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ATR-FTIR CHARACTERIZATION OF THE WHITE WILLOW BARK EXTRACT USED AS A COPPER CORROSION INHIBITOR

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Abstract
As proved inhibitor of copper corrosion in saline environment, the white willow bark (WWB) extract was characterized using the Attenuated Total Reflectance-Fourier Transform Infrared spectroscopy (ATR-FTIR) method. By identifying the bands typical for phenolic profile of WWB extract, the anti-corrodic properties of WWB were explained. The hydrogen-bonded O-H stretching vibrations present in WWB extract is attributed to the phenolic hydroxyl groups and alcoholic hydroxyl groups within glycosides. The C-H stretching vibrations typical for salicin and for glucoside part of salicin aromatic were also identified, as well as the C=C ring stretching vibrations and C-O stretching vibrations that can be attributed to phenolic and alcoholic groups. The presence of these functional groups confirms the presence of a protective film of the WWB extract on the copper surface, protecting the metal from the corrosive effect of chloride ions.

Keywords: *white willow bark, ATR-FTIR, copper, corrosion inhibitor*

1. INTRODUCTION

Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy is a frequently applied method for the analysis of environmentally friendly corrosion inhibitors for metals [1,2]. Corrosion inhibitors are useful for avoiding the dissolution of metal in different corrosive environments [1,3]. The effectiveness of organic inhibitors, including those derived from plants, is related to the chemical structure and physicochemical properties. These include functional groups, electron density at the donor atom, p-orbital character, and the electronic structure of the molecule [4,5]. The performance of organic inhibitors depends on several factors, such as the adsorption of the molecules or their ions on anodic and/or cathodic sites, an increase in cathodic and/or anodic over voltage, and the formation of a protective barrier film [4]. The ATR-FTIR method is significant for examining the film formation and functional groups of molecules that participate in the adsorption process, providing a detailed analysis of corrosion inhibitors [6]. For example, functional groups such as azole, thiol functional groups, and carboxylate tail group can influence the adsorption of corrosion inhibitors on the copper surfaces in a chloride environment. The thiol group improves the adsorptive interaction with the surface, while the carboxylate groups provide additional intermolecular attraction [7].

Recent research indicates the possibility of using white willow bark (WWB) extract can inhibit copper corrosion in a 0.5 M NaCl solution [8]. Also, WWB extracts have anti-inflammatory, antipyretic, and analgesic effects, making them popular in sports performance and weight loss products. Although these extracts are generally standardized to salicin, they also contain other beneficial ingredients, including other salicylates, polyphenols, and flavonoids, which may play prominent roles in the therapeutic actions [9]. In addition to the use of white willow bark for pharmaceutical purposes, research shows that it can be used for phytoremediation [10,11].

In this paper, the ATR-FTIR results for WWB extract obtained by extraction with distilled water are shown. The goal is to determine the functional groups present in the extract and to explain in more detail their role in inhibiting copper corrosion in a 0.5 M NaCl solution.

2. EXPERIMENTAL

2.1 Preparation of white willow bark extract

WWB extract was obtained by extracting the white willow bark sample with distilled water and then evaporating it. Distilled water was chosen as a cheap, universal, and environmentally friendly solvent. The dry and ground WWB was manufactured by "Adonis" company, located in Sokobanja, Serbia. The dry bark mass was poured with hot distilled water (95 ℃) in a solid:liquid ratio of 1:3. After 12 h at room temperature, the mixture was filtered using a Buchner funnel with filter paper No. 1. The filtered solution was evaporated on a rotary evaporator Buchi R-210 (72 mbar, 40 ℃). WWB extract and hydrolate were obtained as products, as shown in Figure 1.

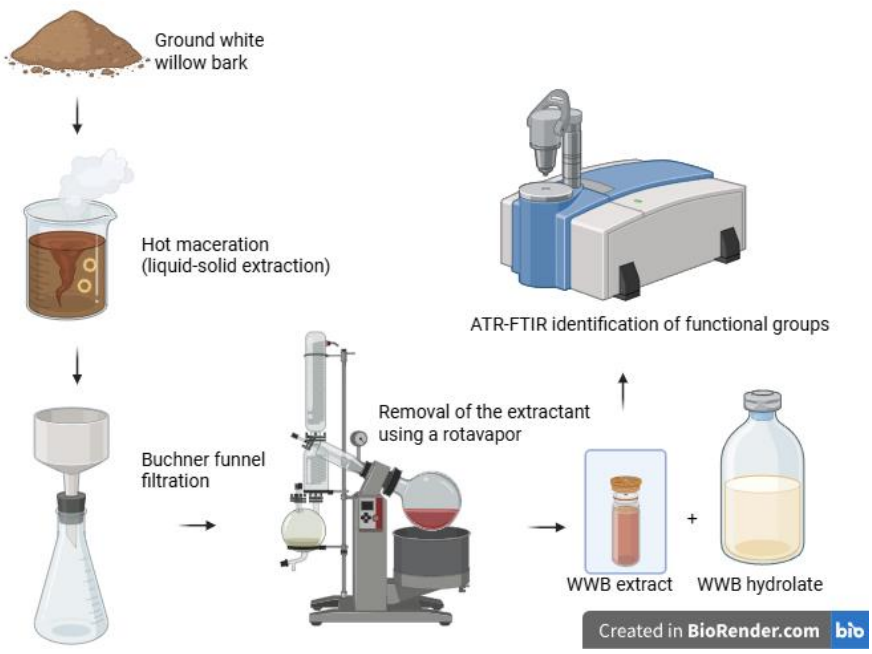

Figure 1. Scheme of obtaining WWB extract and its hydrolate

2.2 ATR-FTIR analysis

The ATR-FTIR characterization of the WWB extract was conducted using a Smart iTR Nicolet iS50 FTIR spectrophotometer (Thermo Fisher Scientific, USA), as reported elsewhere [12].

3. RESULTS AND DISCUSSION

The ATR-FTIR spectra (Figure 2) of the WWB extract reveals characteristic bands consistent with its expected main constituents, such as salicin and its derivatives, other phenolic glycosides, along with tannins and flavonoids [13]. The prominent and broad band at ~3246 cm^{-1} (with percentage transmittance of 64%) indicates the presence of hydrogen-bonded O-H stretching vibrations, attributed to the phenolic hydroxyl groups and alcoholic hydroxyl groups in glycosides. The signal at 2933 cm^{-1} (79%), appearing as a shoulder to O-H band, indicates C-H stretching vibrations, typical for salicin [14]. The bands at ~1604 cm^{-1} (60%) and ~1521 cm^{-1} (73%) correspond to aromatic C=C ring stretching vibrations. Furthermore, C-H bending, indicated by a band at 1374 cm^{-1} (62%), is characteristic of the glucoside part of salicin. Finally, C-O stretching vibrations are indicated by the band at ~1246 cm^{-1} (61%), whereas a strong peak at ~1032 cm^{-1} (36%) can be attributed to phenolic and alcoholic groups.

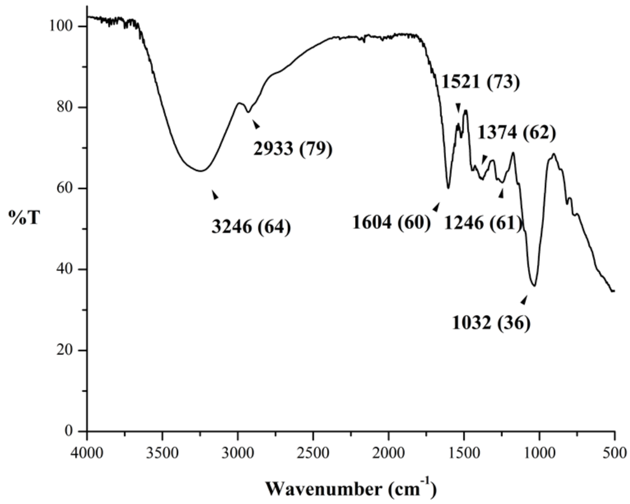

Figure 2. ATR-FTIR spectrum of WWB extract with the most prominent bands marked

The presence of certain functional groups affects the molecular interface adsorption. Some studies have shown that some coordination compounds exhibit good adsorption on the metal surfaces [15]. Heterocyclic compounds containing functional groups such as –OH, $–NH_2$, $–OCH_3$, –NHMe, –NMe_2, –CN, $–CONH_2$, $–COOC_2H_5$, –O–, $–NO_2$ have proven to be effective inhibitors of metal corrosion. Extensive conjugation in the form of non-bonding and π electrons of hetero and homo electrons, such as >C=O, >C=N–, >C=S, –C≡N, –N=O, –N=S, >C=C<, –N=N–, and –C≡C,– interact with metal surfaces as electron-rich adsorption centers [16]. On the other hand, organic compounds with electron-donor functional groups (–OH, $–NH_2$ and $–CH_3$) have a positive effect on the inhibition of metal corrosion, while those with electrons-acceptors groups (–CN, –$COOC_2H_5$, and $–NO_2$) have a negative effect, *i.e.* reduce the effectiveness of corrosion inhibition [17].

The presence of functional groups determined by the ATR-FTIR method confirms the capacity of WWB extract to act as an inhibitor of copper corrosion in saline environment. The hydrogen-bonded O-H stretching vibrations, attributed to the phenolic and alcoholic hydroxyl groups within glycosides, were determined. Previous research confirms the effect of herbal extracts containing glycosides and polysaccharides moieties are effective green and cost-efficient corrosion inhibitors [18]. The C-H stretching vibrations, aromatic C=C ring stretching vibrations, and C-O stretching vibrations are typical indicators of copper corrosion inhibitors [19,20,21,22].

4. CONCLUSION

The identification of functional groups in the WWB extract using the ATR-FTIR method indicates the presence of numerous functional groups that act as metal corrosion inhibitors. The presence of hydrogen-bonded O-H stretching vibrations, attributed to the phenolic hydroxyl groups and alcoholic hydroxyl groups within glycosides, C-H stretching vibrations, typical for salicin, aromatic C=C ring stretching vibrations, C-H bending characteristic for glucoside part of salicin, and C-O stretching vibrations attributed to phenolic and alcoholic groups was confirmed. This confirms the potential of WWB extract as an inhibitor of copper corrosion in chloride conditions.

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