from each other depending on their origin [4].

Humic acids, coal and peat can be used as green fertilizer and/or soil conditioners to improve soil quality [3]. These organic acids can then be leached from soils into groundwater and surface water. Also, a number of technological operations (e.g. washing processes, transport in coal-water slurry, storage piles exposed to water spray) of coal and peat may be associated with the release of humic acids from the matrix. Hence, there may be an increase in the amount in the pedosphere and hydrosphere. The occurrence of humic acids in different environments allows interactions with metallic materials and influence corrosion behaviour [3,4].

Dick and Rodrigues reported that humic acid in sulphate solution promoted corrosion of the PI 5LX65 steel [5]. They related the acceleration of corrosion to the complexing ability of humic acid. Other authors have reported that general corrosion occurred when carbon steel was exposed to fresh lake water with humic acid [6]. The presence of humic acid accelerated corrosion and led to the formation of weakly bound complexes with corrosion products. These organic molecules can also initiate barrier corrosion protection in the case of the galvanized steel surface [7]. Humic acid precipitation on the surface of galvanized steel formed a thick layer of deposits acting as a physical barrier between the steel component and corrosive environment. Doskočil et al. performed corrosion tests of low carbon steel in 3.5% NaCl in the presence of a water-soluble fraction obtained from humic acid [8]. The authors found that there was a deterioration of corrosion process during short-term measurements, but longer-term tests suggested that there may be an improvement in corrosion resistance. In another paper, Doskočil et al. investigated the effect of humic acid in 3.5% NaCl on the corrosion of magnesium alloy AZ31 [9]. They observed that the corrosion rate slowed down slightly at pH 5 and 9, while corrosion accelerated at pH 7.

The aim of this work is to investigate the effect of lignitic humic acid on low carbon steels in 0.1 M NaCl at pH 7 using potentiodynamic measurements. Surface characterization of the corrosion products was also carried out.

2.   MATERIAL AND METHODS

The low carbon steel used in the experiments had the following the nominal composition, with mass ratios of 0.17 % C, 0.25 % Si, 1.4 % Mn, 0.035 % P and 0.035 % S. The steel bar with a diameter of 1.5 cm was cut into circular samples. These samples were ground using a silicon carbide abrasive papers with 800 and 1200 grit, rinsed with water and isopropanol and dried by hot air.

An amount of 0.1 grams of lignite humic acid was dissolved in 1 L of 0.1 M NaOH containing 0.1 M NaCl. The dissolved humic acid was precipitated by lowering the pH to 7. A pH value of 7 was maintained for one day. The solution was filtered through a 0.45 μm pore size filter to separate precipitated humic acids insoluble at pH 7. The obtained filtrate of humic acid fraction (HA7) containing 0.1 M NaCl was used for corrosion tests.

Total organic carbon (TOC) was determined by accredited testing laboratory LABTECH using a Shimadzu TOC 5000A analyser according to Czech technical standard ČSN EN 1484. Based on the TOC analysis, three corrosion solutions of 0.1 M NaCl containing 10, 25 and 50 mg/L of humic acid carbon were prepared.

Fourier-transform infrared (FTIR) spectrometry (Nicolet iS50 spectrometer) was used in Attenuated Total Reflection (ATR) mode. FTIR spectrum was recorded over the range 4000–400 cm^{-1} at 4 cm^{-1} resolutions and was the average of 128 scans. The spectrum for air on a clean dry ATR germanium crystal was used as the background for the infrared measurements.

Electrochemical measurements were carried out using VSP-300 potentiostat (Biologic, Seyssinet-Pariset, France) at laboratory temperature. The corrosion medium (200 ml) at an initial pH of 7 included 0.1 M NaCl and 10, 25 and 50 mg/L HA7 in 0.1 M NaCl. Conventional three electrodes glass cell was used with saturated calomel electrode as reference electrode with Luggin capillary bridge, platinum counter electrode and the sample with geometric area 1 cm^2 as working electrode. The open circuit potential (OCP) was stable within 16 h and then potentiodynamic measurement was performed between -350 and 500 mV vs. OCP at a scanning rate of 1 mV/s.

The immersion test was carried out for low carbon steel of about 1 cm^2 in 200 ml of 0.1 M NaCl solution with and without 10 mg/L HA7 at initial pH 7. The test was run at laboratory temperature for seven days. The corroded steel surface was characterized in terms of appearance and chemical composition.

The morphology of steel surface was analysed using a Zeiss EVO LS-10 scanning electron microscope (SEM) (Carl Zeiss Ltd., Cambridge, UK) and energy-dispersive X-ray spectroscopy (EDS, model OXFORD INSTRUMENTS X-MAX 80 mm^2).

3.   RESULTS AND DISCUSSION

FTIR spectrum of HA7 is shown in **Figure 1** and its interpretation was based on the literature [10-13]. The band located in the region 3390-3270 cm^{-1} can be attributed to hydroxyl groups. Aliphatic groups, including methyl and methylene groups, are indicated by the 2901 and 2972 cm^{-1} bands. These groups were also confirmed by the 1450 cm^{-1} band. The strong band around 1380 cm^{-1} can be attributed to methyl aromatics. The band at 1580 cm^{-1} is related to aromatic substances. The band around 1650 cm^{-1} may include carboxyl groups, aromatic groups (conjugated ketonic structures). Spectra also contained alcohols (around 1060 cm^{-1}) and phenols and ethers (around 1230 cm^{-1}). Out-of-plane C-H deformation bands were found in the 900–700 cm^{-1} region.
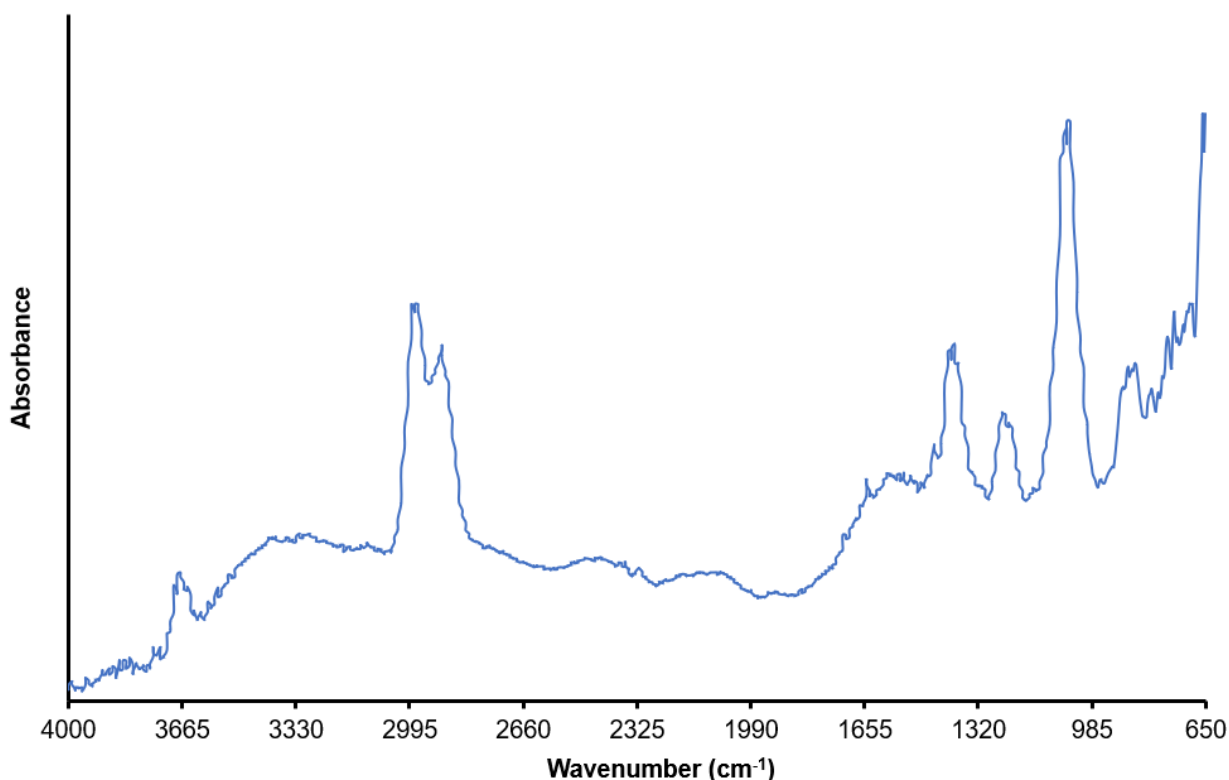
Figure 1 FTIR spectrum of HA7

The potentiodynamic polarization curves are shown in **Figure 2** and the determined parameters are summarized in **Table 1**. The results show that the presence of humic acid caused the acceleration of corrosion of low carbon steel in 0.1 M NaCl. The increase was about twofold after the addition of 10 mg/L HA7 to 0.1 M NaCl. Increasing the HA7 concentration from 10 mg/L to 50 mg/L had only a slight effect on the corrosion current density value i_{cor} (from 2.67 to 2.90 µA/cm^2). The negative effect of HA7 on steel corrosion is also manifested by a more negative corrosion potential value E_{cor} compared to 0.1 M NaCl. However, the E_{cor} value at 10 mg/L HA7 was almost the same as that of 0.1 M NaCl. The shape of the potentiodynamic curves in the anodic region indicates that HA7 influences the anodic reaction of the low carbon steel.

This is consistent with the notion of the role of HA7 during corrosion as pointed out in the literature [5-8]. The deterioration of low carbon steel corrosion by HA7 can be related to the complexing reaction between the released iron ions and oxygen groups such as carboxylic groups. The depletion of iron ions effectively reduces the formation of corrosion products that could form a barrier against the corrosive environment entering the steel surface. The occurrence of oxygen functional groups in HA7 was detected by FTIR analysis.
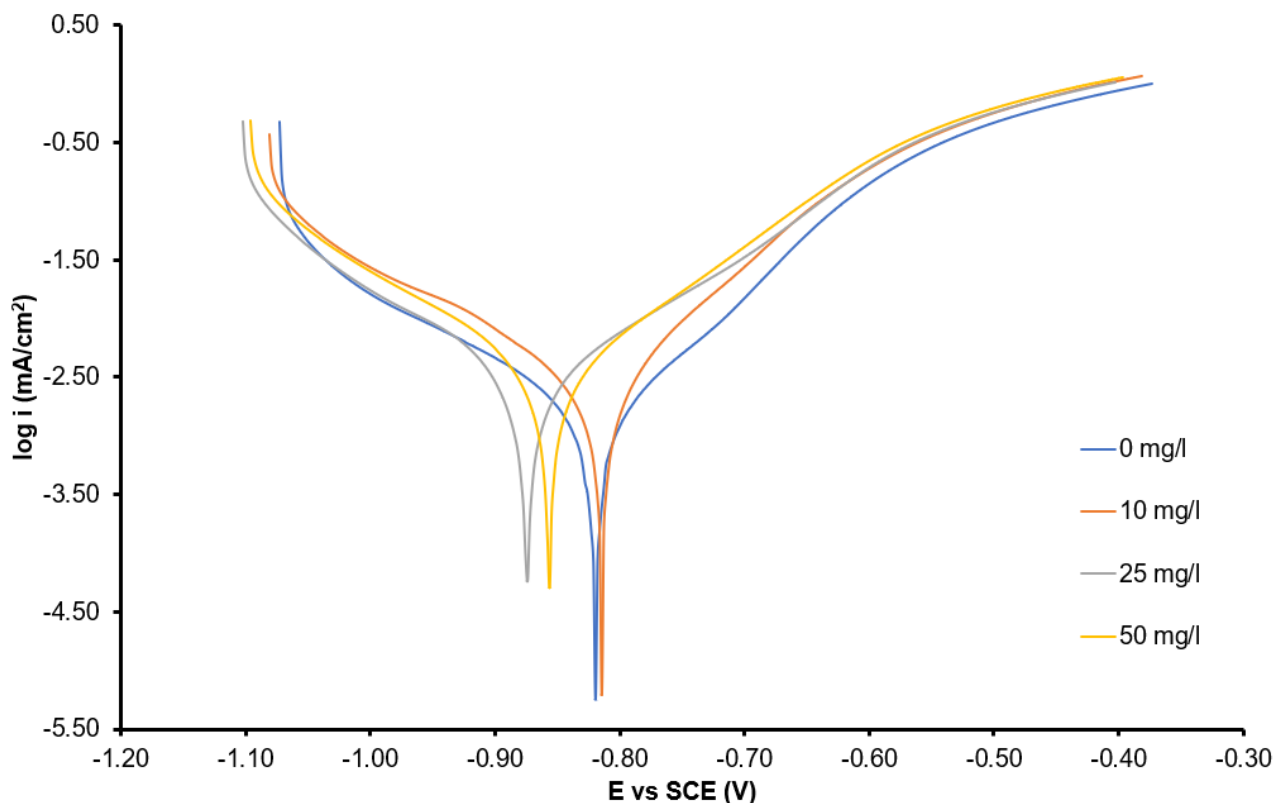
Figure 2 Potentiodynamic curves for different concentrations of HA7 in 0.1 M NaCl. Dependence of logarithm of current density (i) on potential (E)

**Table 1** Electrochemical parameters for different concentrations of HA7 (c_{HA7})

c_{HA7} (mg/L)	E_{cor} (V)	i_{cor} ($\mu A/cm^2$)
0	-0.82	1.18
10	-0.81	2.98
25	-0.87	2.67
50	-0.85	2.90

The surface of the steel after the immersion test in 0.1 M NaCl was mostly covered with black coloured corrosion products, while the central part of the surface appeared to be brownish-black in places. In contrast, the surface of the steel corroding in the presence of HA7 was completely covered with a brown layer of corrosion products. This layer was characterised by poor cohesiveness and adhesion to the steel surface, as the layer was easily detached by rinsing and/or drying after removal from the corrosive environment.

SEM images for the steel surface after corrosion in 0.1 M NaCl is shown in **Figure 3A, B**. The morphology of the black coloured corrosion products is shown in **Figure 3A**. The composition is given in **Table 2**, which according to the atomic ratio of O/Fe can be attributed to Fe_3O_4 (magnetite) [14,15]. The surface with no discernible layer of corrosion products revealed the microstructure of the steel. The recognizable ferritic grains were preferentially dissolved compared to the perlitic grains. Moreover, the surface was weakly distorted with fine particles that could be attributed to FeOOH based on the atomic ratio of O/Fe and the shape of the crystals.

The morphology of the corrosion products formed on steel in a humic acid environment is shown in **Figure 3C**. The surface was formed by fine crystals with an atomic ratio of O/Fe that corresponded to the chemical

composition of FeOOH. Based on literature, appearance and composition, the corrosion product was related to lepidocrocite [14,15]. Surface analysis was also carried out at the point from which the corrosion coating layer was removed. **Figure 3D** documented that iron dissolution preferentially took place on the ferrite grains, as the perlite grains are more well preserved.
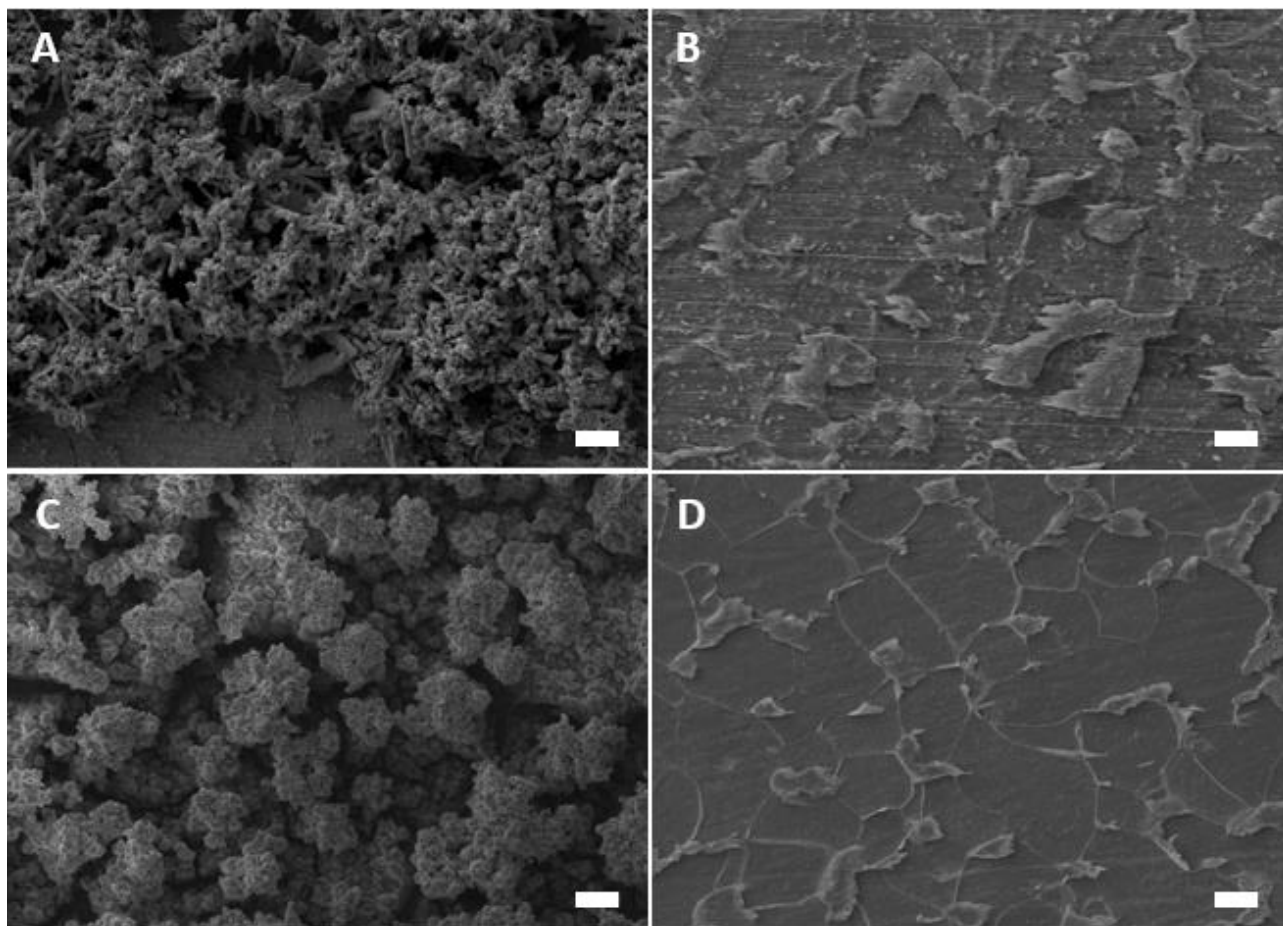
Figure 3 SEM images of steel surface after immersion tests (7 days) in 0.1 M NaCl (A, B) and in 0.1 M NaCl containing 10 mg/L HA7 (C, D). Bar represents 100 µm

Table 2 Elemental analysis of corrosion products after one week of corrosion in 0.1 M NaCl with and without 10 mg/L HA7

Used environment	0.1 M NaCl	0.1 M NaCl with 10 mg/L HA7
Element	Average (at%)	Average (at%)
C	0	25.1
O	58.8	49.7
Fe	41.2	25.2

4.   CONCLUSION

The results showed that lignitic humic acid in 0.1 M NaCl at pH 7 accelerated the corrosion of low carbon steel. Potentiodynamic curves indicate that humic acid affects the anodic corrosion reaction of steel. The aggravation of corrosion was explained by the formation of complexes with the released iron ions, thereby reducing the formation of corrosion products. Humic acid induced the formation of a continuous brown coating on the

surface of the steel, which was mainly of a composition corresponding to FeOOH. In contrast, the steel surface in 0.1 M NaCl in the absence of humic acid incoherently coated with black corrosion products with a chemical composition attributed to Fe_3O_4.

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