ELECTROLYTIC REDUCTION OF AROMATIC NITRO COMPOUNDS USING TITANIC SULPHATE ADDITION

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Galvanostatic polarisation measurements on a copper cathode in presence of titanic sulphate and nitrobenzene are presented. An electrolytic reduction method for the preparation of various amines from the corresponding nitrocompounds using titanous-titanic redox system and a deposited copper cathode has been developed. The process has been scaled up to make aniline in a 1000 A cell. Results obtained in the scaled-up cell are presented.

Electrolytic reduction of various aromatic nitrocompounds like nitrobenzene[1–6], paranitrophenol[7], orthonitrophenol[8], m-dinitrobenzene[9] and 2, 4 dinitrotoluene[10] to their respective amines have been studied to examine the possibility of preparing them on an industrial scale. In presence of a redox system like Ti^{4+}/Ti^{3+} the reduction is made possible even in aqueous medium and the conversion is quantitative without any side products. Use of redox system has been highlighted in our reviews earlier[11,12]. Since same electrolyte can be used several times, nitrocompound added can be recovered as amine sulphate after each use and as the number of cycle increases the acid used becomes less and thereby the cost of production also decreases. Since amine can be obtained by neutralising the amine sulphate by an alkali like ammonia the cost of production will be still less if ammonium sulphate can be recovered. Electrochemical method is unique by its novel advantages as for the reasons stated below :

i) It gives purest of the compound than any other method ;

ii) It is possible to produce the compound with simple equipments, and equipments like high pressure autoclaves hydrogen generators are not needed ;

iii) It is possible to design a plant on any scale starting from few kilograms to hundreds of tonnes ;

iv) It is possible to control the reaction at any stage ;

v) Pollution and explosion hazards are minimum ; and

vi) Same equipment can be used for the production of different compounds.

Reuse of electrolyte makes the process economical as compared with other methods as it consumes less acid and alkali. Studies were made to know the yield with increase in the number of reuse. Same yield was observed even after ten uses. Based on the laboratory scale experiments a semiindustrial unit on 1000 A scale was designed and the experiment gave same yield as with bench scale experiments. Hence, it is possible to design a cell of higher amperage for an industrial unit. But for fine chemicals it is sufficient to manufacture on 1000 A scale. Reduction of nitrobenzene to aniline can be considered as a model unit for other chemicals also as the unit operations are almost similar. In an electrochemical unit mass transport depends mainly on three factors viz , i) diffusion ii) migration and iii) mechanical movement. Since the reduction efficiency mainly depends on mass transport, one can choose a stationary electrode, rotating electrode or any other electrode by which the mass transport is maximum with minimum energy loss. Since hydrogen evolution can bring down the current efficiency thereby accounting for major loss of energy, current versus potential studies were made for the stationary as well as rotating electrodes in presence of the redox system to know the reduction characteristics at different current densities.

EXPERIMENTAL

Electrolytic reduction of nitro compounds like nitrobenzene, p nitrophenol, orthonitrophenol, metadinitrobenzene and 2, 4 dinitrotoluene were carried out at the conditions mentioned in table 1, and the yields of the respective amines, current efficiencies and power consumption in terms of kilowatt hour kilogram amine produced are given in table 2.

From table 2, it is observed that the electrolytic reduction of nitrobenzene, orthonitrophenol paranitrophenol, metadinitrobenzene and 2,4 dinitro toluene give their respective amine compounds quantitatively.

Reuse of electrolyte was studied for the electrolytic reduction of nitrobenzene to aniline under the following condition and the results are given in table 3.

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Table 1 : Conditions for the reduction of nitrocompounds to their respectives amines

No	Compound studied	Vol. of catholyte ml ($20\%H_2SO_4V/V$)	Wt. of Ti $(SO_4)_2$ added to catholyte in TiO_2 equivalent (g)	Wt. of Nitro-compound added (g)	Area of cathode S-Stationary ; R-Rotating (dm^2)	Current (A)	Current density (A/dm^2)	Temperature °C	Voltage (V)
1	Nitrobenzene	1000	10	180	1.8 R	18	10.0	30 – 35	6 – 7.0
2	P-Nitrophenol	1000	10	100	1.5 S	25	16.7	55 – 60	3 – 4.0
3	o-Nitrophenol	1000	10	495	2.0 S	30	15.0	50 – 60	3 – 4.5
4	m-Dinitrobenzene	1000	10	1250	1.8 S	30	16.7	80 – 90	5 – 6.0
5	2,4 Dinitro toluene	900	10	200	2.0 R	30	15.0	70 – 90	5 – 6.5

Table 2 : Results of the reduction of nitrocompounds to their respective amines

No	Aminocompound studied	Weight of nitro compound recovered (g)	Weight of amine accounted (g)	Yield (%)	Current efficiency (%)	Energy consumption Kwh/kg amine produced
1	Aniline	.....	129.6	95	95.0	12.4
2	P-Aminophenol	.....	77.9	99	99.0	9.5
3	o-Aminophenol	.....	378.0	97	97.0	7.7
4	m-Phenylene diamine	8.5	790.0	99	98.7	18.7
5	2,4 Diamino toluene	10.0	124.0	97	85.0	18.6

Table 3 : Results on the reuse of electrolyte for the reduction of nitrobenzene to aniline

No of use	Weight of nitro-benzene taken (g)	Weight of nitro-benzene recovered (g)	Weight of aniline sulphate recovered as solid (g)	Weight of aniline estimated in solid aniline sulphate (g)	Weight of aniline estimated in liquor after removing solid aniline sulphate (g)	Total aniline accounted (g)	Yield (%)
1	513	.....	695.0	268.6	134.0	402.6	.....
2	342	.....	402.5	107.2	233.3	340.5	94.2
3	342	.....	895.0	254.8	189.3	441.1	90.6
4	342	.....	1830.0	425.6	124.7	550.3	
5	342	.....	837.0	160.1	91.9	252.0	92.0
6	342	.....	557.4	186.9	295.0	461.9	99.8
7	342	.....	994.5	368.3	94.8	463.1	95.1
8	342	.....	614.0	220.6	129.7	350.3	95.6
9	399	.....	1050.0	295.9	111.0	406.9	95.2
10	342	.....	928.6	202.0	95.2	297.2	93.0

Conditions :

Catholyte	: 900 ml 25% H_2SO_4 (V/V)
Anolyte	: 200 ml ,,
Titanic sulphats added to catholyte	: 200 ml solution containing $Ti(SO_4)_2$ equivalent to 10.2 g TiO_2
Current density	: 30 A
Cathode	: Stationary copper of area 1.8 dm^2
Current	: 16.7 A/dm^2
Temperature	: 50 - 60°C
Diaphragm	: Ceramic porous pot
Nitrobenzene added (Purity over 99%)	: 450 ml
Voltage	: 5 - 6V

Titanic sulphate solution was prepared by dissolving pure TiO_2 in concentrated sulphuric acid at temperatures between 190– 200°C with constant stirring[13]. The solution was diluted such that it contained 25% free sulphuric acid (V/V). It was estimated by standard methods[14].

After reduction the solution was cooled to room temperature and aniline sulphate separated out was filtered, washed and dried. Washings were added to mother liquor and estimated for aniline before next use. The aniline present in aniline sulphate (solid) was also estimated. The solution was made up by adding sufficient acid that it contained 25% free acid (V/V). Thus the same solution was used ten times and the results are indicated in table 3.

Table 4 : Material balance for the sulphuric acid used in the electrolytic reduction of nitrobenzene to aniline

No of use	Sulphuric acid added to catholyte (g)	Sulphuric acid added to anolyte (g)	Total sulphuric acid used (g)	Volume of liquor (ml)	Wt of free sulphuric acid in the liquor (g)	Weight of solid aniline sulphate (g)	Wt of free sulphuric acid in the solid aniline sulphate (g)	Total Sulphuric acid accounted (g)
1	588.0	90	678 0	...	...	695 0	128.0	...
2	468.3	90	558.3	...	...	402.5	87.9	...
3	180.3	90	270.3	...	...	895.0	148.4	
4	108.3	90	198 3	...	...	1830.0	163.0	...
5	306.3	90	396.3	...	...	837.0	58.1	...
6	414.3	90	504.3		...	557.4	24.4	
7	306.3	90	396.3	...	...	994.5	173.6	...
8	288.3	90	378.3	...	...	614.0	87.6	...
9	360.4	90	450.4	...	...	1050.0	154.5	...
10	378.3	90	468.3	500	22.7	928.6	216 3	2690.7*

* This figure was obtained by adding free sulphuric acid in solid aniline sulphate and mother liquor left behind and also the acid taken up by the total aniline formed.

Material balance for the use of sulphuric acid in the above experiment is shown in table 4. Since fresh anolyte was prepared for each experiment, this could not be accounted. Hence the difference 3398.8 - 2690.7 = 708 1 g sulphuric acid could not be accounted. This must have migrated towords the anode[15]. This accounts for about 20% of the sulphuric acid used for catholyte only. If the sulphuric acid used for anolyte had also been taken into account the percentage of unaccounted acid would be still less. For large scale experiments the anolyte is diluted and used for subsequent experiments.

Electrolytic reduction of nitrobenzene to aniline at 1000 A cell :

The cell used was made of 1/8" thick copper sheet with the dimensions 2a = 90 cm ; 2b = 45 cm and h = 40 cm where 'a' and 'b' are radii of the major and minor axis respectively as the cell was of elliptical shape and h is the height of the cell (Fig. 1). The total weight of the cell was 33kg and volume was about 120 litres. It was provided with a jacke ted vessel in G. I. for passing water as the temperature had to be maintained between 50-60°C. The cell was provided with

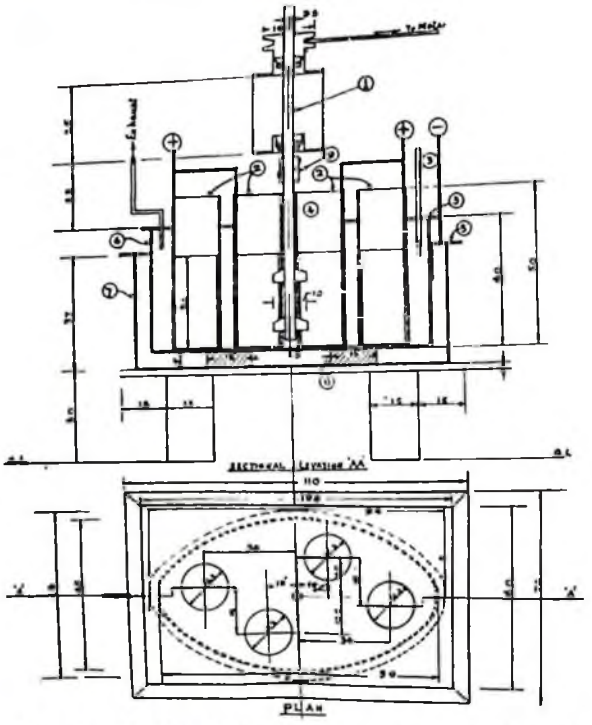


Fig. 1 1000 AMPS Electrolytic Cell for Aniline

1. Stirrer 2. Porous Pots 3. Thermometer
4. Condenser 5. Wooden Cover
6. Cell Container (Copper) 7. Cooling Tank
8. Non-conducting Material

a wooden cover with provision for 4 ceramic porous pots, mechanical stirrer, condenser and thermometer. Condenser was to reflux the nitrobenzene escaping from the cell. It was kept under mild suction arrangement. The ceramic porous pots served as anode chambers. The porous pot had a dimension of 15 cm diameter and 45 cm height having a wall thickness of about 0.5 cm. Lead anodes were in cylindrical shape with perforated sheets of thickness 1/8" and whose dimension was 13.5 cm diameter and 40 cm height. Total active area of anode was 94.3 dm^2 when the cell was filled to a height of 30 cm. Mechanical stirrer was provided with a wooden stirrer and a ½ h.p.motor. Stirrer was provided with paddles to give efficient agitation. When 1000 A current was passed cathode current density was 11.2 A/dm^2 and anode current density 9.2 A/dm^2. Thus the ratio between cathode and anode area was 1 : 1.04 Catholyte volume was 42 litres and anolyte volume 19 litres. Thus the ratio between anolyte volume and catholyte volume was 1 : 2.25. Other codintions were as shown below :

Conditions :

Titanic sulphate added to catholyte	:	Equivalent to 495g (1.1% W/V of the catholyte)
Anolyte	:	19 lit 25% H_2SO_4(V/V)
Catholyte	:	45 lit ,,
Cathode area	:	90.5 dm^2
Copper sulphate added to	:	45g (0.1% W/V of the
the catholyte	:	catholyte)
Nitrobenzene (Purity 95%)	:	15 lit or 17.24 kg
Anode weight	:	44.05 kg
Theoretical current for complete reduction	:	23540 amp hrs
Theoretical current for conversion of Ti^{4+} to Ti^{3+}	:	166 amp hrs
Total theoretical current reqd	:	23706 amp hrs
Cell voltage	:	4.3 – 6V
Temperature	:	50 – 60°C
Actual quantity of current passed	:	26100 amp hrs
Duration	:	26.5 hrs
Quantity of acid added to the catholyte during the course of reduction	:	5 litres
Quantity of water added to the anolyte	:	3.7 × 4 litres

After reduction the solution was free from nitrobenzene smell. Hence it was neutralised with soda ash and the liberated aniline was recovered by steam distillation in the usual manner.

Results of the experiment :

Weight of aniline recovered as oil	:	9.88 kg
Weight of aniline estimated in the	:	
distilled water and left over	:	2.77kg
solution in the still		
Total aniline accounted	:	12.65 kg
Current efficiency	:	83.8%
Yield	:	97%
Current consumption per kg	:	12.4 kwh
Sulphuric acid recovered from	:	16 kg
the anolyte		
Wt of anode after reduction	:	42 kg
Loss in weight of anode	:	2.05 kg (4.65%)
Purity of Aniline	:	99.6%

Same yield as observed on bench scale was observed for the experiment on 1000 A scale. Hence it is possible to scale it up further using same parameters. Based on the above results a complete block type flow sheet diagram for the production of aniline is prepared (Fig. 2).

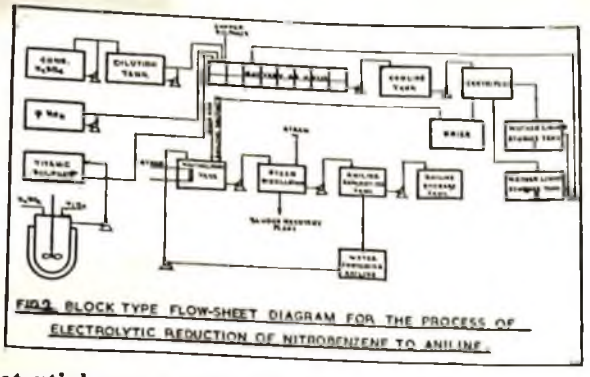


FIG 2. BLOCK TYPE FLOW-SHEET DIAGRAM FOR THE PROCESS OF ELECTROLYTIC REDUCTION OF NITROBENZENE TO ANILINE.

Potential versus current density studies for the electro reduction of nitrobenzene to aniline at stationary and rotating copper cathodes :

The cell used was a one litre beaker with provision for diaphragm, condenser, thermometer and stirrer or rotating electrode. For stationary electrode a glass stirrer was used. For rotating cathode a copper electrode of cylindrical type having an area 0.28 dm^2 was used. For stationary cathode a flat type electrode made of copper of same area as that of rotating cathode was used Catholyte consisted of 1 litre 25% sulphuric acid (V/V). For studies with titanic sulphate, the same equivalent to 10g TiO_2 was added. A ceramic porous pot was used as diaphragm. Anode was a strip of lead which was kept immersed in anolyte which consisted of 150 ml 25% sulphuric acid (V/V). Hundred ml of nitrobenzene was added for experiments with nitrobenzene. Cathode potential was recorded from a V T.V.M connected through a luggin capillary for the current density under study. Temperature was maintained between 50-60°C by external heating or cooling. Potential versus log current density was plotted for 25% sulphuric acid alone, 25% sulphuric acid containing 1% TiO_2 in the form of titanic sulphate, 25% sulphuric acid containing nitrobenzene (1·0 ml) and 25% sulphuric acid containing 1% TiO_2 and nitrobenzene (100 ml) for stationary as well as rotating cathodes and they are shown in fig. (3) and (4) respectively

Results and discussion :

Fig (3) represents depolarisation studies for a flat type copper cathodes under stationary electrode condition with a mechanical stirrer and fig (4) represents depolarisation studies for a cylindrical electrode under rotating condition. Since the current distribution varies from a cylindrical electrode to a flat electrode depolarisation characteristics also varies accordingly and hence the curves representing rotating electrode and stationary electrode were plotted separately.

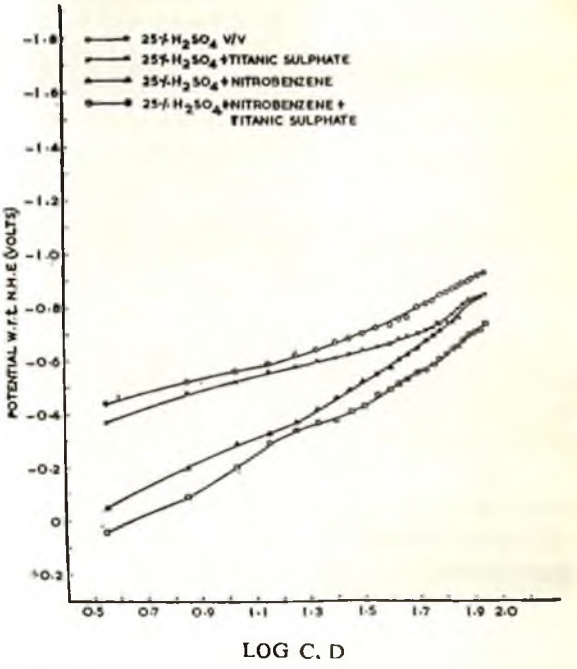


Fig. 3

The mechanism at the rotating cathode is that the layer adjoining the cathode surface moves very fast relative to the bulk of the solution whereas in a stationary cathode the bulk of the solution moves very fast relative to the layer adjoining the cathode surface.

It is reported that reduction of aromatic mononitrocompounds lead primarily to the successive formation of nitroso, and hydroxylaminocompounds. The final reduction product, the amino compound, predominates only when the conditions of reduction are such that the secondary reactions are held in subordination to the electrolytic reduction i.e., a very fast reduction velocity combined with a low rearrangement (in order to decrease the formation of aminophenols) to the formation of the largest amounts of amines according to the equation :

$$C_6H_5NO_2 \rightarrow C_6H_5NO \rightarrow C_6H_5NHOH \rightarrow C_6H_5NH_2$$

When titanic sulphate is added to the catholyte it gets reduced to titanous sulphate by virtue of its ionic

nature. This titanous sulphate reduces nitrobenzene present in the catholyte to aniline and thereby it gets oxidised to titanic sulphate again. Titanic sulphate once again gets reduced to titanous sulphate at the cathode and thus the cycle repeats. Meanwhile nitrobenzene which has reached the cathode surface by mechanical movement will also get reduced to nitrosobenzene. Before any nitrosobenzene intermediately formed reaches the cathode surface it will be reduced to aniline by the titanous sulphate which is in large excess at the cathode surface. Thus reduction to phenylhydroxylamine stage is prevented and no p-aminophenol is formed. Thus titanic sulphate and nitrobenzene are reduced resulting in the final product aniline only. Rate of nitrobenzene reaching the cathode surface is governed by diffusion only as other parameters like strength of supporting electrolyte, rate of stirring, temperature etc are constant. Hence the rate of nitrobenzene reaching the cathode surface is almost constant. But the rate of titanic ion reaching the cathode surface depends on current density. As the current density increases more and more titanic ions move towards the cathode surface. At high current density the rate of titanic ion reduction is high and nitrobenzene is reduced only chemically by titanous ions.

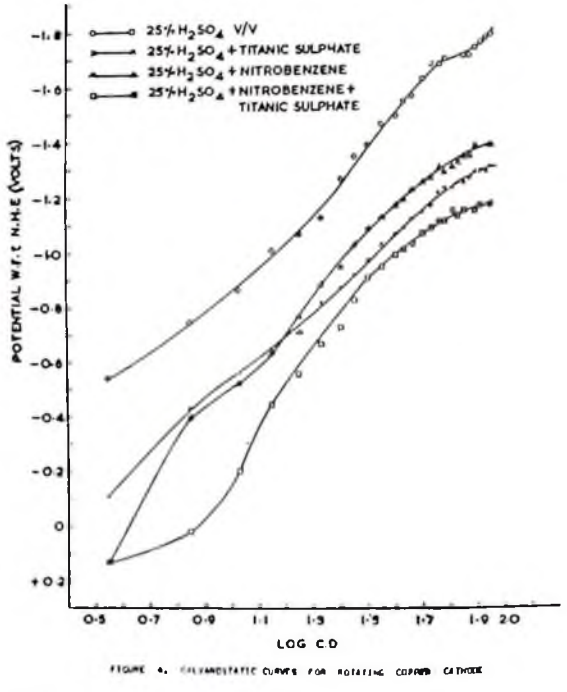


FIGURE 4. GALVANOSTATIC CURVES FOR ROTATING COPPER CATHODE

For a stationary cathode at a current density 3.55 A/dm² depolarisation due to individual addition of titanic sulphate and nitrobenzene is 0.07V and 0.38V respectively (Fig. 3). But when nitrobenzene and titanic sulphate are added together depolarisation is 0.48V for the corresponding current density. Upto a current density 14 A/dm² depolarisation due to lone addition of titanic sulphate decreases to a value of 0.02V but increases to a value 0.1V up to a current density of 63 A/dm². This remains almost constant afterwards i.e, up to a current density of 89 A/dm². Depolarisation due to lone addition of nitrobenzene shows a constant decrease from a value of 0.38V to 0.08V with increase in current density from 3.55 A/dm² to 89 A/dm². For joint addition of nitrobenzene and titanic sulphate the depolarisation value rapidly decreases from 0.48V to 0.27V for current densities from 3.55 A/dm² to 17 8 A/dm² but the decrease is slow afterwards. It decreases to 0.19V at a current density 89 A/dm². It is observed from the above results that titanic sulphate gets reduced to titanous sulphate at higher current densities at a greater rate and nitrobenzene at a lesser rate. Hence the current density 17.8 A/dm² upto 89 A/dm² reduction of nitrobenzene is mainly due to titanic sulphate which gets reduced to titanous sulphate thereby resulting in chemical reduction of nitrobenzene to aniline. At the lower current density ranges i.e., from 3.55 A/dm². It decreases to 0.19V at a current density 89 A/dm². It is observed that from the above results that titanic sulphate gets reduced to titanous sulphate at higher current densities at a greater rate and nitrobenzene at a lesser rate. Hence the current density 17.8 A/dm² upto 89 A/dm² reduction of nitrobenzene is mainly due to titanic sulphate which gets reduced to titanous sulphate thereby resulting in chemical reduction of nitrobenzene to aniline. At the lower current density ranges i.e., from 3.55 A/dm² to 17.8 A /dm² nitrobenzene may also get reduced but it will not go upto phenyl hydroxylamine stage as it will get reduced to aniline by titanous sulphate before that stage.

For a rotating cathode, at a current density 3.55 A/dm² depolarisation due to individual addition of titanic sulphate and nitrobenzene are 0.43V and 0.66V respectively (Fig. 4). Depolarisation due to nitrobenzene and titanic sulphate together also has got a value of 0.66V corresponding to that current density. At 7A/dm² depolarisation due to lone addition of titanic sulphate and nitrobenzene shows a value 0.3V and 0.34V respectively. But their joint addition shows a value 0 75V corresponding to that current density. This value is maximum for the range studied. At a current density 10.7 A/dm² depolarisation due to lone

addition of titanic sulphate and nitrobenzene are same as that of the current density 7 A/dm² i.e., 0.3V and 0.34V respectively. But the joint addition of titanic sulphate and nitrobenzene shows a depolarisation value 0.65V at 7A/dm². This values goes on decreasing up to a minimum value of 0.45V at a current density of 22.4 A/dm² and again goes on increasing up to a value of 0.63V at a current density of 89 A/dm². At a current density of 14 A/dm² depolarisation due to individual addition of titanic sulphate and nitrobenzene registers the same depolarisation value viz., 0.36V. Afterwards, depolarisation due to lone addition of titanic sulphate is more than the depolarisation due to lone addition of nitrobenzene throughout the range studied. Minimum value registered by low addition of nitrobenzene is 0.25V at a current density 15.9 A/dm². It goes on increasing up to 0.4V at 89 A/dm². Lone addition of titanic sulphate also behaves similarly i.e., the depolarisation value increases from 0.36V to 0.48V from a current density 14 A/dm² to 89 A/dm². These results prove that the reduction of nitrobenzene is mainly due to chemical reduction by the reduced titanous sulphate at higher current density ranges viz., from 14 A/dm² to 89 A/dm² though at a lesser rate at low current density ranges from 3.55 A/dm² to 14 A/dm².

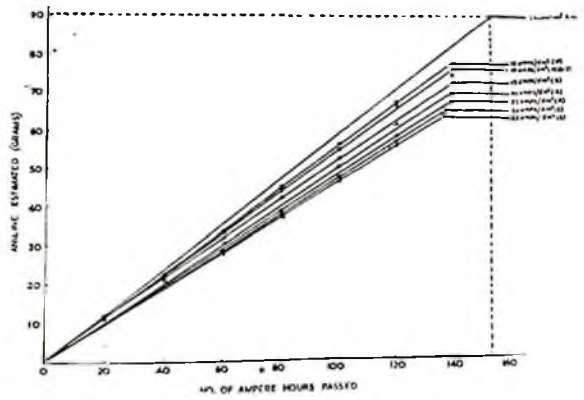


Fig. 5 Yield vs. No. of Amp. Hrs Passed for Electrolytic reduction of Nitrobenzene to Aniline at various Current Densities R-Rotating Cathode, S-Stationary cathode.

Yield versus number of ampere hours passed was plotted for different current densities viz.. 10 A/dm², 15 A/dm², 20 A/dm² and 25 A/dm² for stationary electrode as well as rotating electrode under identical conditions (Fig. 5). The cell used was the same as that used for previous studies. Theoretical line representing the weight of aniline formed with number of ampere hours is also shown on the graph. The deviation from ideal behaviour with increase in current density can be observed from each curve. Taking 60g aniline as a standard unit the number of ampere hours required for rotating cathode and stationary cathode was found out for all the current densities studied. The results are shown in table 5.

Table 5: Comparative studies of stationary and rotating cathodes in the electrolytic reduction of nitrobenzene to aniline under identical conditions.

Current density	Rotation cathode		Stationary cathode	
	Extra no. of amp hrs for theoretical value	Percentage	Extra no. of amp hrs for theoretical value	Percentage
10	8.0	7.9	8.0	7.9
15	6.0	5.9	14.0	13.8
20	18.7	18.5	25.3	25.0
25	22.7	22 4	28.7	28.3

From table 5 it is obsereyd that the reduction efficiency is better for a rotating cathode than a stationary cathode for current densities 15 A/dm², 20 A/dm² and 25 A/dm². It makes no difference at a current density 10 A/dm² for both the electrodes. In the experiment with 1000 A capacity, a current density of 11.2 A/dm² was used. For the complete reduction 10% extra quantity of current was passed. Thus the table gives an approximate quantity of current to be passed for complete reduction for current densities ranging from 10 A/dm² to 25 A/dm² for stationary as well as rotating electrodes under the said conditions.

Conclusion: It is shown by above experiments that reduction of nitrobenzene and other nitro compounds are quantitative in presence of a redox system like Ti^{4+}/Ti^{3+}. For current densities up to 10 A/dm² stationary electrode can be used and above that current density rotating cathode can give better efficiency.

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