



Electrochemical synthesis of schiffs base of 4-{(2E)-2-[(2E)-3-phenylprop-2-en-1-ylidene]hydrazinyl} benzene-1,3-diamine using Zinc Cathode with surface morphology and biological activity

S. A. Srikanta

Department of chemistry, Sahyadri Science College, Shivamogga, Karnataka, India

Corresponding author affiliation: Department of Chemistry, Sahyadri Science College, Shimoga, Karnataka-577203, India

Ph: +91-9449497629 (Off), Fax: +91-08182 – 241793, Email address: shreekanta.camistry@gmail.com

To Cite this Article

S. A. Srikanta. Electrochemical synthesis of schiffs base of 4-{(2E)-2-[(2E)-3-phenylprop-2-en-1-ylidene]hydrazinyl}benzene-1,3-diamine using Zinc Cathode with surface morphology and biological activity. International Journal for Modern Trends in Science and Technology 2022, 8(06), pp. 641-645. <https://doi.org/10.46501/IJMTST0806107>

Article Info

Received: 12 May 2022; Accepted: 10 June 2022; Published: 27 June 2022.

ABSTRACT

This paper presents an innovative green organic electrosynthesis to prepare schiff base product by the reduction of 2,4 Dinitrophenyl hydrazine followed by condensation on Zinc Cathode in aqueous alkaline ethanol media in presence of cinnamaldehyde at room temperature. The main characteristic of this proposal is electro-reduction and electro condensation. The bulk Electrolysis at constant potential was performed in a three-electrode undivided cell to prepare schiff base. In this case, good yields and easy purification were achieved. Results indicate that the reduction produce high current in the cell and succeed a green chemistry process. Products were characterized by IR, NMR (¹H, ¹³C), and SEM.

Graphical abstract

Keywords: Electrolisis, Surface morphology, Organic electro-synthesis, cathode

INTRODUCTION

As in the last several decades, chemist have shown their interest in the electrochemical reduction of organic compounds by bringing the organic compound into contact with a cathode, wherein the cathode comprises a support made of an electrically conductive material and an electrically conductive, cathodically polarized layer formed thereon in situ by alleviation [1-5]. This analysis has to be guided by a series of factors such as physicochemical parameters of the organic compound, chemical composition, particle size, structure and morphology or environmental.

The electrochemical reduction of nitro organic compounds has been used for the cathodic dimerization of acrylonitrile. Because current densities were inadequate in economic terms, which meant that space-time yields (STY) were too small, current yields were too low, hydrogen was being formed, selectivities with a view to a number of possible reduction steps were too low, the special catalytically active cathodes were not sufficiently available on a technical scale. At present, more information is required on electrochemical behavior for electrochemical reduction on cathodes to be utilized industrially [6-10].

It is also known, from publications on preparative organic electrochemistry that anodes and cathodes used in preparative electrochemistry must have special electrochemical characteristics. Such electrodes are often used for metal-organic frame works represents a class of hybrid materials comprised of ordered networks formed via combining metal ions with organic ligands. Metal-organic frame works have been used as efficient electrodes in fuel cell systems [11-15].

The electrodes and electrolytes are crucial in electrocatalysis and different electrodes and electrolytes can induce different products. The modifying the surface of electrodes to provide some control over how the electrode interacts with its environment has been one of the most active areas of research interest in electrochemistry within the last 30 years [16-25].

The absorption of the drugs is especially affected by particle size because the bioavailability is, in most cases, dissolution-rate controlled. In the pharmaceutical industry several conventional techniques have been utilized for particle size reduction, such as spray drying, freeze drying and liquid antisolvent precipitation [26-30].

A drawback of these established fabrication methods is that the electrodes, after inactivation of the catalytically active layer, often have to be removed from the electrolytic apparatus and subjected to external regeneration, The drawback is the laborious preparation of the catalytically active layer as such and the difficulties in achieving adequate bonding to the support electrode [31-34].

In view of the prior art set forth herein above it is an object of the invention to provide a process for reducing organic compounds, which on the one hand gives high space time yields, permits high selectivity in the case of multiple reducible compounds, which avoids the formation of hydrogen during the reduction and can be used on an industrial scale. [35,36].

The mean particle size of the particles forming the above defined layer and the thickness of the layer are always chosen so as to ensure an optimum ratio of filter pressure drop and hydraulic through put and enable optimum mass transfer. The mean particle size is generally from about 1 to about 400 μm , preferably from about 30 to about 150 μm , and the thickness of the layer is generally from about 0.05 mm to about 20 mm, preferably from about 0.1 to about 5 mm.

After the reduction is complete or when the catalytically active layer is spent, it can be separated from the support, by a simple switch of the flow direction, and can be disposed of or regenerated, independently of the reduction. After the spent layer has been completely removed from the system, it is then possible once more to recoat the support with the particles forming the layer and after said particles have been completely alluviated, to continue the reduction of the organic compound. Organic compounds suitable for use in the process according to the invention in principle comprise any organic compounds containing reducible groups as starting materials. The products which can be obtained in the process include, depending on the total electric charge introduced, both partially reduced compounds and completely reduced compounds [37,38].

Materials and methods

All chemicals were analytical grade from Aldrich chemicals and solvent for electrochemical process were methanol, ethanol from Aldrich chemicals. The water obtained from double distillation. The reported melting point was uncorrected and the purity of the compound

was checked by TLC on glass plates coated with silica gel as absorbent, using acetone: methanol in 1:1 ratio. The IR spectra were taken in KBr beam splitter on a Thermo Nicolet avatar 370.

^1H NMR was recorded on a BrukerAvance III, 400MHz. instrument using DMSO as solvent and TMS as internal standard. JSM-6390 scanning electron microscope at the accelerating voltage of 10-20 Kv was used for SEM analysis. CHNC-13, all spectral analysis were carried out at the sophisticated analytical Instrumentation Facility, cochin university and technology, cochin, Kerala, India.

Experimental

Procedure for Electrolysis

The electrochemical reduction of 2,4-dinitrophenyl hydrazine was carried out in an undivided cell. (0.38 g, 1 mmol) 2,4-dinitrophenyl hydrazine was taken in an undivided cell along with 75 mL of ethanol and 25 mL of water. To this mixture a 10% aqueous solution of sodium hydroxide (1g) was added drop wise at room temperature. The undivided cell was equipped with a zinc cathode (0.014cm²), platinum anode (Pt) and calomel electrode. The constant potential was supplied with DC power supply (8.5 V). The reaction was electrolysed with constant stirring using a magnetic stirrer for 30 minutes and electrolysis was stopped. To this electrolysed solution cinnamaldehyde (0.108 g, 1 mmol) was added slowly with stirring, the whole electrolysed solution was immediately converted into pale red solid. The solid was washed with ethanol and water repeatedly and recrystallised from mixture of solvent (DMSO and DMF) to get the pure product. The isolated yield was 98 % (0.58 g).

Procedure for antibacterial and antifungal activity:

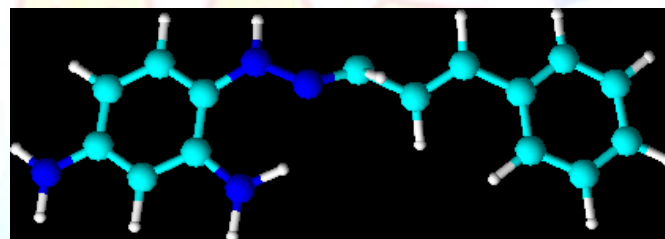
The in-vitro antibacterial activity carried out by well diffusion method using nutrient agar as the medium, DMSO as the control and streptomycin used as a standard bactericide and fluconazole as standard fungicide. The newly synthesized compound was screened for antibacterial activity against *Staphylococcus aureus*, *Bacillus cereus*, *Streptococcus Sp*, *Proteus mirabilis*, *Staphylococcus epidermidis*, *Enterobacter aerogenes*, *Shigella flexneri*, *Klebsiella pneumonia*, *Vibrio cholerae* and species of fungi against *Aspergillus flavus*, *Aspergillus niger*, *Cryptococcus neoformans*, *Curvularia sp*, *Trichosporon sp*, *Candida albicans* by well-in agar method. The synthesized

compounds (1mg mL⁻¹) and the controlled drugs were dissolved in redistilled DMSO for determining both antibacterial and antifungal activity. The zones of inhibition were determined at the end of an incubation period of 24 hours at 37 °C. During this period, the test solution diffused into the medium and the growth of inoculated microorganism was affected. The antifungal activities were determined at 26-28°C for 48 hours.

Results and Discussion

The preparative electrolysis of the dinitrocompound in aqueous alkaline alcoholic media has been studied. The compound

4-[(2E)-2-[(2E)-3-phenylprop-2-en-1-ylidene]hydrazinyl]benzene-1,3-diamine has been reduced on a zinc cathode at a cathode potential of -2.3 V and produced pale yellow solid A while stirring the solution with benzaldehyde. The speed of the reaction between the reduction product and the aldehyde is very interesting because the same reaction takes more than two hours in conventional method.

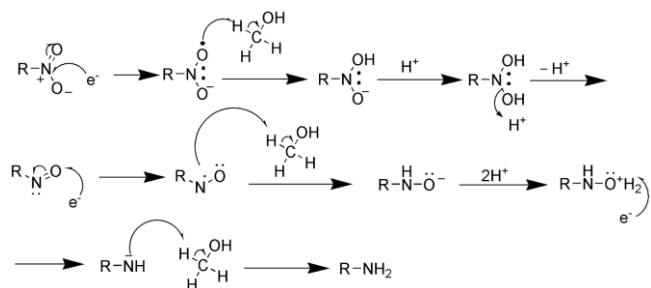


The preparative electrolysis of the dinitrocompound in aqueous alkaline alcoholic media has been studied using DC suppliers operated at a standard output of 0.5 to 2.5 A / 0 – 35 V. These were connected with ammeter and voltmeter in series. The electrode reactions have been performed successfully in an undivided cell which is a simple beaker type apparatus. The solution was stirred using a magnetic stirrer. The calomel electrode was used as reference electrode to monitor the operating potential.

MECHANISM:

The reaction which proceeded through one electron reduction of the nitro compounds to form corresponding nitro free radical anion and followed by protonation in which nitro compound is reduced to amino compound which have been further condensed with benzaldehyde producing Schiff base.

The one electron transfer from cathode to nitro compound followed by protonation occurred as shown below.



Surface morphology of electrode before and after electrolysis was studied. The surface morphology was analysed by SEM analysis and it was observed that there is a difference in the morphology of the surface of zinc cathode, this is due to the reduction of 2,4-dinitro phenyl hydrazine on the surface of zinc cathode. The SEM image of A on the surface of zinc cathode are shown in figure c and d (after electrolysis). The scanning electron microscope (SEM) images of surface of zinc cathode were shown in figure a (before electrolysis). The SEM image of 4-[(2E)-2-[(2E)-3-phenylprop-2-en-1-ylidene]hydrazinyl]benzene-1,3-diamine were shown in figure b (before electrolysis). The product was proved by spectroscopic study.

The average diameter of these particles is about 840 nm. The SEM micrographs show slab like crystallites of average particle dimensions approximately 840 nm. The technique is a new way of doing electron diffraction with an SEM. In standard SEM-based electron diffraction, the researcher analyses patterns that are formed by electrons that bounces back after striking atoms in the sample. If the sample is a crystalline material, with a regular pattern to the arrangement of atoms, these diffracted electrons form a pattern of lines that reveals the particular crystal structure or "phase" and orientation of the material. Scanning Electron Microscope (SEM) is the method of choice to investigate particle size shape and structure. According to the SEM images in figure c and d, the obtained structure has a uniform morphology. Scanning electron micrographs (SEMs) were used to study the morphology of the compounds and to observe the interfacial quality between the phases. Fractured surfaces of the samples from the notched impact tests were coated with a gold/palladium alloy and observed

at a voltage of 20 kV. The surface morphology and cross sectional morphology of Schiff base of the reduction product

4-[(2E)2benzylidenehydrazinyl]benzene-1,3-diamine (figure c and d) were characterized by SEM. The SEM images showed a microporous and fibrous structure. The expected interactions between the formation of imine linkage which make the Schiff base derivatives stable with many hydrophilic sites at the surface. The cross sectional morphology of the same showed the fine interaction with pores and micro voids. The pores are effective in increasing the functional surface in the Schiff bases which enabled the same to be used promising material.

The Schiff bases of the reduction product 4-[(2E)2benzylidenehydrazinyl]benzene-1,3-diamine was evaluated for their anti-bacterial activity in vitro by using zone inhibition technique against gram negative and gram positive bacteria such as *Pseudomonas aeruginosa* and *Bacillus subtilis* at different concentration (10 µg, 50 µg, 100 µg, and 200 µg). The results obtained were compared with the standard drug streptomycin as a standard bactericide and fluconazole as standard fungicide. The electrochemically produced Schiff' base showed promising antibacterial and antifungal activity. The zone of inhibition is given in table 1 and 2.

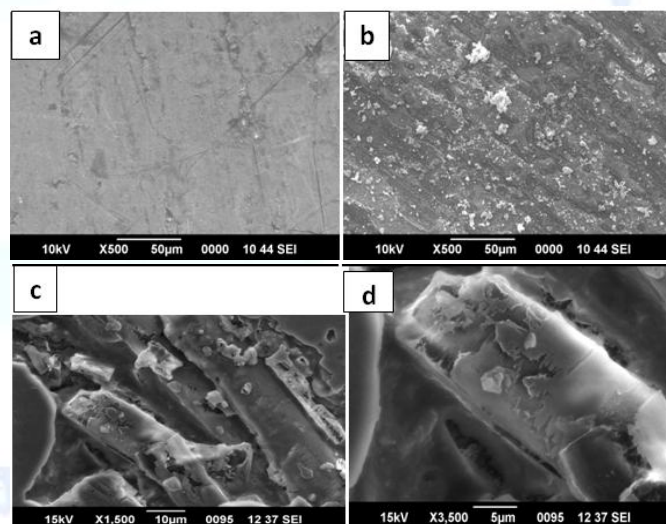


Figure 1 The SEM images of the morphologies of electrolysis product A

Spectroscopic Analysis

In the FTIR spectrum of the electrochemical product, the stretching frequency for N-H₂ the broad peak appears at 3500cm⁻¹, the stretching frequency for N=CH appears

at 1620 cm⁻¹. In the ¹H NMR spectrum, one imine proton appears at 9.07 ppm, NH₂ proton appears at 6.69 ppm. mp 170-182 °C

Table-1 Antibacterial activity (zone of inhibition in mm)

Sl. No.	Bacterial strains used	Zone of inhibition in mm
1	<i>Staphylococcus aureus</i>	40
2	<i>Bacillus cereus</i>	15
3	<i>Streptococcus sp</i>	40
4	<i>Proteus mirabilis</i>	15
5	<i>Staphylococcus epidermidis</i>	16
6	<i>Enterobacter aerogenes</i>	30
7	<i>Shigella flexneri</i>	37
8	<i>Klebsiella pneumoniae</i>	40
9	<i>Vibrio cholerae</i>	30

Standard streptomycin

Table-2 Antifungal activity (zone of inhibition in mm)

Sl. No.	Type of fungi	Zone of inhibition in mm
1	<i>Aspergillus flavus</i>	35
2	<i>Aspergillus niger</i>	15
3	<i>Cryptococcus neoformans</i>	44
4	<i>Curvularia sp</i>	16
5	<i>Trichosporon sp</i>	15
6	<i>Candida albicans</i>	37

Standard fluconazole

CONCLUSION

The study of the electrochemical reduction of 2,4-dinitrophenyl hydrazine in presence of cinnamaldehyde was investigated in a basic, water / ethanol homogeneous medium. The main attention was first paid to the following key parameters, the cathode material, the cathode potential and water/methanol. For conventional electrolysis, the best experimental conditions for Schiff base of 4-[(2E)2benzylidenehydrazinyl]benzene-1,3-diamine are the use of a zinc cathode and the potential of -2.1 V/SCE. The bulk synthesis of Schiff base was achieved in single step in an undivided cell.

Conflict of interest statement

Authors declare that they do not have any conflict of interest.

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