

An electrochemical technique for the reduction of aromatic nitro compounds

M. NOEL, P. N. ANANTHARAMAN, H. V. K. UDUPA

Central Electrochemical Research Institute, Karaikudi 623006, India

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A preparative technique for the electroreduction of aromatic nitro compounds using a copper cathode, a lead anode and a porous pot diaphragm with 30–40% H₂SO₄ as the anolyte and 30–40% H₂SO₄ containing 2–3% Ti(SO₄)₂ as the catholyte is reported. Nitrobenzene, dinitrobenzenes, nitrotoluenes, phenols, phenetoles and nitrochlorobenzenes have been reduced by this method. Slightly modified techniques were employed for some compounds such as 2-nitro-*m*-xylene. The results of some pilot plant studies are also reported. The studies indicate that on smaller scales this technique may be competitive with metal/acid systems with the additional advantage of less pollution problems.

1. Introduction

Aromatic nitro compounds are reduced to their corresponding amines by catalytic hydrogenation on very large scales and by metal/acid systems on medium and small scales [1]. The higher temperatures and pressures, and high purity catalysts required in the first process restricts its utility to very large scale operations. The latter method is more widely used at present. It involves the use of high purity metal powders which are becoming very costly. A more serious objection, however, is the problem of handling large quantities of metallic sludges. If the electricity which goes into the production of the metal powders could be used immediately as the reducing agent, it would result in the saving of energy and materials. An electrochemical method would also be pollution-free.

Direct electrochemical reduction of aromatic nitro compounds can result in various products such as nitroso, hydroxylamine, azoxy, azo and hydrazo compounds. With copper cathodes in an HCl medium under well stirred conditions, good yields of amines could be obtained for a few compounds such as *m*-nitro-toluene [2]. Using this method, as the amount of nitro compound added was increased the current efficiency was found to decrease (Table 1). This may be due to a hydrogen evolution reaction enhanced by the proton carrying capacity of the amines formed. Moreover, this

method was not satisfactory for many other nitro compounds. The immiscibility of many nitro compounds in aqueous media was considered to be the cause. Hence attempts were made to use various redox systems in the cell to act as catalysts in the reduction of aromatic nitro compounds.

Titanous salts have been shown to be very good reducing agents for aromatic nitro, nitroso and hydroxylamine compounds [3]. In fact this method is being used for the analytical estimation of aromatic nitro compounds. Using titanous sulphate as an addition agent resulted in very good yields of amines. The electroreduction of nitrobenzene to aniline was reported as early as 1972 [4]. Since then a number of compounds have been successfully reduced by this method. A few modifications to the general technique have been made for a few compounds. Some processes have been studied at pilot plant scale. These are the main contents of the present paper.

2. Optimization studies

2.1. Approach

The optimization studies were carried out at 5–30 A scales. In the selection of the parameters such as cathode current density and temperature, linear optimization was assumed, i.e. each factor was considered to affect the process independently.

The electrolysis was carried out under galvano-

Table 1. Effect of depolarizer concentration on the electroreduction efficiency of *m*-nitrotoluene
 Conditions: Cathode, cylindrical Cu; Catholyte, 10% H_2SO_4 containing 0.5% $CuSO_4 \cdot 5H_2O$; Current density, $15 A dm^{-2}$; Temperature, $70-80^\circ C$; Anolyte, 10 H_2SO_4 ; Anode, Pb

No.	Depolarizer ratio	Current efficiency (%)	
		Rotating cathode	Stationary cathode
1	1:50	—	42.0
2	2:50	—	43.6
3	3:50	53.2	41.8
4	4:50	63.0	38.3
5	5:50	90.0	24.2
6	6:50	64.7	—
7	7:50	60.2	—

static conditions using 10% more current than theoretically required. The product amine was then isolated using the same technique for each compound. The yield and current efficiencies reported are based on the amount recovered from the catholyte rather than the amount estimated to be in solution after the electrolysis. From these studies the optimal conditions were chosen. Typical experimental results for the electroreduction of *m*-nitrotoluene are presented in Table 2.

2.2. Compounds studied

The compounds studied were based on their industrial utility rather than on their mechanistic

importance. However, a host of compounds were studied to make a general analysis possible. Table 3 lists the compounds studied with the typical experimental conditions used and the results. They include nitrobenzene, dinitrobenzene, nitrotoluenes, phenols, xylene, benzoic acid, sulphonic acid and even a stilbene derivative. The important parameters which control the efficiency of the process are discussed below.

2.3. Cathode material

Among the cathode materials studied, a copper cathode gives a maximum yield of amines from the reduction of aromatic nitro compounds. Copper may also be used to construct the cell. In the reduction of nitrobenzene, a copper cathode was shown to give the best yields. In the reduction of other nitro compounds, also, no side products were obtained.

2.4. Electrolyte and anode

In earlier studies on the electroreduction of aromatic nitro compounds, HCl was generally used as the electrolyte. In this process, however, the anodic reaction is the evolution of chlorine. This results in a pollution problem and anode dissolution. Hence attempts were made to conduct the electrolysis in H_2SO_4 . Pb or Pb-Ag alloy could be used as the anode material which showed good stability. The anodic reaction results only in oxygen evolution.

Table 2. Electroreduction of *m*-nitrotoluene
 Conditions: Cathode, cylindrical Cu vessel $1.4 dm^2$; Anode, lead; Catholyte, $200 cm^3$ 35% H_2SO_4 containing 2.4% $Ti(SO_4)_2$ and 0.1% $CuSO_4 \cdot 5H_2O$; Anolyte, $50 cm^3$ 35% H_2SO_4 ; Volume of *m*-nitro-toluene, $30 cm^3$

Experiment No.	Current density ($A dm^{-2}$)	Temperature ($^\circ C$)	Cell voltage (V)	Estimated yield (%)	Current efficiency (%)
1*	5.0	45-50	5.2	58.5	56.0
2	5.0	45-50	4.6	97.4	86.1
3	7.5	45-50	4.7	94.0	83.3
4	10.0	45-50	4.9	86.1	74.6
5	5.0	55-60	5.0	66.7	61.6
6†	5.0	45-50	4.4	98.3	87.4

* Electroreduction without titanous sulphate.

† Electroreduction with 0.01% CTAB as an addition agent.

Table 3. Electroreduction of aromatic nitrocompounds with Ti^{3+}/Ti^{4+}

General experimental conditions: Catholyte, 30–40% H_2SO_4 containing 3% titanous sulphate; Anolyte, 30–40% H_2SO_4 ; Cathode, stationary Cu with stirring; Anode, Pb; Current density, 5–20 $A\ dm^{-2}$; Temperature, 45–80° C; Cell voltage, 3–4.5 V; Diaphragm, ceramic porous pot

Sample No.	Starting compound	Product	Cell current (A)	Current efficiency (%)	Yield (%)	Energy consumption ($kWh\ kg^{-1}$)	Reference
1	Nitrobenzene	Aniline	18	95.0	95.0	12.4	[4]
2	<i>o</i> -Nitrophenol	<i>o</i> -Aminophenol	30	97.0	97.0	7.7	[5, 6]
3	<i>p</i> -Nitrophenol	<i>p</i> -Aminophenol	20	92.0	98.0	9.5	[8, 9]
4	<i>m</i> -Nitrophenetole	<i>p</i> -Phenetidine	100	90.5	81.0	12.0	[10]
5	<i>m</i> -Dinitrobenzene	<i>m</i> -Phenylenediamine	30	98.7	99.0	18.7	[11, 12]
6	2,4-Dinitrotoluene	2,4-Diaminotoluene	30	85.0	97.0	18.6	[13, 14]
7	<i>p</i> -Nitrochlorobenzene	<i>p</i> -Chloraniline	20	82.6	98.2	7.3	[15, 16]
8	<i>o</i> -Nitrotoluene	<i>o</i> -Toluidine	25	70.0	80.0	7.0	[17]
9	<i>p</i> -Nitrotoluene	<i>p</i> -Toluidine	150	80.0	90.0	5.5	[18]
10	<i>m</i> -Nitrotoluene	<i>m</i> -Toluidine	20	69.8	74.9	13.7	[19, 20]
11	<i>p</i> -Nitrobenzoic acid	<i>p</i> -Aminobenzoic acid	25	85.0	93.0	4.0	[21]
12	<i>o</i> -Nitroanisole	<i>o</i> -Anisidine	20	70.0	67.0	7.6	[15, 16]
13	<i>m</i> -Nitrobenzene sulphonic acid	Metanilic acid	6	76.3	87.5	6.8	[22]
14	2-Nitro- <i>m</i> -xylene	<i>m</i> -Xylidine	10	73.0	79.0	8.2	[23]
15	2,4-Dinitrophenol	2,4-Diaminophenol	15	81.0	87.7	8.9	[24]
16	4,4-Dinitrostilbene-2,2'-disulphonic acid	4,4'-Diaminostilbene 2,2'-Disulphonic acid	3	86.0	91.9	3.9	[25, 26]

In general it was observed that a higher acid concentration favours the para transformation of any hydroxylamine formed. However, when titanous sulphate is used as an addition agent, lower acid concentration results in the hydrolysis of titanous sulphate. The catholyte becomes a milky white semi-solid material. At higher acid concentrations, however, titanous sulphate solution is quite stable. Since the chemical reaction between titanous salts and the hydroxylamine is sufficiently faster than para transformation, such side products were not observed. In general the acid concentration ranged from 30 to 40% H_2SO_4 .

2.5. Addition agents

When a redox system is used as an addition agent to reduce an organic compound, the following criteria should be considered.

(a) The reduction potential of the species of the redox system must be more positive when compared with the reduction potential of the organic compound. This criteria may be fulfilled by almost all inorganic redox systems.

(b) The reduced species of the redox system should be unstable when compared to the oxidized species. In other words the reduced species should be an active reducing agent. This condition is fulfilled by Ti^{3+}/Ti^{4+} , Sn^{2+}/Sn^{4+} , Fe^{2+}/Fe^{3+} and a few other systems.

(c) The chemical reaction rate between the reduced species and the organic compound should be very fast and it should result in the desired product. Ferrous sulphate reduces nitro compounds slower than titanous sulphate. Stannous, thalous and other similar salts reduce nitro compounds faster and hydroxylamines slower thus resulting in para transformation. Hence, among the redox systems available, titanous sulphate is the best for reducing the nitro compounds to amines. Experiments carried out with various redox systems also confirmed the above conclusion.

Among the various concentrations of titanous sulphate considered, a concentration range of 2–3% was found to give good results. Lower concentrations result in lower current efficiencies. Higher concentrations do not result in any higher current efficiency.

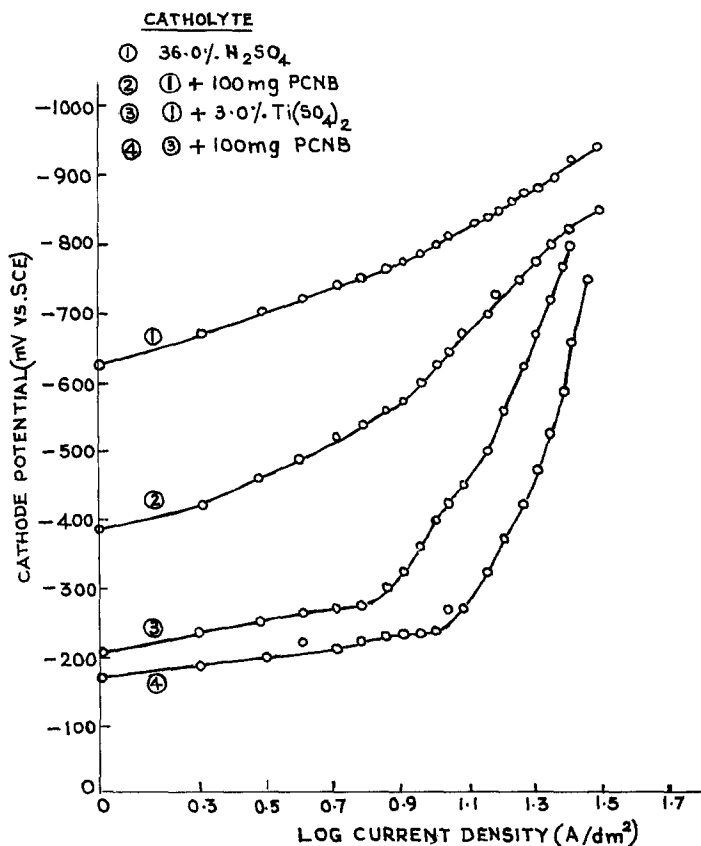


Fig. 1. Galvanostatic polarization curves for *p*-chloronitrobenzene at $70 \pm 1^\circ \text{C}$ using a Cu cathode.

2.6. Temperature of electrolysis

In choosing the temperature three considerations should be made.

(a) The chemical reaction rate should be fast. In general titanous sulphate reduces nitro compounds at a sufficiently fast rate at about $50\text{--}60^\circ \text{C}$. In certain cases, e.g. *m*-nitrotoluene, a higher temperature favours hydrogen evolution thereby reducing current efficiency.

(b) The nitro compounds should be sufficiently miscible with the catholyte. When solid nitro compounds such as *p*-chloronitrobenzene, are reduced the temperature of electrolysis is $75\text{--}80^\circ \text{C}$ which is very close to its melting point (83°C). However, if the solid nitro compounds are slightly soluble in water, a lower temperature may be employed. Nitrophenols, for example, are reduced at much lower temperatures when compared to their melting points.

(c) The nitro compounds should not be lost due to volatility. This consideration applies especially

to liquid nitro compounds. Temperatures in such cases are generally kept below 60°C . In addition, reflux condensers are used with the cell to collect volatile material.

2.7. Cathode current density

The optimum cathode current density was arrived at by carrying out experiments at various current densities for each compound. However, in general it was observed that 10 A dm^{-2} is the optimum current density with stationary cathodes. With rotating cathodes slightly higher current densities could be employed. However, this advantage is outweighed by the simpler cell design and higher cathode area available per unit volume in stationary cathode cells.

Galvanostatic polarization curves were traced for each compound to confirm the experimental observations. Typical polarization data are presented in Fig. 1 for the reduction of *p*-chloronitrobenzene. It may be observed that the cathode

Table 4. Re-use of catholyte in the electroreduction of *p*-nitrophenol

Conditions: Cathode, Cu; Catholyte, 35% H_2SO_4 + 2.4% $Ti(SO_4)_2$; Anolyte, 35% H_2SO_4 ; Cathode current density, 10 A dm^{-2} ; Temperature, 50–55° C; Cooling temperature after electrolysis, 30° C

Electrolysis No.	Wt of <i>p</i> -nitrophenol added (g)	Number of amp hours passed	Wt of <i>p</i> -Aminophenol sulphate obtained (g)
1	450.0	516.0	288.0
2	175.0	200.0	216.0
3	150.0	175.0	130.0
4	150.0	162.5	125.0
5	125.0	155.0	160.0
6	125.0	155.0	150.0
7	200.0	262.5	210.0
<i>p</i> -Aminophenol sulphate estimated in solution:			202.0
∴ Overall yield			96.6%

potential shifts sharply to more negative values at higher current densities indicating hydrogen evolution. This figure also indicates the depolarization of nitro reduction by titanous sulphate addition, i.e. the catalytic nature of the electroreduction process. Polarography also indicates the catalytic influence of titanous sulphate under similar conditions.

2.8. Product build-up and catholyte re-use

The electroreduction of nitro compounds in acidic medium has an additional advantage. The amine product formed is fixed as its sulphate in solution. The nitro compound is generally added in smaller portions as reduction continues. When the amine sulphate reaches a limiting concentration, it separates out as a solid sulphate at lower temperatures. This property is made use of to isolate the product as solid sulphate and to re-use the catholyte. Before re-use the catholyte acid concentration is adjusted. In the case of the production of *p*-aminophenol from *p*-nitrophenol the catholyte has been re-used seven times (Table 4). In general the catholyte may be re-used ten times for all nitro compounds.

2.9. Product recovery

In some cases the amine sulphate product may be used as it is. For example, 2,4-diaminophenol sulphate may be used as such in photographic development. Some sulphates such as aniline

sulphate may be converted to sulphanilic acid by direct heat treatment.

When the free base is required, neutralization by bicarbonate liberates amine from a solution of amine sulphate in water. If the product is a solid it can be filtered from the solution. If the product is a liquid, it may be recovered by steam distillation.

The products obtained by this method are extremely pure and are free from metallic ions.

3. Some variations in the technique

The general experimental technique employed is described in the previous section. Some nitro compounds are not reduced fully under such conditions. Accordingly some slight modifications were attempted to the general technique.

3.1. *o*-nitroanisole

In this case when the general technique is employed, a very low current efficiency was noted. However, along with the required product of *o*-anisidine, *o*-aminophenol was also obtained. This was supposed to be due to the acid catalysed hydrolysis of *o*-nitroanisole. Hence *o*-nitroanisole was added in very small amounts, always keeping an excess of titanous sulphate in the catholyte. A slightly lower temperature was also employed. These modifications brought about an improvement in the current efficiency.

Table 5. Electroreduction of 2-nitro-*m*-xylene to 2-amino-*m*-xylene

Conditions: Catholyte, 35% H_2SO_4 (w/v) + 2.4% $Ti(SO_4)_2$; Cathode, Cu; Anolyte, 35% H_2SO_4 ; Anode, Pb; Diaphragm, ceramic porous pot

Experiment No.	Type of cathode*	Current density ($A\ dm^{-2}$)	Cell voltage (V)	Temperature range ($^{\circ}C$)	Concentration of CTAB (% w/v)	Recovery yield (%)	Current efficiency (%)
1	R	17.4	6.0	50-60	—	17.3	10.4
2	S	4.4	5.4	50-60	—	34.3	18.4
3	R	5.8	4.2	50-50	—	38.0	19.0
4 [†]	S	4.4	6.2	50-60	—	35.5	15.2
5	S	4.4	4.0	60-70	0.1	54.7	46.0
6	S	4.4	4.0	50-60	0.05	71.0	70.3
7	S	5.8	4.2	50-60	0.01	79.0	72.9
8	R	5.8	3.8	40-50	0.01	64.8	58.9
9	S	10.7	4.4	50-60	0.01	43.4	23.9
10	S	5.8	4.0	60-70	0.01	79.3	73.1

* Stationary (S) or Rotating (R).

[†] System without titanic sulphate.

3.2. 2-nitro-*m*-xylene

When the general technique was employed a very poor yield was again obtained. But after electrolysis the major portion of 2-nitro-*m*-xylene still remained as a separate phase totally immiscible in

water. Hence to improve the miscibility a cationic surfactant, cetyltrimethylammonium bromide was added. This improved the current efficiency greatly (Table 5). Galvanostatic polarization studies (Fig. 2) indicate that the cetyltrimethylammonium bromide (CTAB) retards the hydrogen

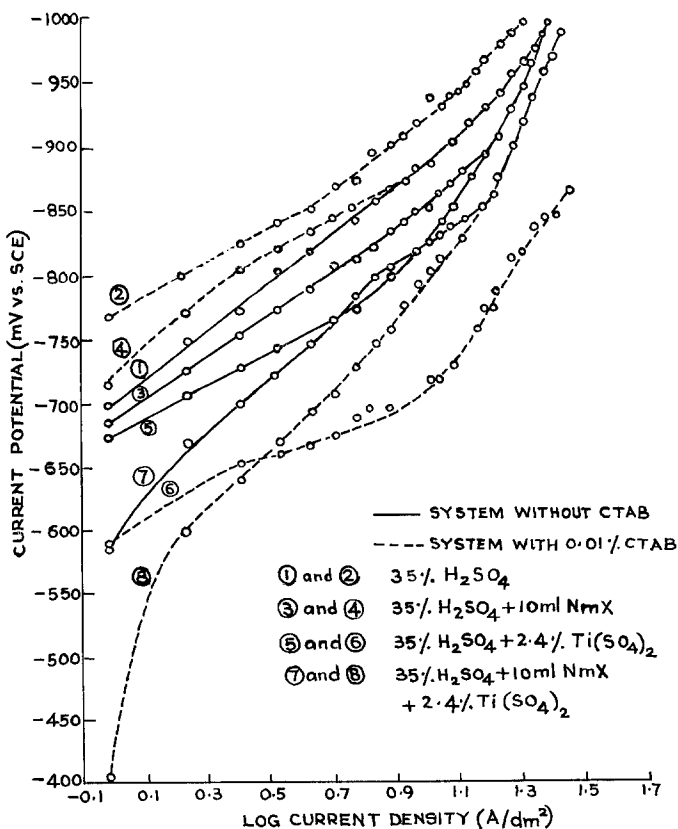


Fig. 2. Galvanostatic polarization curves for 2-nitro-*m*-xylene using a Cu cathode with and without cetyltrimethylammonium bromide (CTAB) at $50 \pm 2^{\circ}C$.

evolution reaction and direct electroreduction of nitro compound, and enhances the titanous sulphate reduction. Hence in addition to improving the miscibility of the nitro compounds CTAB also influences the electrode reactions favourably [23].

3.3. 4,4'-dinitro stilbene-2,2'-disulphonic acid

The reduced product of this compound finds extensive application in the optical whitener industry. When the general technique is employed, even in the presence of titanous sulphate, direct electroreduction of nitro compounds is observed. The catholyte shows different colours during electrolysis. However, it was noticed that both the starting material and the product are insoluble in highly acidic media.

Hence a two-stage indirect electroreduction was developed in this case. Highly concentrated titanous sulphate solution is prepared in the electrochemical cell using a Cu or Pb cathode and a Pb anode with ceramic porous pot or blue asbestos fibre as the diaphragm. This solution is used to reduce the nitro compound outside the cell. The product is filtered and the electrolyte is re-used as in the previous cases [25].

4. Pilot plant studies

Using the optimized conditions arrived at from the bench-scale experiments, pilot plant experiments have been completed for at least four compounds. Other work is in progress.

The experiments were carried out using 300–1000 A scale unit cells. The cells were made of Cu. Cylindrical and elliptical cell designs were tested. The cells may contain Cu baffles arranged symmetrically around the inner part of the vessel in order to increase the cathode area and enable a uniform current distribution. Ceramic porous pots were used for the diaphragm with lead anodes.

The detailed cell design and pilot plant scale experimental data for the reduction of nitrobenzene to aniline are reported elsewhere [27]. The details of other studies will be reported later. However, typical results obtained in the reduction of a few compounds are reported in Table 6.

5. Conclusions

The economic feasibility of the process has been estimated for a few nitro compounds which were studied at the pilot plant level. These considerations indicate that even on a small scale of 30–60 tons per annum production capacity this technology may be utilized successfully. At these scales, although capital investment is slightly higher, this process competes successfully with the usual metal/acid method employed in small scale work. It is necessary to note that the general thinking that the electrochemical industry requires a large capital investment is very misleading. It has been pointed out frequently that in the electro-organic industry only around 30% of the capital investment is due to the electrochemical process itself. Other investments are common to both the chemical and electrochemical industries.

Hence, it may be hoped that the new electrochemical technique developed for the reduction of aromatic nitro compounds will be used widely in the near future as a pollution free technique. It may be noted here that a few Indian manufacturers have already started employing this technique.

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Table 6. Results of pilot plant scale electroreduction of aromatic nitro compounds

No.	Starting material	Product	Cell current (A)	Current efficiency (%)	Yield (%)	Energy consumption (kWh kg ⁻¹)
1	Nitrobenzene	Aniline	1000	83.8	97.0	12.4
2	<i>p</i> -Nitrophenol	<i>p</i> -Aminophenol	1000	92.0	98.0	9.5

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