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Electroreduction of nitrobenzene to *p*-aminophenol using voltammetric and semipilot scale preparative electrolysis techniques

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Abstract

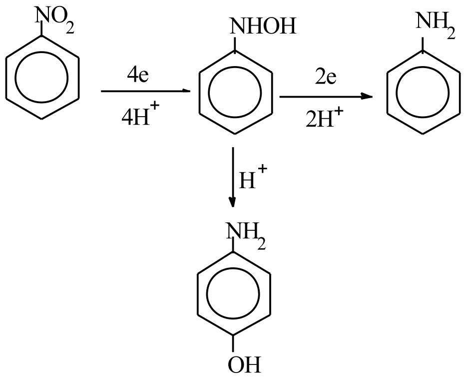
This paper describes an investigation of the reduction of nitrobenzene to *p*-aminophenol by the use of CV, RDE and preparative electrolysis with Cu and Cu(Hg) electrodes. The preparative electrolyses of nitrobenzene were carried out at controlled current and controlled potential conditions using copper and amalgamated copper using a new semipilot (laboratory) scale system in the absence of an organic cosolvent. The effects of redox reagents and the concentration of nitrobenzene in catholyte added to the medium were also examined. The best results were obtained with 2.3% $BiCl_3$ at nitrobenzene concentration of 0.144 g cm^{-3} catholyte. The most suitable electrode material was found to be amalgamated copper and the reduction of nitrobenzene to *p*-aminophenol was found to follow an ECE mechanism.

1. Introduction

The electrolytic reduction of nitrobenzene to *p*-aminophenol was first carried out by Gattermann using a Pt cathode, ambient temperature and highly acidic reaction medium [1,2] where nitrobenzene (I) was converted into *p*-aminophenol (III) by the rearrangement of the phenylhydroxylamine (II) intermediate as follows:

$$\underset{(I)}{C_6H_5\text{–}NO_2} \rightarrow \underset{(II)}{(C_6H_5\text{–}NHOH)} \rightarrow \underset{(III)}{NH_2\text{–}C_6H_4\text{–}OH(p)} \qquad (1)$$

The Gattermann method was modified by Darmstadler [3] and Thatcher [4], and used by Eastman Kodak [5] for the large-scale production of *p*-aminophenol. Although this method was more popular than the chemical method it was not as commercially promising as the method developed by Dey et al. [6]. These workers developed a new method using cheap cathode materials such as copper, monel and nickel and H_2SO_4 at very low concentration. Wilson and Udupa [7] obtained high current densities by rotating the electrodes at very high speeds. Fleishmann et al. [8] proposed the following reaction scheme:



(2)

After these studies, much attention has been given to the effects of temperature, H_2SO_4 concentration, cathode material, type of diaphragm and the reducing agent employed, on the reduction of nitrophenol to the *p*-aminophenol [9–17].

Here, we report the effects of cathode material, electrode rotation speed, the concentration of the electroactive compounds and additives such as $SnCl_2$ and $BiCl_3$ on the yield of *p*-aminophenol.

2. Experimental details

Copper (Johnson Mathey, 99.9% with dia. 1 mm), graphite (IR grade with dia. 5 mm) amalgamated copper and copper-coated copper electrodes were mounted in Teflon rods filled with an acryl (Merck) polymer. The amalgamation and bismuth coating of copper electrodes were carried out as described in the literature [15, 18, 19].

The supporting electrolyte used in the CV and RDE studies was 2 M H_2SO_4 in a solution of 50% organic solvent/50% water (v/v).

All the voltammetric studies were carried out with a Wenking Lb75L laboratory model potentiostat, a Wenking model V5G72 wave generator, a Yokogowa Technicorder 3077 type recorder and a 1KA-WERK TYP RM 18 rotating disc electrode using a standard H-type cell. The counter electrode was a helical Pt wire in the CV and a cylindrical Pt cage placed around the working electrode in the RDE experiments; the reference electrode was the saturated calomel electrode (SCE).

Except for the electrolytically coated electrodes, all the electrodes used in the voltammetric studies were first subjected to mechanical treatment using rough and then fine emery paper, and then kept in trichloroethylene to remove any grease from the surface. They were shaken in doubly distilled water for a few minutes and wiped with drying paper before being placed into the electrolytic cell. The electrolytic cell was purged with oxygen-free nitrogen for thirty minutes prior to the electrochemical experiments. It was observed that the reduction peak currents decreased with the number of scans to an increasing extent when the electrodes had not been subjected to this pretreatment. The curves obtained with the pretreated electrodes were found to be highly reproducible.

All the reagents used in the experiments were analytical grade (Merck) and used without further purification. All the solutions were prepared with double distilled water.

The preparative electrolyses were carried out using the system depicted in Figure 1. The cathode was a Cu or Cu(Hg) plate with the dimensions of 13 cm × 9 cm × 0.1 cm rolled into a cylindrical form. The anode compartment was a ceramic porous cup with dimension 16 cm × 2.8 cm × 0.4 cm. The capacities of the anode and cathode compartments were 200 and 120 cm^3. The anolyte was 20% H_2SO_4 and the catholyte was 20% H_2SO_4 containing nitrobenzene at various concentrations.

The catholyte was transferred to the cell using a peristaltic pump (Prominent Electronics) with an output rate of 8.9 $dm^3\ h^{-1}$. The solution was purged with purified nitrogen for two hours with constant stirring. The preparative electrolyses were carried out by circulating the electroactive compound over the surface of the cathode without using organic cosolvent. The use of organic cosolvent proves to be a problem when high temperatures are employed. The system used here is a novel one and avoids these problems. The circulation of the catholyte also reduces the cost of the raw material, namely sulphuric acid. The catholyte temperature was kept constant at 70–75 °C using a thermostat. The charge passing through the circuit in constant potential electrolyses was monitored with an electronic integrator (Sistem Teknik, model 274). The constant current electrolyses were carried out using a 250V/25A power source (Deniz Elektronik ve Makine Sanayi Tic.).

3. Results and discussion

3.1. *Cyclic voltammetric investigation*

The cyclic voltammetric curves obtained with Cu are shown in Figure 2. The curves show a single irreversible peak at all scan rates; the peak shifts in the negative direction as the scan rate is increased.

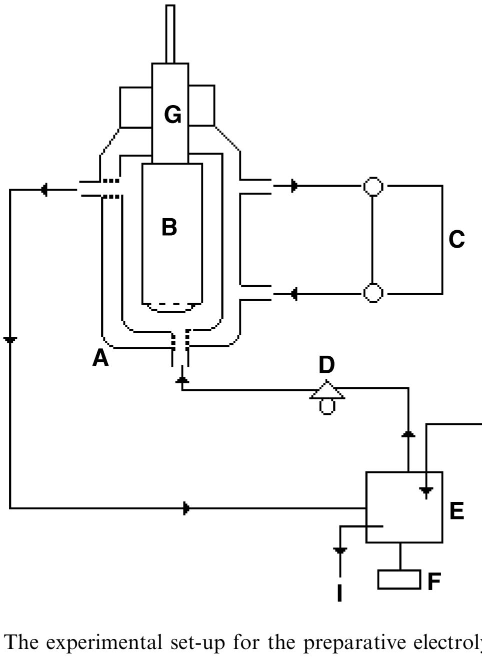


Fig. 1. The experimental set-up for the preparative electrolyses. Key: (A) electrolytic cell, (B) cathode, (C) thermostat, (D) peristaltic pump, (E) electrolyte reservoir, (F) magnetic stirrer with a heater, (G) anode compartment, (H) N_2 inlet, (I) N_2 outlet.

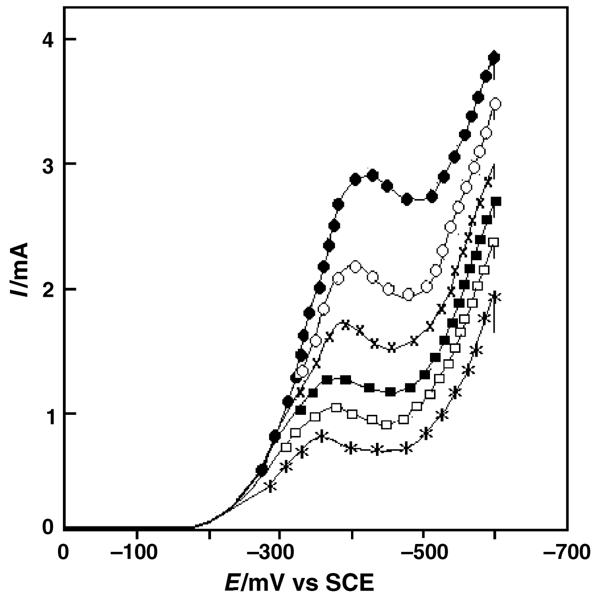


Fig. 2. Cyclic voltammograms of nitrobenzene (3.0 mM) in 2.0 M H_2SO_4 containing 50% water – 50% 2-propanol (v/v) on Cu at: (∗) 10, (□) 20, (■) 40, (×) 80, (○) 160 and (●) 320 mV s^{-1}.

Table 1. Cyclic voltammetric results of NB (3 mM) on graphite in a medium of 2 M H_2SO_4 in 50% water – 50% 2-propanol (v/v)

v/mV s^{-1}	$-E_p$/mV	$-E_{p/2}$/mV	I_p/mA	$I_p/v^{1/2}$ C	$E_{1/2}$/mV	αn_a	$E_p - E_{p/2}$/mV
10	320	245	1.686	178	285	0.640	75
20	330	250	2.033	152	290	0.600	80
40	335	255	2.772	146	295	0.533	90
80	350	260	3.788	141	305	0.533	90
160	365	260	5.036	133	315	0.533	90
320	380	260	7.346	137	320	0.384	125

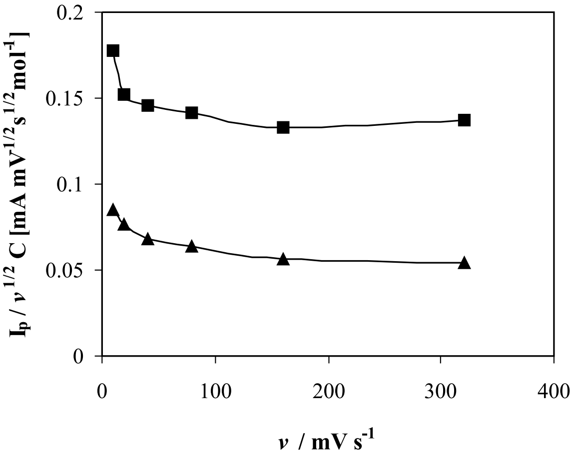


Fig. 3. Change of current function with scan rate on Cu (▲) and graphite (■).

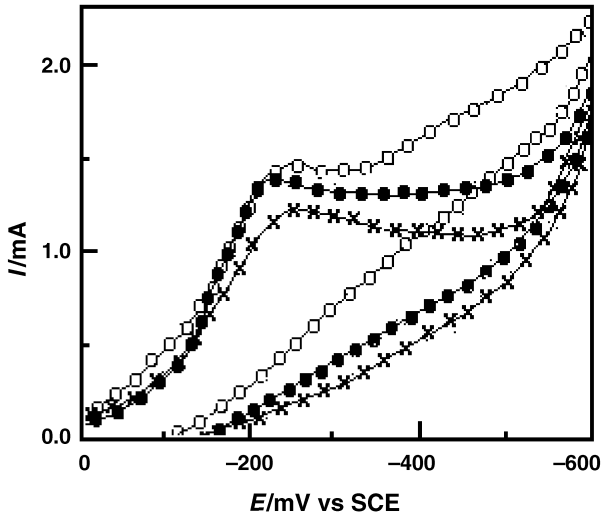


Fig. 4. Cyclic voltammograms of nitrobenzene (2.0 mM) on coated Cu at a scan rate of 40 mV s^{-1} (×) Bi coated Cu; (●) Cu coated Cu; (□) amalgamated Cu.

Table 1 lists the cyclic voltammetric data obtained with graphite under the same conditions employed for Cu. Figure 2 and Table 1 show that the results obtained with both these electrodes are similar, except for a more negative reduction potential, higher current and current function values and lower charge transfer coefficient (αn_a) with graphite.

The plot of I_p against $v^{1/2}$ gave a straight line, while the graph of current function against the scan rate was a concave curve decreasing towards the higher scan rates for both copper and graphite (Figure 3).

In another study with copper the effect of the concentration of the nitrobenzene in the electrolyte was investigated.

Figure 4 gives the cyclic voltammograms obtained with coated electrodes. The peak potential shift towards more positive values and the current and hydrogen overvoltage is much higher compared with those obtained with Cu and graphite. The reduction peak of nitrobenzene to phenylhydroxylamine appears at −225 mV with Cu/Cu and Cu(Hg) and −250 mV with Cu/Bi. The rate of hydrogen evolution reaction is highest on Cu(Hg) and almost the same on Cu/Cu and Cu/Bi.

The effect of salts such as $SnCl_2$ and $BiCl_3$ as reducing agents on the reduction of nitrobenzene on Cu and graphite was also investigated. The data obtained by the addition of these salts into the reaction media using copper and graphite are given in Table 2. The highest current efficiency was obtained with $BiCl_3$. It appears that the peak potentials in media without reducing agent shift to more positive values and hydrogen evolution takes place at more negative potentials.

Table 2. Effect of redox compounds on the reduction of nitrobenzene (2 mM) in 2 M H_2SO_4 containing 50% water – 50% 2-propanol (v/v) on copper and graphite at a scan rate of 40 mV s^{-1}

Redox compounds	Electrodes	$-E_p$/mV	I_p/mA	$-E_H$/mV
$SnCl_2$	Cu	325	1.35	520
$BiCl_3$	Cu	325	1.50	520
–	Cu	375	1.28	500
$SnCl_2$	Graphite	210	3.00	600
$BiCl_3$	Graphite	210	3.30	600
–	Graphite	335	2.80	580

The current increases linearly with scan rate and nitrobenzene concentration with Cu and graphite indicating that the reduction process is diffusion-controlled. The current function does not correlate with the scan rate, which shows that the electron transfer is preceded by a chemical reaction. Otherwise, these two parameters would be expected to correlate linearly [22]. The parameter $(\mathrm{d}E_p/2)/\,\mathrm{d}\log v$ was found to be 35–45 mV which complies well with the criterion of $(\mathrm{d}E_p/2)/\,\mathrm{d}\log v = 30/\alpha n_a$ (mV) for ECE reactions [23].

The charge transfer coefficient (αn_a) for the irreversible system was calculated using

$$E_p - E_{p/2} = 48/(\alpha n_a) \qquad (3)$$

The (αn_a) values at scan rates ranging between 10 mV s^{-1} and 320 mV s^{-1} were found to be 0.640–0.800 on Cu and 0.384–0.640 on graphite. The fact that the value of charge transfer coefficient is lower on graphite compared to one on copper is probably due to the stronger adsorption and blockage of the products on graphite.

The transfer coefficients decrease and the E_p values shift to more negative potentials, as is known to be the general case for irreversible reactions [25]. This was observed for both electrodes.

The fact that there was no anodic peak after reversal from the hydrogen evolution potential shows that the total reduction process and the chemical reaction are irreversible and the product of chemical reaction is electrochemically inactive. In previous reports on the same reaction it was pointed out that the total reduction and the chemical reaction was totally irreversible and the rate of chemical reaction was 100 times higher than that of the electrochemical reaction [16].

The reduction of phenylhydroxylamine to aniline by taking an electron from the cathode surface and its conversion to *p*-Ap though a chemical rearrangement reaction in the solution is competitive [9, 16, 17, 25]. Therefore the higher the rate of the chemical reaction the higher the yield of *p*-aminophenol.

Studies carried out in this area show that the reduction of phenylhydroxylamine into aniline takes place in parallel with hydrogen evolution [6]. Therefore, the yield of *p*-aminophenol is expected to be higher on metals having a higher hydrogen overvoltage. Accordingly, graphite, which has a higher hydrogen evolution potential than copper, is a more suitable cathode material for *p*-Ap synthesis.

The fact that hydrogen overvoltage and current are higher on Cu(Hg) than on Cu/Cu and Cu/Bi can be explained on the basis of a stronger adsorption of *p*-Ap on the amalgamated surface. That is why Cu(Hg) appears to be a more suitable electrode material in the synthesis of *p*-Ap.

The addition of redox compounds such as $SnCl_2$, $TiCl_3$ and $BiCl_3$ has a synergistic effect on the yield of *p*-Ap as indicated in previous studies and it was claimed that these ions were capable of reducing the nitro compounds in the solution [9, 12]. This was also observed in our study and the addition of $SnCl_2$ and $BiCl_3$ to the reaction medium changed the shape of the voltammograms obtained with both electrodes employed (Cu and graphite) and increased the hydrogen overvoltage and the current densities as mentioned previously.

3.2. *Rotating disc electrode results*

The RDE studies were carried out with Cu and Cu(Hg) at a rotation speed of 200–2000 rpm (Figures 5 and 6). The voltammograms obtained with both electrodes are similar in appearance. However, the current and hydrogen overvoltage on Cu are much lower than on Cu(Hg). The current increases with rotation speed and the peaks become broader as the rotation speed is increased. The plots of $I/\omega^{1/2}C$ against $\omega^{1/2}$ and $1/I_p$ against $1/\omega^{1/2}$ gave a curve and a straight line, respectively, which shows that reaction is ECE type and diffusion controlled.

The kinematic viscosity of the solution under the experimental conditions was 0.0435 $cm^2\ s^{-1}$. The heterogeneous rate constant was obtained in the usual manner from the intercepts of the linear $1/I$ against $1/\omega^{1/2}$ plot [26].

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{0.62\, nFAC_0^{\infty} D_0^{2/3} \nu^{-1/6} \omega^{1/2}} \qquad (4)$$

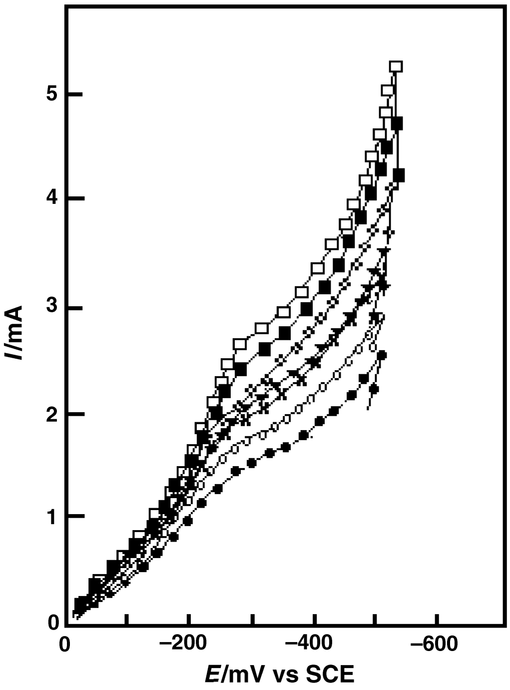


Fig. 5. RDE curves of nitrobenzene (3.0 mM) in 2.0 M H_2SO_4 containing 50% water – 50% 2-propanol (v/v) on Cu at: (●) 200, (○) 400, (×) 600, (▼) 1000, (✣) 1200, (■) 1600 and (□) 2000 rpm keeping the scan rate at 40 mV s^{-1}.

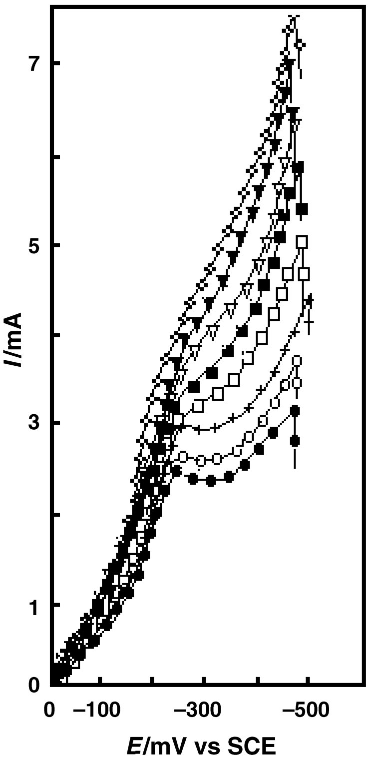


Fig. 6. RDE curves of nitrobenzene (3.0 mM) in 2.0 M H_2SO_4 containing 50% water – 50% 2-propanol (v/v) on Cu(Hg) at: (●) 200, (○) 400, (+) 600, (□) 1000, (■) 1200, (▽) 1600, (▼) 1800 and (✣) 2000 rpm keeping the scan rate at 40 mV s^{-1}.

where

$$I_k = nF\vec{k}C_0^\infty \qquad (5)$$

n is the number of electrons transferred, C_0^∞ is the bulk concentration of the reactant, ω is the rotation speed of the electrode, v is the kinematic viscosity of the solution and A is the surface area of the electrode. The diffusion coefficient and the heterogeneous rate constant for nitrobenzene were determined as 5.98×10^{-6} cm^2 s^{-1} and 9.24×10^{-8} cm s^{-1}.

The rotating disc electrode experiments revealed that the number of electrons transferred was 6 at low (200–600 rpm), 4 at medium (600–1200 rpm) and 2 at high rotation speeds above (>1200 rpm) as calculated by the use of the Levich equation. Thus, the most suitable range of rotation speeds in the reduction of nitrobenzene to *p*-Ap was 600–1200 rpm.

The literature indicates that the rotation speed has a marked effect on the yield of *p*-Ap [7, 9, 16]. It was also found that the current function $1/\omega^{1/2}C$ was independent of rotation speed.

The sharp peaks obtained at lower rotation speeds can be explained by the fact that the intermediates remain at the surface of the electrode for a much longer period, which increases their chance of reaction and reconverting to aniline. This makes the total number of electrons transferred correspond to $n_1 + n_2$. The increase in rotation speed apparently increases the rate of phenylhydroxylamine molecules leaving the electrode surface by diffusion, and convection and this leads to a decrease in reaction time for organic molecule reduction. In other words, the amount of phenylhydroxylamine on the surface increases. The reason why the peaks get broader at higher rotation speeds is possibly the result of the fact that the reduction of nitro compounds is continuing while phenylhydroxylamine is leaving the electrode surface to give chemical reaction in the solution. This shows that chemical reaction competes with electrochemical reaction.

3.3. *Preparative electrolyses*

The electrolyses were carried out at constant potential and current conditions using Cu and Cu(Hg) and the effects of the current, redox reagents and the concentration of nitrobenzene in catholyte were investigated. The parameters such as acid concentration and temperature were not separately examined and kept at 20% H_2SO_4 and 75 °C. The same parameters were employed in previous studies [12, 20, 21].

The results obtained in constant potential electrolyses are given in Table 3 which shows that the highest yield of *p*-Ap in preparative electrolyses was obtained with Cu(Hg) at potential controlled conditions which is supported by the cyclic voltammetric and RDE data. The formation of resinous compounds remained low at nitrobenzene concentration less than 0.144 g cm^{-3} and increased at concentrations higher than that. The amount of aniline formed remained constant. The increase in nitrobenzene concentration increases the

Table 3. Results of constant potential electrolyses of nitrobenzene on Cu and Cu(Hg)

Cathodes	$-E$/mV	Product yields				Conversion/%	Selectivity/%		Unreacted NB/mol	Resinous Compounds/g
		p-Ap		AN			*p*-Ap	AN		
		/mol	/%	/mol	/%					
Cu	375	0.160	68.4	0.062	26.4	94.8	72.2	27.8	0.0122	1.05
Cu(Hg)	225	0.180	76.9	0.044	18.8	95.7	80.4	19.6	0.0098	0.92

Catholyte: 20% H_2SO_4 (200 cm^3) + 0.144 g NB/cm^3 catholyte; anolyte: 20% H_2SO_4, anode: graphite; temperature: 75 °C; *Q*: 85 603 C (4 F mol^{-1}).

Table 4. Effect of nitrobenzene concentration in catholyte for electrolyses carried out on Cu at −375 mV (the electrolyses was carried out at the same conditions set in Table 3)

NB /g/catholyte	Q/C (4 F mol^{-1})	Product yields				Conversion /%	Selectivity/%		Unreacted NB/mol	Resinous Compounds/g
		p-Ap		AN			*p*-Ap	AN		
		/mol	/%	/mol	/%					
0.144	85603	0.160	68.40	0.062	26.40	94.80	72.20	27.80	0.0122	1.04
0.300	175992	0.296	60.66	0.160	32.79	93.45	64.91	35.09	0.0320	2.70
0.400	235814	0.375	57.69	0.236	36.31	94.00	61.37	38.63	0.0390	3.20

Table 5. Results of constant current electrolyses of nitrobenzene on Cu and Cu(Hg), cf. Table 3, $i = 5.85$ mA cm^{-2}, $Q = 90\ 312$ C (4 F mol^{-1})

Cathodes	Product yields				Conversion/%	Selectivity/%		Unreacted NB/mol	Resinous Compounds/g
	p-Ap		AN			*p*-Ap	AN		
	/mol	/%	/mol	/%					
Cu	0.097	41.50	0.126	54.00	95.50	43.50	56.50	0.0106	1.90
Cu(Hg)	0.158	67.40	0.070	29.90	97.30	69.30	30.70	0.0065	1.50

Table 6. Effect of redox compounds added to reaction medium in the reduction of nitrobenzene on Cu ($E = -325$ mV) and all other conditions are as same as those listed in Table 3)

Redox compounds	%	Product yields				Conversion/%	Selectivity/%		Unreacted NB/mol (× 10^{-3})
		p-Ap		AN			*p*-Ap	AN	
		/mol	/%	/mol	/%				
$SnCl_2$	1.7	0.100	42.70	0.128	54.70	97.40	43.80	56.20	6.00
$BiCl_3$	1.7	0.130	55.60	0.099	42.30	97.90	56.80	43.20	5.00
$SnCl_2$	2.3	0.168	71.80	0.062	66.50	98.30	73.00	27.00	4.00
$BiCl_3$	2.3	0.175	74.80	0.055	232.90	98.72	75.80	24.20	3.00
$SnCl_2$	5.2	0.112	47.90	0.120	51.30	99.10	55.20	44.80	2.00
$BiCl_3$	5.2	0.115	49.10	0.117	50.00	99.10	49.50	50.50	2.00

chance of nitrobenzene intermediate phenylhydroxylamine giving reaction at the cathode surface. This reaction is promoted as the amount of undissolved nitrobenzene increases.

The *I–Q* graph of potential controlled electrolysis data gave the number of electron as 4.

The effect of the nitrobenzene concentration was also investigated at constant potential (all the other parameters being the same as Table 3) and the results are given in Table 4. Table 5 lists the results obtained from the constant current electrolyses of nitrobenzene Cu and Cu(Hg). The effects of the reducing agent added to the catholyte are given in Table 6. It is observed that the *p*-Ap yield is dependent on the potential employed according to the data presented in Table 3 and Table 4.

Table 6 indicates that the addition of redox compounds to the reaction medium increases the *p*-Ap yield and percentage conversion, which proves that these redox species reduce the nitro compounds in the solution. It was observed that the highest selectivity and product yield of *p*-Ap were obtained when the amount of both redox agents was 2.3% and $BiCl_3$ gave better results compared with $SnCl_2$.

3.3.1. *Separation of the electrolyses product*

The unreacted NB was separated from the reaction medium by steam distillation, purified with ether extraction and dried over $CaCl_2$ after evaporation of ether. The remaining solution was neutralized with NH_4HCO_3 to pH 6–7 and resubjected to steam distillation to separate aniline. Aniline was extracted with ether from the aqueous solution. The solution was then boiled with active carbon, filtered and cooled to 0 °C. The *p*-aminophenol crystals were filtered off, washed with benzene and 1% sodium bisulfite, recystallized from hot water and dried in a vacuum dessicator (mp 188–189 °C lit., [28] mp 189.5–190 °C). The flow chart of the system is depicted in Figure 7.

In conclusion, the highest *p*-Ap yield is obtained by using Cu(Hg), $BiCl_3$ and 0.144 g cm^{-3} catholyte concentration, respectively.

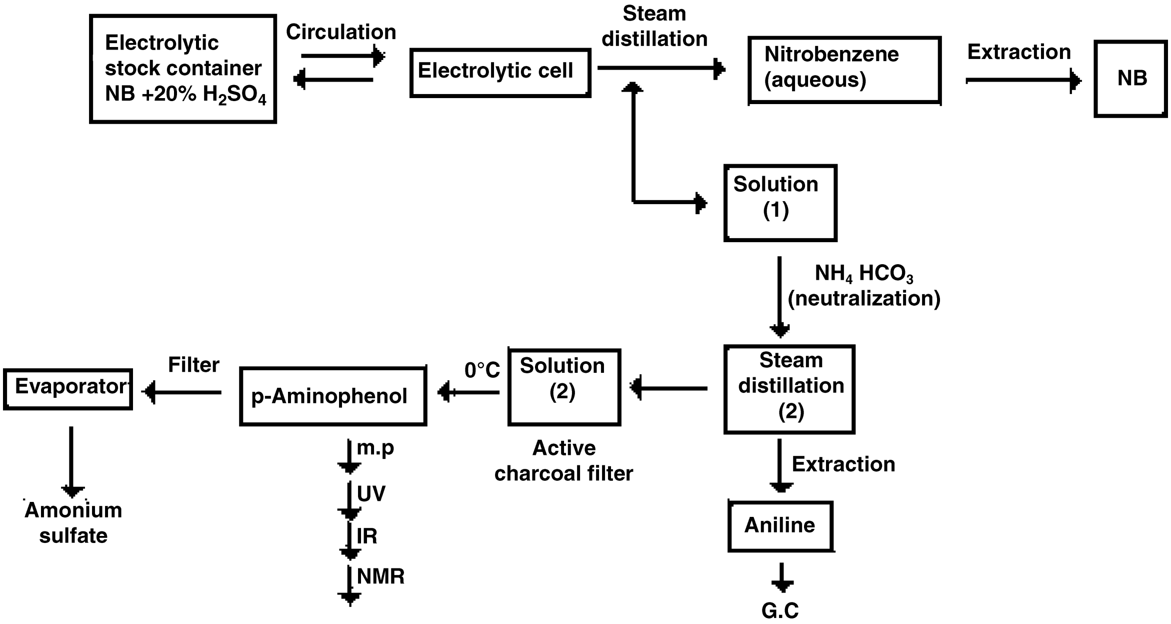


Fig. 7. Flow-chart for the electrochemical production of *p*-aminophenol.

This is a preliminary study for the continuous electrolyses of nitrobenzene to *p*-aminophenol on an industrial scale. The results are promising and studies to scale up this semipilot (laboratory) system to pilot scale are continuing.

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