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Current Chemistry Letters

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Chitosan – hydrogen iodide salt supported graphite electrode: A simple and novel electrode for the reduction of nitro group under electrochemical condition**P. L. Deena^{a*}, Savariraj Joseph Selvaraj^b and K. Joby Thomas^c**^aDepartment of Chemistry, St. Joseph's College (Autonomous), Tiruchirappalli, 620 002, Tamil Nadu, India^bAffiliated to Bharathidasan University, Tiruchirappalli 620 024, Tamilnadu, India^cDepartment of Chemistry, St. Thomas' College (Autonomous), Thrissur- 680 001, Kerala, India**CHRONICLE***Article history:*

Received March 20, 2023

Received in revised form

June 17, 2023

Accepted November 1, 2023

Available online

November 1, 2023

*Keywords:**Chemoselective reduction**Quaternary ammonium**chloride**Chitosan**Acetic acid**Nitro group***ABSTRACT**

The present investigation provides a unique, simple, selective and efficient method for the electrochemical reduction of aromatic nitro groups into amines using chitosan-hydrogen iodide salt supported graphite electrode. 3:1 tetrabutyl ammonium chloride and acetic acid mixture was used as the medium for electrolytic process and a constant voltage of 5 V applied between the modified electrodes. The reaction was found to be selective and further reduction of amines was not observed. The purity of the products was checked with HPLC and characterized using spectroscopic tools. The electrochemical synthesis resulted in moderate to good yields of amino compounds which were higher than the reduction using conventional graphite electrodes. Quaternary ammonium chloride behaved as supporting electrolyte during synthesis and the reaction did not progress in the absence of acetic acid. The redox characteristic of the process was studied by cyclic voltammetry of the reaction mixture.

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1. Introduction

The widespread application of aromatic amines in different industries, including agrochemicals, textile dyes, medicines, the rubber industry, fine chemicals etc. demonstrates their great utility as intermediates and building blocks in organic synthesis.¹⁻⁵ One of the most prevalent techniques for getting various aromatic amines is via reducing nitro groups.^{6, 7}

The conversion of a nitro group (-NO₂) to an aromatic amine (-NH₂) can be accomplished in organic chemistry in a variety of ways. The most widely used technique for converting nitro groups into aromatic amines is catalytic hydrogenation. It involves the use of a metal catalyst (usually Pd, Pt or Ni) and hydrogen gas under high pressure and temperature.⁸ In the iron reduction process, nitro groups are transformed into aromatic amines using iron powder and an acid (typically acetic acid).⁹ Zinc reduction involves the use of zinc dust and an acid (usually hydrochloric acid) to reduce nitro groups to aromatic amines.¹⁰⁻¹² Under benign conditions, aromatic nitro compounds are converted to amines via the sodium borohydride reduction technique, which uses NaBH₄ and an acid (often acetic acid).^{13,14}

In spite of the requirement of high pressure, possibility for potential accident and costly catalyst/reagent, these reductions are more preferred in the synthetic laboratories. Nitro compounds and their derivatives are important in biological, pharmaceutical and industrial fields.^{15,16} The reduction of nitro group under electrochemical conditions is another approach that has been widely explored but is not as frequently used. The reaction can be carried out under mild conditions and is often utilized to reduce nitro compounds that are challenging to reduce using alternative techniques.¹⁷⁻¹⁹

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In addition to the conventional techniques, electrochemically stimulated reactions in organic synthesis have created novel avenues for synthetic transformation.²⁰⁻²⁴ Making the reaction as environmentally friendly as possible while adhering to green chemistry principles is of the utmost importance.²⁵⁻²⁷ It is a powerful method for selectively reducing benzyl groups in organic molecules, providing a versatile tool for the synthesis of a wide range of benzylic compounds.²⁸⁻³⁰ Oxidation of toluene, benzyl alcohol, benzyl chloride, 3-phenylpropene are just a few examples of electrochemical oxidation reactions.³¹⁻³³ The electrochemical reduction of organic compounds is a versatile and promising field that continues to be explored for various applications, contributing to both chemical synthesis advancements and sustainable technologies. Electrosynthesis of alcohols, electrochemical hydrogenation, electrochemical reduction of α,β -unsaturated ketones etc. are the few examples which showcase the diverse applications of electrochemical reduction in various fields, ranging from chemical synthesis to environmental remediation and energy storage.³⁴ By adjusting the applied current or voltage, electrochemical reactions enable control of chemoselectivity.

Chitosan is a polymer of carbohydrate which is made up of β - linked D- glucosamine and N-acetyl D-glucosamine units. It is obtained from the basic hydrolysis of chitin (**Fig. 1**) isolated from the shells of shrimp. The $-\text{NH}_2$ unit present in the chitosan is the central focus of the chemists and is modified to specific applications particularly to serve as ligand for several transition metals. Commercially available chitosan is categorized as low, medium and high based on their molecular weight.

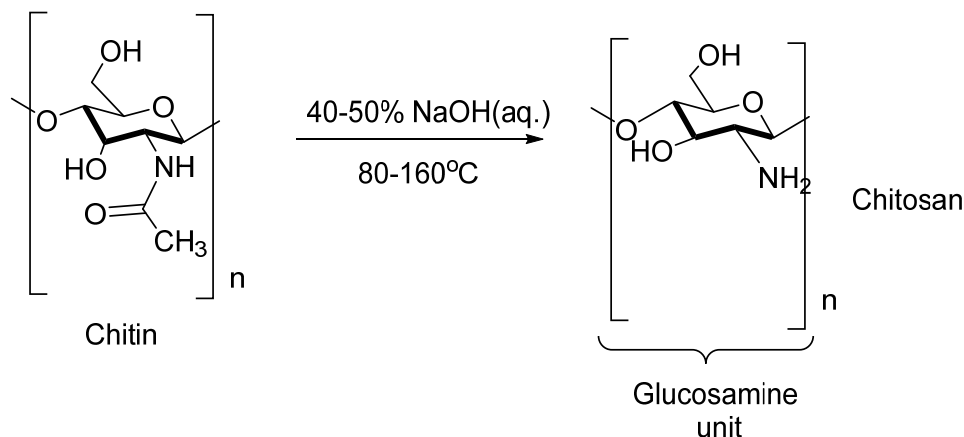


Fig. 1. Chitosan Preparation from chitin

Chitosan, due to its unique chemical structure, has several properties such as biocompatibility, biodegradability and adsorption capability, making it useful in various biomedical applications.³⁵⁻³⁷ However, chitosan is not conductive, which limits its use in electronic applications. In contrast, graphite is advantageous for use in electronic equipment because it is an excellent conductor of electricity and has a wide surface area. By impregnating chitosan with graphite, the resulting composite material has improved adsorption properties of chitosan and the conductivity of graphite. In the acid, the free $-\text{NH}_2$ group of chitosan gets protonated, and the resulted salt is soluble in water. Upon evaporation the dissolved chitosan-acid salt results in a translucent film with high tensile strength. We envisaged that this film could be used as electrode by impregnating graphite powder (G-Ch).

In this communication, we report the preparation of a novel electrode in which graphite is impregnated on Chitosan – Hydrogen iodide salt and investigated the use of this electrode for the reduction of nitro group under electrochemical conditions. This electrode can act both as the reservoir of H^+ ions and supplier of electrons. We anticipate that under mild conditions, the H^+ ions in the electrode will facilitate the reduction. Furthermore, enhanced surface area of the electrode may boost current flow through the medium. The yield of the amino compounds was compared with the yield obtained by the reduction using graphite electrode.

2. Results and discussion

2.1. SEM analysis of the G-Ch film

Though the film looks homogeneous with even distribution of graphite, the SEM image clearly shows that the graphite powder is randomly distributed, and the surfaces are not uniform and smooth (**Fig. 2**). In the SEM image, it is observed that small flakes of chitosan –HI is adhered on the surface which is around 20 μm in size.

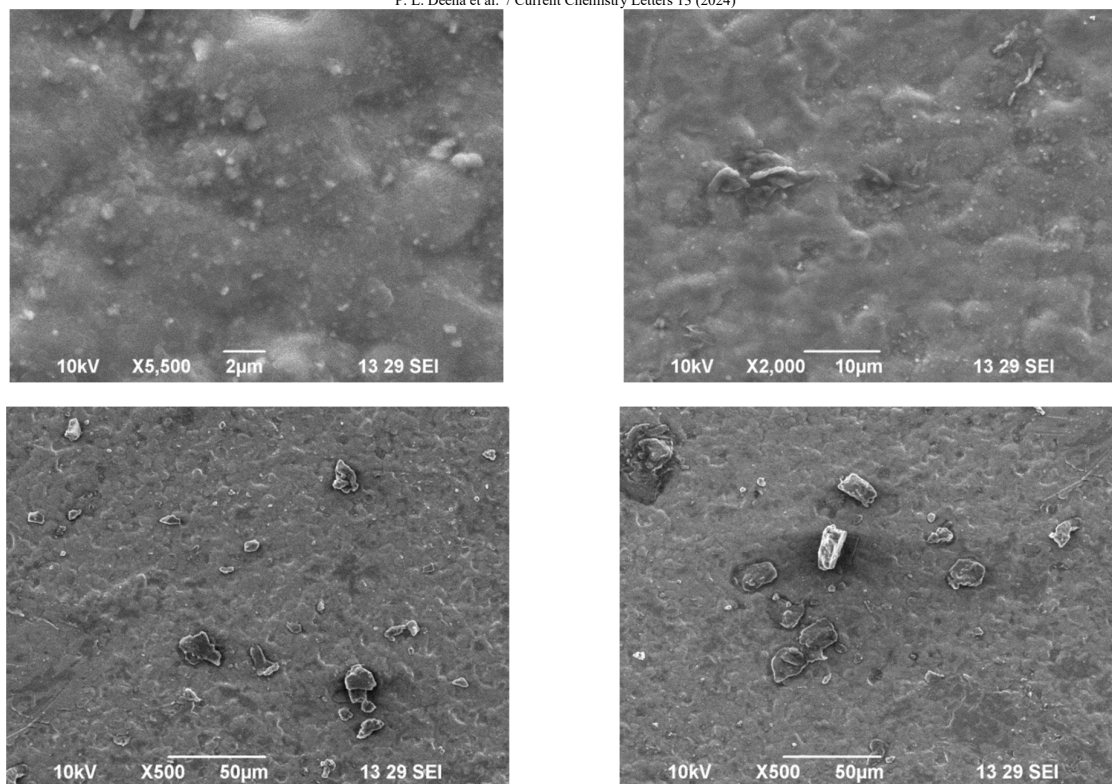


Fig. 2. SEM image of the graphite impregnated chitosan (1g of graphite/1g of chitosan)

2.2. XRD studies of the G-Ch film

The diffractogram of the Chitosan-graphite film displayed two sharp peaks at $2\theta = 26.795^\circ$ and 54.826° which is attributed to the peaks of crystalline chitosan (130) and graphite (004). The appearance of sharp peaks is an indication of crystalline behaviour of the composite material than pure low molecular weight chitosan.³⁸ The XRD spectrum of G-Ch is depicted in **Fig. 3**.

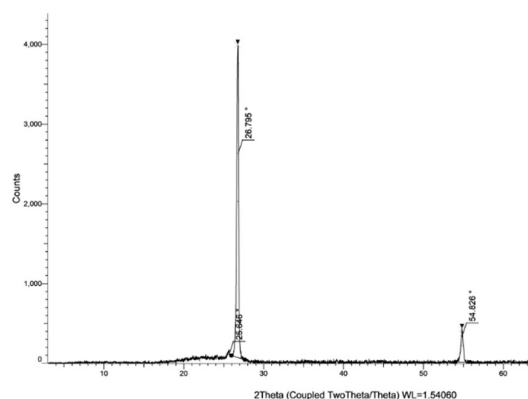


Fig. 3. X-ray diffractogram of chitosan-graphite composite material

2.3. FTIR spectral studies

FTIR spectrum of chitosan and the composite film (G-Ch) is shown in **Fig. 4**. The O-H and N-H stretching frequencies appeared at 3340 and 2878 cm^{-1} respectively in the spectrum of G-Ch. These peaks were slightly shifted to low energy region when compared to IR spectrum of chitosan. This confirms the interaction of chitosan-HI salt with graphite. C-N stretching frequencies of the composite film (1622 and 1525.5 cm^{-1}) also appeared in the lower frequency region of the FTIR spectrum when compared to the peaks of pure low molecular weight chitosan. The strong spectral peak of chitosan corresponds to C-O-C vibrations (1077 cm^{-1}) were also shifted to lower frequency side in the composite film spectrum (1062 and 1020 cm^{-1}).

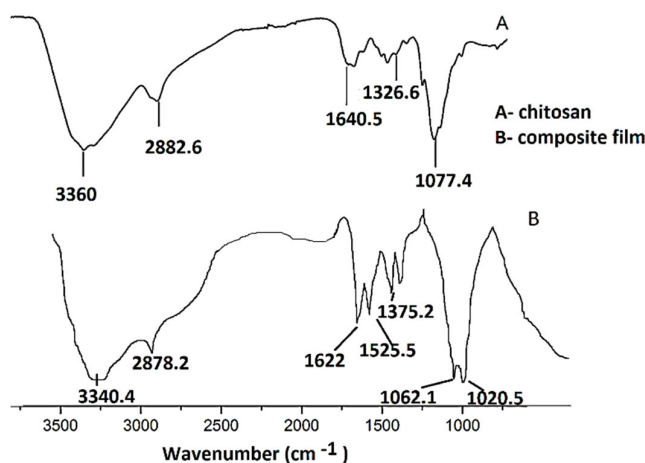


Fig. 4. FTIR spectrum of A) chitosan and B) composite film

2.4. Conductivity of composite film

Initially we studied the conductivity of the films prepared (2 x 5 cm) using $n\text{Bu}_4\text{N}^+\text{Cl}^-$: AcOH (3:1mmol) as electrolyte and MeOH (30 ml) as solvent (**Table 1**). Additionally, we attempted to find out conductivity in EtOH. In the methanol medium, conductivity values were seen to be relatively superior. Moreover, we chose MeOH solvent since it has high dielectric constant and does not dissolve the chitosan-HI film. A constant voltage of 5 V was applied between the graphite impregnated chitosan-HI films. The current flow was found to increase slightly as the amount of graphite is increased in the film. A slight fluctuation of the current was observed during measurement.

Table 1. Conductivity study of the graphite impregnated polymer film

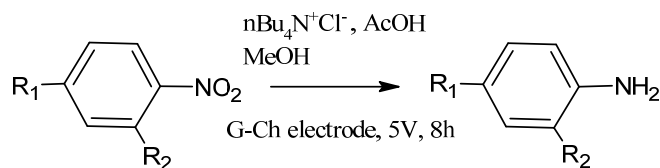
Sl. No	Chitosan (g):Graphite (g)	Solvent	Current (A)
1	10:1	MeOH	0.03
2	10:2	MeOH	0.05
3	10:4	MeOH	0.06
4	10:5	MeOH	0.08
5	10:10	MeOH	0.08
6	10:1	EtOH	0.02
7	10:2	EtOH	0.05
8	10:4	EtOH	0.06
9	10:5	EtOH	0.07
10	10:10	EtOH	0.07

2.5 Electrochemical synthesis

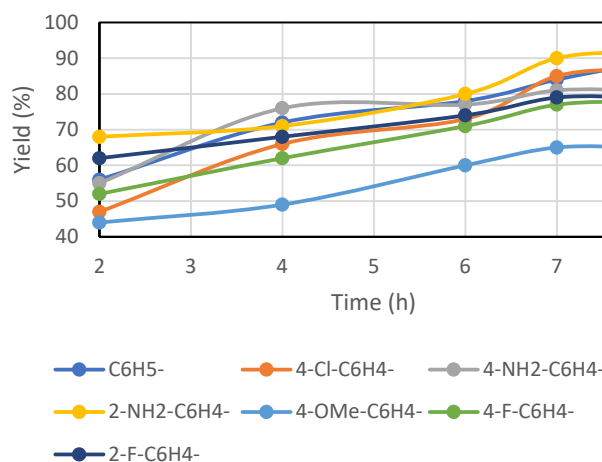
Same reaction condition was applied to a number of substituted aromatic nitro compounds and the outcome is shown in **Table 2**. 3mmol nitro compounds were subjected to electrochemical reduction using $n\text{Bu}_4\text{N}^+\text{Cl}^-$: AcOH (3:1 mmol) and MeOH (30 ml) as electrolyte and solvent respectively. Modified electrodes (1g graphite : 1g chitosan : 800 mg HI) having dimensions (2 x 5cm) were used for all investigation. A constant potential of 5 V was applied between the electrodes for a period of 8 h. The purity of the products was checked with HPLC and characterized using NMR and FTIR spectroscopic tools. The efficiency of the processes in the presence of the conventional graphite electrode was also determined parallelly and reported in **Table 2**.

From the experimental data, it was noticed that majority of nitro compounds gave higher yields of reduced amino form in the presence of G-Ch electrodes during electrochemical transformation than the reduction using graphite electrodes. Exceptionally very high yield of 2-nitro aniline was obtained when compared to the synthesis using conventional graphite electrodes. Slightly low yield was noticed for the reduction of 4-methoxy nitro compound when compared to the electrochemical synthesis using graphite electrodes. The increased efficiency of the G-Ch electrodes in converting the aromatic nitro compounds into the corresponding amino compounds may be due to the potency of the electrodes to supply the H^+ ions (from HI) readily from their surface which is an essential condition of reduction.

In the absence of acetic acid, it was also observed that the electrochemical synthesis did not advance. It can be assumed that repeated release of H^+ ions from the G-Ch surface and the absorption of protons from the acetic acid continuous till the completion of the reaction. The G-Ch electrode (cathode) itself acted as the reservoirs of both H^+ ions and electrons for the reduction of nitro compounds.

Table 2. Substrate scope for nitro reduction under electrochemical condition

Sl. No	R ₁ , R ₂	Yield (%) G-Ch electrode	Yield (%) Graphite electrode
1	R ₁ =H, R ₂ =H	89	85
2	R ₁ =Cl, R ₂ =H	87	82
3	R ₁ =NH ₂ , R ₂ =H	81	81
4	R ₁ =H, R ₂ =NH ₂	92	76
5	R ₁ =OMe, R ₂ =H	65	68
6	R ₁ =F, R ₂ =H	78	75
7	R ₁ =H, R ₂ =F	79	68

**Fig. 5.** Variation of reaction time with the yield of amino compounds

The approximate duration of the electrochemical process was also estimated in this work. It was found that the entire electrochemical reduction process took 6 to 8 hours to complete. The optimal time for the synthesis of aromatic amino compounds was determined to be 8 hours. The variation of reaction time with the yield of the aromatic amino compounds is depicted in **Fig. 5**. It is understandable that the molecules such as 4-amino nitrobenzene, 4-methoxy nitrobenzene and 2-fluoro nitrobenzene underwent complete reduction at 7 h.

For the electrochemical reduction of nitro compounds, it was also examined how the applied voltage (1–5 V) varied with the yield of product (**Table 3**). Since there was a good yield of the products and a discernible rate of reaction at 5 V potential, this voltage was selected to be the optimum condition for the reduction.

Table 3. Variation of the applied potential with the yield (%) of the product

Compound	1V	3V	5V
aniline	78	84	89
p-chloroaniline	79	83	87
p-phenylenediamine	72	79	81
o-phenylenediamine	78	86	92
4-methoxy aniline	60	63	65
4-Fluoroaniline	68	74	78
2-Fluoroaniline	67	75	79

The resulting anilines were pure as demonstrated by chromatographic and spectroscopic methods.

The NMR spectral data and the M. P/B. P of various amino compounds are listed below.

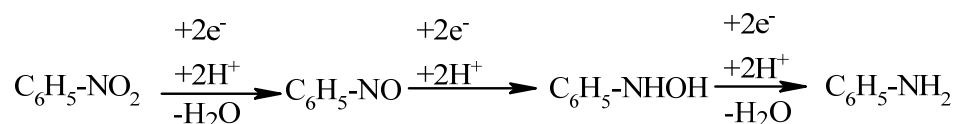
C₆H₅-NH₂: B. P. 185.2 °C; ¹Hnmr (ppm): δ 6.64-7.13 (Ar-H), 3.54 (-NH₂); ¹³Cnmr (ppm): δ 115.1, 118.5, 129.4, 146.5. **4-Cl-C₆H₄-NH₂**: M. P. 73.1 °C; ¹Hnmr (ppm): δ 6.57-7.11 (Ar-H), 3.57 (-NH₂); ¹³Cnmr (ppm): δ 145.07, 116.22, 122.9, 129.07. **4-NH₂-C₆H₄-NH₂**: M. P. 140.3 °C; ¹Hnmr (ppm): δ 6.54 (Ar-H), 3.37 (-NH₂); ¹³Cnmr (ppm): δ 138.68, 116.65. **2-NH₂-C₆H₄-NH₂**: M. P. 104.5 °C; ¹Hnmr (ppm): δ 6.34, 6.57 (Ar-H), 4.37 (-NH₂); ¹³Cnmr (ppm): δ 116.38, 147.32. **4-OMe-**

C₆H₄-NH₂: M. P. 58.1 °C; ¹Hnmr (ppm): δ 6.77, 6.92 (Ar-H), 3.43 (-NH₂), 3.73 (-OCH₃); ¹³Cnmr (ppm): δ 56.31, 114.32, 116.41, 140.82, 152.33. **4-F- C₆H₄-NH₂**: B. P. 187.5 °C; ¹Hnmr (ppm): δ 6.53, 6.83 (Ar-H), 3.46 (-NH₂); ¹³Cnmr (ppm): δ 115.431, 116.7, 148.22, 156.72. **2-F- C₆H₄-NH₂**: 182.2 °C; ¹Hnmr (ppm): δ 6.92-7.62 (Ar-H), 3.71 (-NH₂); ¹³Cnmr (ppm): δ 111.62, 116.42, 126.33, 129.64, 134.5, 154.51

The electrode remains undissolved in the reaction medium. After the reaction, the electrode was washed with methanol and air dried. It had the same nature after two hours and its usability had been verified. It is worthwhile to mention that almost the same yield of the amino compounds was obtained for the second process.

2.6. Cyclic voltametric studies

The mechanism of nitro group reduction under electrochemical method had been thoroughly investigated by cyclic voltammetry studies. We performed CV studies using G-Ch electrodes and Ag/AgCl reference electrode. 2-nitroaniline (1 mmol) was chosen as the substrate (**Fig. 6**). Initially, the reaction mixture was scanned over a potential range of -2 to +2 V to observe the active regions. After that the experiment was repeated with a fresh mixture in the potential range -2.0 to 0 V which found as the active region of the electrochemical process. The curve shown in the figure represents the cyclic voltammogram for the reduction of 2-nitro aniline. The voltammogram displayed three small reduction peaks at -0.68, -1.2 and -1.41 V which corresponds to three stage reduction of the nitro group. A strong oxidation peak at -0.66 V was also visible in the CV diagram. Based on CV investigations, the reduction mechanism for the nitro group can be explained as depicted in **Scheme 1**.



Scheme 1. Mechanism of nitro group reduction under electrochemical conditions

The G-Ch electrode initially provides two electrons and two H⁺ ions to the nitro group, which then changes into C₆H₅N(OH)₂ at -0.68 V. Due to the initial product's instability, it loses one water molecule and converts into aromatic nitroso compound (C₆H₅NO). The nitroso compound further captures two electrons and two H⁺ ions from the electrode to form the hydroxyl amine (C₆H₅NHOH). This process took place at -1.2 V. The third step of the reduction process occurred at -1.4 V, when the hydroxyl amine accepts two H⁺ ions and electrons from the G-Ch electrode to produce the corresponding amino compound.

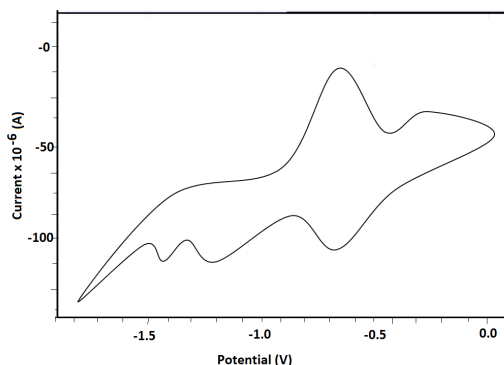


Fig. 6. Cyclic voltammogram of 2-nitro aniline

3. Conclusion

In conclusion, we have developed chitosan-HI supported graphite electrode and used it for the reduction of nitro group of aromatic compounds. We have demonstrated the effectiveness of G-Ch electrodes in reducing the nitro group into amino group and compared with that of conventional reduction using graphite electrodes. The electrode acted as the reservoir for both electrons and H⁺ ions. Most of the nitro compounds gave better yields of amines compared to the reduction using graphite electrodes. Presence of nBu₄N⁺Cl⁻ : AcOH (3 : 1) electrolyte in MeOH gave better results for the reduction of nitro compounds using 1g graphite : 1g chitosan : 800 mg HI composite electrode. Among the investigated reductions, the 2-nitroaniline reduction at 5 V for 8 h displayed the highest yield of o-phenylenediamine (92 %). The three-stage reduction process involved in the electrochemical reduction was verified using cyclic voltametric studies. The reusability of the G-Ch electrode was checked after cleaning it with methanol. Almost same yield of the amines was obtained when the reduction was conducted again using the same electrode.

4. Experimental

4.1. Preparation of chitosan-hydrogen iodide salt supported graphite electrode

Commercially available low molecular weight chitosan (Sisco Research Lab) was taken in 100 ml beaker and added 30ml water. To this suspension, stoichiometric amount of hydrogen iodide (Merck Millipore) is added dropwise with constant stirring. Chitosan gets dissolved completely to produce highly viscous gelatin like chitosan – HI salt. To this viscous material graphite powder (purchased from Aldrich) was added and stirred with mechanical stirrer for 30 minutes to ensure complete dissolution of chitosan and proper mixing of graphite powder. After 30 minutes, the viscous black colour liquid was poured into petri dish covered with perforated filter paper and allowed to dry in the open atmosphere. (Oven drying alters the nature of film that is produced). After two days of drying, the film is peeled off from the petri dish and cut into the desired shape and size (2 x 5 cm). The graphite powder was discovered to be well bound within the film and washing with an organic solvent did not remove any graphite powder from the film. Following this method, we impregnated 100 mg, 200 mg, 400 mg, 500 mg and 1000 mg of graphite in 1000 mg of chitosan. The film was found to be insoluble in CH₂Cl₂, CHCl₃, THF, MeOH and ethanol. The film with less graphite (100 mg – 500 mg) undergoes deformation and is flexible when dipped in ethanol. Better rigidity is obtained when 1000 mg of graphite powder was impregnated on the polymer.

4.2 Spectroscopy, microscopy and XRD studies

Shimadzu prestige 20 FT-IR spectrophotometer was used to record IR spectra with NaCl crystal as the sample holder. The Attenuated Total Reflection (ATR) method was used to perform FTIR analysis. SEM was performed using SEM EDX MB.1051. XRD of chitosan-hydrogen iodide salt supported graphite electrode were recorded by DW-XRD-2700A instrument. Utilizing a Bruker 300 MHz FT-NMR apparatus, the NMR spectra of the products were determined.

4.3 Cyclic voltammetric studies

Cyclic voltammetric studies of the reaction mixture were performed using G-Ch electrodes (0.5 x 3 cm) and Ag/AgCl reference electrode. 2-nitroaniline (1 mmol) was chosen as the substrate in order to analyze the overall behaviour of the nitro reduction process. Voltammetric studies were performed using electrochemical workstation (CH instrument, Model: CH1660D) at a scan rate of 50 mV/s in 3:1 quaternary ammonium chloride and acetic acid mixture as the electrolytic medium. Total volume of the electrolytic solution was 8 ml.

4.4. Procedure for the selective nitro reduction

Due to its reasonable rigidity and resistance to deformation in organic solvent, we selected 1g graphite powder impregnated chitosan HI (1g graphite: 1g chitosan: 800 mg HI) sheet as the electrodes. The electrode was taken as a rectangle with dimensions of 2 cm width and 5 cm height. The weight of the rectangle film was around 650 mg-700 mg.

In a typical experiment, the electrolytic cell is charged with nitro compound (3 mmol), MeOH (30 ml) and 3: 1 tetrabutyl ammonium chloride (TBAC) and acetic acid mixture as electrolyte (40 ml). During synthesis, TBAC acted as a supportive electrolyte. The best agents for a significant dissolution of the reactants were TBAC, AcOH and MeOH in combination. The modified electrodes were immersed in the reaction mixture and a constant voltage (5V) was applied for 8 h. During the reaction the colour of the solution turns brown, and the colour deepens as the reaction progressed. In order to assure sufficient current flow to convert the reaction intermediates into amines, we conducted the reaction for a period of 8 h. After completion of the reaction, as identified by the TLC, the reaction mixture was evaporated, and aniline was separated by acid-base treatment and then purified by column chromatography using alumina.

To compare the efficiency of graphite impregnated chitosan electrode with that of pure graphite electrode, we conducted the reduction of various nitro compounds using graphite electrode (1.5 cm diameter and 5 cm height) in the same electrolytic conditions.

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