

## Synthesis of 2,5-furandicarboxylic acid using biosynthesized silver and gold nanoparticles as catalysts

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Received: November 13, 2021; Revised: December 08, 2021

In the recent years there is a constant search for replacement of fossil fuel-derived chemicals and polymers produced on their basis. The furan derivatives and especially 2,5-furandicarboxylic acid (FDCA) obtained from renewable resources (carbohydrates) are among the most promising substances. Therefore, the present study focused on the possibility to synthesize FDCA employing bio-synthesized gold and silver nanoparticles. One-pot two-step synthesis starting from mucic acid was considered. In the first step mucic acid was dehydrated in the presence of *p*-toluenesulfonic acid through intermediate 5-hydroxymethyl-furfural (5-HMF) and FDCA was obtained with yield 28±0.5% and the 5-HMF conversion was 75±0.9%. In the next step the mixture was alkalized and bio-synthesized gold (SiO<sub>2</sub>/AuNPs) or silver (SiO<sub>2</sub>/AgNPs) nanoparticles loaded on silica at 2.5, 5, 7.5 and 10% (w/w) were added. The final yield of FDCA increased to 33±0.4% for the SiO<sub>2</sub>/AuNPs experiments (at 5% load). For SiO<sub>2</sub>/AgNPs (at 5% load) added as catalyst the total yield of FDCA increased insignificantly (29±0.3%) due to formation of 5-hydroxymethyl-2-furancarboxylic acid (partially oxidized product) as main compound and lower yield of FDCA.

**Keywords:** bio-synthesis; gold nanoparticles; silver nanoparticles; mucic acid; 2,5-furandicarboxylic acid.

### INTRODUCTION

Nowadays our everyday life relies on vast amounts of plastic polymeric materials. These polymers are exclusively prepared from fossil resources. However, with the rising prices of fossil-based starting materials, diminishing quantities and the recycling problems with the plastic wastes there is an urgent need for searching alternatives and switching to a more sustainable model of development. In this regard, bio-based raw materials and, in particular carbohydrates from undervalorized biomass wastes, are promising starting feedstocks for the production of added-value chemicals, such as: esters, diols, hydroxyl-acids and esters, lactones, carbonyl compounds, cyclic ethers, di-amines, amino acids, lactams, alkenes, acrylics and conjugated dienes [1]. Among them very promising precursors for biopolymer synthesis are considered the derivatives of furan and in particular 2,5-furandicarboxylic acid (FDCA) [2]. Polyesters made using FDCA had found various applications but the most promising one is for replacing polyethylene terephthalate-based products. However, there are many difficulties in front of the successful production, application and utilization of FDCA as promising bio-based material. Attempts on FDCA-based materials development were diffusive in individual scientific investigations and besides cooperation

between scientists and manufacturers has also been occasional, incapacitating and troubling their successful industrialization and market introduction. In order to shed more light and facilitate the FDCA synthesis, applications and economic viability, various initiatives and joint actions were established (for example COST Action CA18220 European network of FURan based chemicals and materials FOR a Sustainable development – FUR4SUSTAIN), which are intended to gather the individual efforts to elaborate novel paths for FDCA and its derivatives synthesis.

Various routes and approaches for obtaining FDCA as a starting material for bio-based polymers were suggested depending on the reactants, catalysts, temperature, pressure, etc. [2–5]. In general, two major approaches are employed: dehydration and oxidation of hexoses (mainly fructose and glucose) with strong acids and selective oxidation of 5-hydroxymethyl furfural (5-HMF). Combined, one-pot syntheses were also reported as alternatives [3], as well as photocatalytic oxidation [6] and microorganisms' assisted bio-synthesis [7]. The main problem in the field is the price of the obtained furan-based monomers and respectively their bio-based polymers. Therefore, new synthetic routes, catalysts and conditions are constantly investigated. The present study employs mucic acid which could be easily produced from the respective hexose by

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dehydration, as a starting material for synthesis of 2,5-furandicarboxylic acid. The reaction was carried out in two steps: acid-catalyzed dehydration (first step) and mild heat treatment in basic medium using as catalysts bio-synthesized silver or gold nanoparticles obtained by reduction with an extract from by-products of rose oil industry (second step).

## MATERIALS AND METHODS

### Materials

The industrial by-products from steam-water distillation of *Rosa damascena* (RD\_SW) were provided by ECOMAAT distillery (Mirkovo, Bulgaria, 2021). After treatment of the fresh rose flowers, the RD\_SW were cooled down, inspected for impurities, dried at 50°C and stored at -18°C until further treatment. The mucic acid was obtained from Riedel-de Haën-Honeywell International Inc. (Germany); silver nitrate (AgNO<sub>3</sub>), chloroauric acid (HAuCl<sub>4</sub>·3H<sub>2</sub>O), silica (nanopowder with specific surface area 175-225 m<sup>2</sup> g<sup>-1</sup> (BET), *p*-toluenesulfonic acid monohydrate (*p*-TSA·H<sub>2</sub>O, 98%), 2,5-furandicarboxylic acid (FDCA), 5-hydroxymethyl-2-furancarboxylic acid (HFCA), levulinic acid and 5-hydroxymethyl furfural (5-HMF) were from Sigma Aldrich Chemie GmbH (Germany).

### Methods

The bio-synthesized silver nanoparticles (AgNPs) were obtained by mixing 0.4 mL of RD\_SW water extract (obtained according to Georgieva *et al.* [8]), 0.4 mL of deionized water and 1.2 mL of 0.01M AgNO<sub>3</sub>. The bio-synthesized gold (AuNPs) nanoparticles were obtained by mixing 0.3 mL of RD\_SW water extract with 1.2 mL of 0.01M HAuCl<sub>4</sub>.

The mixtures of AgNPs and AuNPs were left in dark for two hours, centrifuged for 15 min (6000 rpm, 4°C) and the supernatant was removed by decantation. The nanoparticles were washed three times with deionized water and dried at 50°C.

The silica-supported AgNPs (SiO<sub>2</sub>/AgNPs) or AuNPs (SiO<sub>2</sub>/AuNPs) were prepared as follows: the dried AgNPs or AuNPs were suspended in deionized water at 2.5%, 5%, 7.5% and 10% (w/v) and silica was added at 25% (w/v). The suspension was stirred overnight at room temperature and then heated at 50°C for one hour. After that the mixture was centrifuged for 20 min (12000 rpm, 4°C) and the supernatant was removed. The pellets were dried at 80°C and then heated at 200°C for 3 hours.

The FDCA was synthesized in two steps as a one-pot synthesis: a mixture of mucic acid (420 mg, 2 mmol) and *p*-TSA (768.8 mg, 4 mmol) was

heated in an oil bath at 100°C for 5 min until suspension appeared and then the temperature was raised to 160°C. The mixture was heated for 30 min under constant stirring. The temperature was lowered to 40°C and the pH was brought to 9.5 with 2.5M NaOH. The catalysts were added (SiO<sub>2</sub>/AgNPs – 85 mg or SiO<sub>2</sub>/AuNPs – 94 mg) and the mixture was transferred to a laboratory home-made autoclave (max. temperature 250°C, max. pressure 60 bars, Teflon inlets), purged three times with air and heated at 90°C, 4 bar air pressure for 3 hours. At the end of the reaction the mixture was cooled down and the pH was lowered to 5 using 1M HCl.

In order to follow the reaction progress a sample was taken at the end of the first step (acid-catalyzed dehydration) and every 30 min during the second step, filtered through a 0.45 µm cellulose acetate CA syringe filter (IsoLab, Germany) and properly diluted for HPLC analysis on ELITE LaChrome Hitachi equipped with a VWR Hitachi Chromaster 5450 refractive index detector. The FDCA and HFCA were determined using Bio-Rad Aminex HPX-85H column (250 × 4.6 mm × 5 µm particle size), solvent 5 mM H<sub>2</sub>SO<sub>4</sub> at an elution rate of 0.5 mL min<sup>-1</sup>, column temperature 50°C, and detector temperature 35°C. The 5-HMF was determined on a Supelco Discovery HS C18 RP column (250 × 4.6 mm × 5 µm particle size), solvent CH<sub>3</sub>OH:H<sub>2</sub>O=90:10 (v/v), at an elution rate of 1 mL min<sup>-1</sup>, column temperature 25°C and VWR Hitachi L-2455 diode array detector at 284 nm wavelength.

### Statistical analysis

The experiments and analyses were run three times, and the data were given as mean values. Statistical significance was detected by analysis of variance (ANOVA, Tukey's test; value of *p*<0.05 indicated statistical difference).

## RESULTS AND DISCUSSION

The dried biomass obtained after fresh *Rosa damascena* industrial processing by water-steam distillation, was used to prepare water extracts. The extracts were found to be rich in carbohydrates and polyphenolic compounds which are the main responsible substances for reduction of Ag<sup>+</sup> and Au<sup>3+</sup> to nanoparticles [8, 9]. The synthesis of AgNPs and AuNPs started immediately after the mixture was prepared and visually after the 10<sup>th</sup> minute the solutions turned grey (for the AgNPs) and dark blue (for the AuNPs). The process of synthesis was followed by UV-Vis measurements: Figure 1 (for the AgNPs) and Figure 2 (for the AuNPs). It can be seen that after two hours the NPs

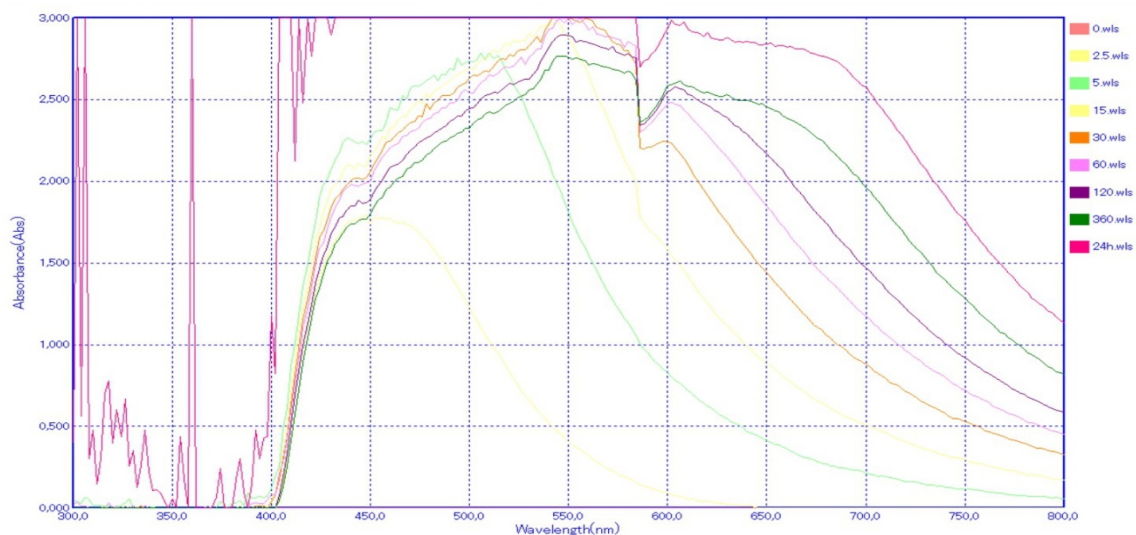
were synthesized and no further increase of the absorption (for the AuNPs) was observed. For the AgNPs a process of agglomeration of the NPs was established and at the 24<sup>th</sup> hour the absorption was out of the range. The lack of absorption maximum in the spectra could be due to the heterogeneous and polydisperse character of the AgNPs and AuNPs. The bio-synthesized nanoparticles (NPs) by this method were previously utilized for assembling of sensors for electrochemical determination of hydrogen peroxide and vanillin [10] and it was found that the prepared electrodes could be successfully utilized for analyses. The other usual application of noble metal NPs is in the field of catalysis and for this reason they were further utilized in this direction.

The preliminary experiments suggested that the

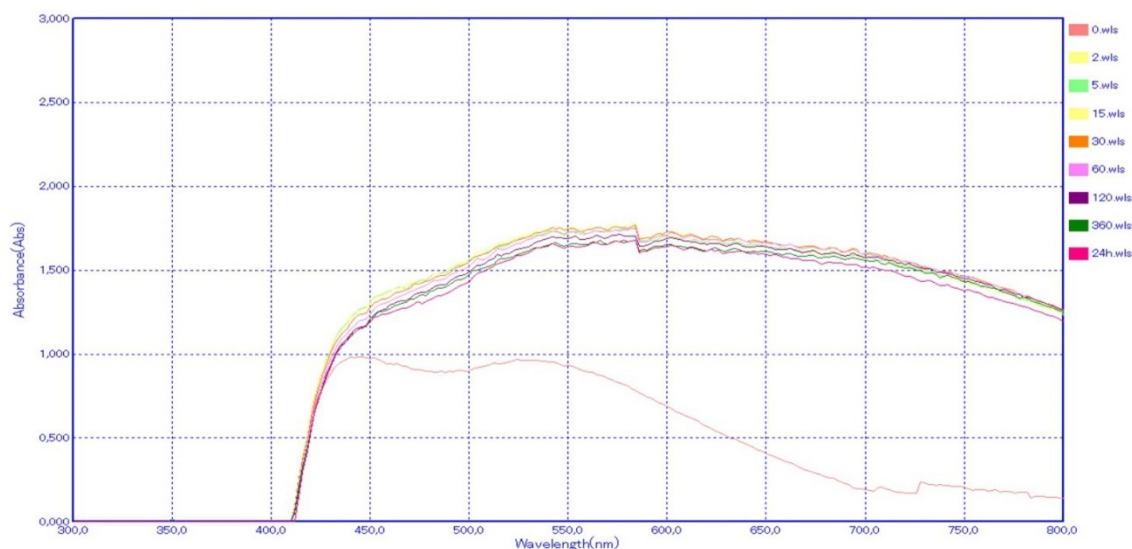
bio-synthesized NPs are difficult to be utilized as catalysts directly, as they are obtained *in situ* with plant extract and other substances are present in the medium, for conversion of aldaric acids or 5-HMF to FDCA. For this reason, the metal NPs were isolated and then were loaded on silica in order to obtain silica-supported AgNPs and AuNPs.

The conversion of hexoses, their respective aldaric acids or 5-HMF to furan derivatives could be successfully performed by heating in the presence of strong acid. The reaction usually takes place at temperatures above 100°C and as an intermediate 5-HMF is obtained (Scheme 1).

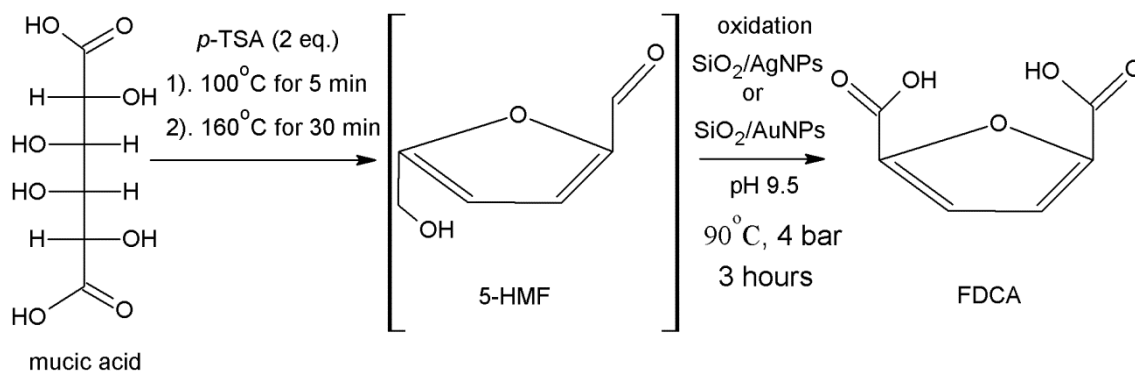
The action of strong acids on mucic acid is leading to formation firstly of 5-HMF. The reaction continues to formation of FDCA by additional loss of water.



**Figure 1.** UV-Vis spectra of AgNPs formation with RD\_SWD water extract (legend: minute of taking the spectra from the beginning of the AgNPs synthesis)



**Figure 2.** UV-Vis spectra of AuNPs formation with RD\_SWD water extract (legend: minute of taking the spectra from the beginning of the AuNPs synthesis)



**Scheme 1.** Synthesis of FDCA from mucic acid in two steps

**Table 1.** Catalysts SiO<sub>2</sub>/AgNPs or SiO<sub>2</sub>/AuNPs application for oxidation of 5-HMF formed in the first step of mucic acid treatment. Reaction conditions: pH 9.5; AgNPs – 85 mg or AuNPs – 94 mg; 90°C for 3 h.

Catalyst	№	Load, %	5-HMF conversion, %	Relative yield <sup>1</sup> , %		Productivity <sup>2</sup> (mol <sub>product</sub> h <sup>-1</sup> mol <sub>metal</sub> <sup>-1</sup> )
				HFCA	FDCA	
SiO <sub>2</sub> /AgNPs	1	2.5	93.1±0.2 <sup>c</sup>	7.0±0.1 <sup>c</sup>	2.0±0.2 <sup>b</sup>	29.3±0.7 <sup>c</sup>
	2	5	97.2±0.3 <sup>a</sup>	10.1±0.1 <sup>a</sup>	2.9±0.1 <sup>a</sup>	35.6±0.5 <sup>a</sup>
	3	7.5	93.6±0.2 <sup>c</sup>	7.6±0.2 <sup>b</sup>	1.9±0.1 <sup>b</sup>	30.4±0.4 <sup>b,c</sup>
	4	10	95.3±0.4 <sup>b</sup>	7.8±0.2 <sup>b</sup>	2.7±0.2 <sup>a</sup>	31.3±0.6 <sup>b</sup>
SiO <sub>2</sub> /AuNPs	5	2.5	92.0±0.5 <sup>d</sup>	3.1±0.1 <sup>c</sup>	8.2±0.1 <sup>c</sup>	28.5±0.3 <sup>d</sup>
	6	5	96.6±0.3 <sup>a</sup>	5.4±0.2 <sup>b</sup>	10.8±0.2 <sup>a</sup>	34.8±0.4 <sup>a</sup>
	7	7.5	93.3±0.4 <sup>c</sup>	5.6±0.3 <sup>b</sup>	9.2±0.1 <sup>b</sup>	30.2±0.8 <sup>c</sup>
	8	10	94.2±0.3 <sup>b</sup>	7.7±0.2 <sup>a</sup>	9.4±0.2 <sup>b</sup>	32.4±0.3 <sup>b</sup>

<sup>1</sup>Relative yield was estimated as the product obtained from the mixture from the first step of the reaction;

<sup>2</sup>Productivity is given as moles of product formed per mole of noble metal and time. For SiO<sub>2</sub>/AgNPs or SiO<sub>2</sub>/AuNPs catalysts, the productivity is given for the major products FDCA and HFCA synthesized, respectively;

<sup>a, b, c</sup> – Values with different letters in a column are statistically significant (ANOVA, Tuckey's post hoc test, *p* < 0.05). Compared were values in the № 1-4 (SiO<sub>2</sub>/AgNPs) and № 5-8 (SiO<sub>2</sub>/AuNPs) experiments.

Disadvantage of this reaction is the formation of side products: levulinic acid, 5-hydroxymethyl-2-furancarboxylic acid, products of 5-HMF degradation and polymeric products (humins) [2, 5]. Moreover, 5-HMF is relatively unstable in acidic medium [5] and it is not completely oxidized to FDCA.

Employing only the first approach in our work (acidic conversion of mucic acid to FDCA) the yield of the final product was found to be 28±0.5% and the 5-HMF conversion was 75±0.9%. Similarly, Zhao *et al.* [3], investigating the process using different acids, found around 30% FDCA yield employing *p*-TSA and heating the mixture for 30 min at 160°C. The authors were able to increase the final yield up to 38-37% increasing the time of treatment. In our studies the time was also increased in order to try to augment the yield but it was observed that significant amounts of humins started to be formed after 45 minutes of heating.

For this reason, different approaches were investigated. The acid-catalyzed dehydration was followed by addition of SiO<sub>2</sub>/AgNPs or SiO<sub>2</sub>/AuNPs in basic medium. The results of the second step conversion are presented in Table 1.

The addition of silver or gold silica-supported NPs catalysts led to additional formation of FDCA and from 28±0.5% yield employing only *p*-TSA as catalyst to 33±0.4% for the subsequent SiO<sub>2</sub>/AuNPs experiments (at 5% load). For SiO<sub>2</sub>/AgNPs added as catalyst the total yield of FDCA increased insignificantly (29±0.3%) due to formation of HFCA (partially oxidized product) as main compound and lower yield of FDCA. In both experiments using SiO<sub>2</sub>/AgNPs or SiO<sub>2</sub>/AuNPs as catalysts the optimal load with NPs was at 5%.

## CONCLUSIONS

The present study focuses on the synthesis of FDCA by combining the two major approaches employed nowadays: acid-catalyzed dehydration and catalytic (metals, alloys, nanoparticles, organic catalysts, etc.) conversion of 5-HMF. Employing *p*-TSA treatment of mucic acid for 30 min at 160°C the yield of FDCA was 28±0.5% and the 5-HMF conversion was 75±0.9%. Additional second step utilizing silica supported AuNPs led to increase of the final yield of FDCA to 33±0.4% but for utilization of SiO<sub>2</sub>/AgNPs as catalyst no significant increase of the final yield was observed. As a side

product partially oxidized HFCA was determined. In both experiments using SiO<sub>2</sub>/AgNPs or SiO<sub>2</sub>/AuNPs as catalysts, the optimal load of NPs on silica was 5%. Optimization of the NPs support and search for alternative approaches is ongoing. The results from the work suggested that biosynthesized gold nanoparticles could be successfully employed for catalytic conversion of mucic acid and synthesis of FDCA.

**Acknowledgements:** This article is based upon work from COST Action CA18220 European network of FURan based chemicals and materials FOR a Sustainable development – FUR4SUSTAIN, supported by COST (European Cooperation in Science and Technology).

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