

DOI: <http://doi.org/10.21698/simi.2024.ab21>

GALLIC ACID DEGRADATION IN AQUEOUS SOLUTION BY FENTON'S REAGENT

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Keywords: *aqueous solution, Fenton reagent, Folin-Ciocalteu reagent, gallic acid, propolis*

Introduction

The basic aim of the proposed work is the determination of polyphenols, including gallic acid, from propolis collected from the Republic of Moldova by the Folin-Ciocalteu method and, subsequently, the removal of gallic acid from wastewater by applying Fenton oxidation.

Republic of Moldova is a predominantly agricultural country where the food industry thrives. This industry, alongside its economic benefits, generates wastewater with high levels of non-biodegradable pollutants, which negatively impact the quality of natural waters. The presence of gallic acid (GA) that is of different origin, can degrade water quality, rendering it unsuitable for agriculture, recreation, or as a drinking water source. The concentration of GA in wastewater can vary significantly depending on the source and type of agro-industrial activity involved.

Removing gallic acid from wastewater is important because excess gallic acid in natural waters has been shown to change the composition of water by increasing color and odor, can be toxic to aquatic organisms, affecting fish, algae and other aquatic life, reduces oxygen levels which can lead to eutrophication and affect biodiversity. Constant exposure to gallic acid through contaminated water can have adverse effects on human health, including skin and mucosal irritations, and at higher concentrations leads to potential systemic toxic effects. Similarly, during the chlorination process of drinking water, carcinogenic by-products are formed, such as trichloroethanes and chloroacetic acids.

Materials and methods

Raw propolis was collected in November 2023 from the southern region of the Republic of Moldova (46°32'23"N 28°55'45"E). Propolis is a source with a high polyphenol content, and for the European region, literature data indicates that the gallic acid content can vary between 0-0.3 mg/g of propolis.

All the experimental samples were analysed for the GA concentration using spectrophotometric equipment (model UV-Vis T80+) at wavelength of 276 and 765 nm. The determination of polyphenols in propolis is essential for quality control and therapeutic studies. Several methods can be used to quantify the polyphenol content in propolis. Here are the commonly used Folin-Ciocalteu method. This colorimetric method is based on the reduction of the Folin-Ciocalteu reagent by polyphenols, resulting in a blue complex measurable at 765 nm. Calculate the polyphenol content

using a calibration curve prepared with a standard like gallic acid (40-200 mg/L). The kinetics of gallic acid from aqueous solutions was estimated by the variation of GA concentration (C_t), determining the reaction rates ($\Delta c/\Delta t$, $\text{molL}^{-1}\text{s}^{-1}$), rate constants (k_t , s^{-1}). The concentration of GA (C_t) was determined from the calibration curve, according to the equation of the line: $y = 0.0016x + 0.003$, where the regression coefficient is $r^2 = 0.9998$. Chemical oxygen demand (COD) was determined according to the Standard Methods with potassium dichromate and oxidation/mineralization was monitored by the variation of residual organic compounds (COD_t).

Results and conclusions

The extraction of raw propolis was performed through maceration and ultrasound-assisted extraction. Experimentally, it was determined that the total polyphenolic compound content in the propolis extracts ranged from 203.70 ± 33.17 to 429.40 ± 17.75 mg GAE/g, depending on the extraction method and the concentration of ethanol used. The maceration extraction process was carried out at room temperature for 10 days with periodic agitation, with a raw material to solvent ratio of 1:10. For obtaining hydro alcoholic propolis extracts, the ultrasound-assisted extraction process was performed under optimized extraction conditions: a raw material to solvent ratio of 1:10, an ultrasonic amplitude of 25 kHz, at 40 °C for 30 minutes. Ethanol concentrations of 60%, 70%, and 80% were used as solvents.

The kinetics of GA ($1.47 \cdot 10^{-5}$ M) in Fenton reactions can be described by pseudo-first-order kinetics. The rate of degradation/mineralization depends on factors such as the concentrations of ferrous ions, hydrogen peroxide, and GA, as well as pH and temperature. Fenton reactions offer efficient means for the oxidation of GA, leading to its degradation (50%) and mineralization (30%) after 5 minutes of reaction. The results, show a slight increase in the COD removal after 60 minutes of reaction. Based on the data acquired, the most effective degradation and mineralization of AG from the aqueous solution occurred when utilizing Fenton's reagent. Thus, the best initial operating conditions, for practical purposes, are $[\text{H}_2\text{O}_2] = 5 \cdot 10^{-4}$ M, $[\text{Fe}^{2+}] = 1 \cdot 10^{-5}$ M, and $\text{pH} = 3.0$. It was found that the conversion kinetics of gallic acid is carried out at the rate constant (k_{avg}) is 0.0057 s^{-1} , the reaction rate ($\Delta c/\Delta t_{\text{avg}}$) is $6.7 \cdot 10^{-7} \text{ Ms}^{-1}$ during 118 s ($\tau_{1/2}$).

Based on the obtained results, it can be concluded that the gallic acid exhibits the highest degree of degradation/mineralization when oxidized with the Fenton reagent. The interaction between the Fenton reagent and GA forms reactive species ($\bullet\text{OH}$), which typically involve the removal of hydrogen atoms from phenolic hydroxyl groups, leading to the formation of intermediate radicals. Subsequent reactions, such as benzene ring cleavage, result in the fragmentation of the GA molecule into smaller, more easily degradable compounds. Gallic acid contains multiple hydroxyl groups, which can undergo hydroxylation reactions under certain conditions. During the oxidation of GA by Fenton reactions, various intermediate and by-products are formed: hydroxylation products, cleavage products such as formic acid, oxalic acid, and acetic acid, harmless by-products etc.

Acknowledgment

This study was supported by the research project No. 010603, Advanced research in computational and ecological chemistry, identification of technological procedures for treatment, formation of water quality and quantity, funded by NARD.