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Electroreduction of nitrobenzene to p-aminophenol at a TiO_2/Ti electrode

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1. Introduction

p-Aminophenol is an intermediate in the manufacture of the photographic developer Metol and of the drug p-acetamol, whose demand in India is estimated to be 2400 tonnes per annum [1]. At present the demand is met by adopting chemical methods of manufacture.

p-Aminophenol is manufactured chemically by several methods: (i) one method consists of the reduction of p-nitrophenol with iron and HCl [2] which causes waste disposal problems; (ii) phenol may be treated with HNO_2, which, on reduction with polysulfide, gives p-aminophenol with very poor yield; (iii) nitrobenzene may be reduced to p-aminophenol in the presence of catalysts such as Pt or Pd and this method is highly expensive.

An alternative method for production of p-aminophenol is by the electrolytic method, which is clean and without pollution problems. The yield is also higher than that in the chemical method, leading to purer product. The electroreduction of p-nitrophenol to p-aminophenol involves $6\,F\,mol^{-1}$ whereas the electroreduction of p-nitrosophenol or nitrobenzene involves only $4\,F\,mol^{-1}$. The maximum yield of p-aminophenol from p-nitrosophenol was only 87% [4].

Earlier workers have done extensive work on the electroreduction of nitrobenzene to p-aminophenol [5–13]. Nitrobenzene was reduced in aqueous 20% H_2SO_4 in a divided cell using amalgamated copper as a stationary or rotating cathode, at a c.d. of $2.7\,A\,dm^{-2}$ and a temperature of 90° C, and the yields reported were 56.5% and 71.7%, respectively for the two types of electrode. It was also reported that different addition agents such as stannous chloride, bismuth chloride and thallus chloride were used individually to study their effect on the yield of p-aminophenol and aniline. The addition of bismuth chloride gave maximum yield of 65–70% p-aminophenol and 5.8% aniline. When amalgamated Monel was used as cathode a yield of 70% p-aminophenol was obtained. The reduction of nitrobenzene was also repeated at amalgamated copper to compare the results with the results obtained with the TiO_2/Ti electrode. The objective of the present investigation was to study the maximum yield of p-aminophenol with minimum aniline formation.

2. Experimental details

2.1. *Preparation of TiO_2/Ti electrode [15]*

Titanium sheet in cylindrical form was treated with 50% HCl at 363 K for about 1 h to give a rough surface for good adherence of the oxide coating. A solution of 0.05 M titanyl acetyl acetonate in isopropanol was prepared and the titanium cylindrical sheet was dipped into this solution and dried in an oven at 100–110° C, followed by further heating at 500° C for 25 min in a muffle furnace. The process was repeated a minimum of 5 times to obtain a good coating of TiO_2 over the titanium.

2.2. *Cell set-up and electrolysis*

The cell consisted of a glass beaker of 500 ml capacity provided with a lead cover having holes for introducing a porous pot (diaphragm), the electrodes, a stirrer (only for stationary electrodes), a thermometer and a reflux condenser. A ceramic porous pot with lead anode served as the anode chamber and TiO_2/Ti electrode served as cathode. The amalgamated copper cathode was prepared by coating mercury over the copper by electrolysing a solution of 1% mercuric sulphate, with a copper cathode and lead anode at a c.d. of $5\,A\,dm^{-2}$ for 10 min. To keep the mercury electrode bright throughout the experiment, 0.1% mercuric sulphate was added to the catholyte in the subsequent experiments. D.c. was passed from a rectifier and the electrolysis was continued until the quantity of electricity was $4\,F\,mol^{-1}$ and the catholyte contained different concentrations of depolarizer (nitrobenzene) in 50% H_2SO_4. The electrolyte temperature was maintained at 80–85° C by keeping it over a hot water bath. The results of the experiments with the TiO_2/Ti electrode are given in Table 1 and for the experiments with amalgamated copper in Table 2.

Total amine was estimated by standard methods [16] from which the aniline value obtained by a method by Day and Taggart [17] was deducted and thus p-aminophenol for each experiment was determined.

3. Results and discussion

It is evident from Table 1 that the yield (or current efficiency) of PAP increases with temperature for the TiO_2/Ti electrode (Nos 1–3) with simultaneous decrease in percentage of aniline. The yield (or c.e.) of p-aminophenol also increases with acid concentration with simultaneous decrease in the percentage of aniline (Nos 3–5 in Table 1).

With increase in c.d. the yield (or c.e.) of p-aminophenol increases with simultaneous decrease in the percentage of aniline for the rotating TiO_2/Ti electrode (Nos 9–11 with variation of nitrobenzene as

Table 1. Electroreduction of nitrobenzene to p-aminophenol (PAP) at TiO_2/Ti electrode. Catholyte: 50% H_2SO_4; temperature: 80–85° C

Exp. No.	*Nitrobenzene taken* (g)	*C.d.* ($A\,dm^{-2}$)	*Wt of PAP estimated* (g)	*Yield of PAP* (%)	*Yield of aniline* (%)	*C.e. for PAP* (%)
(a) With stationary cathode						
1	6[a]	2.5	2.5	46	50.1	49.6
2	6[b]	2.5	3.6	68	28.4	72.7
3	6	2.5	4.7	90	5.5	94.5
4	6[c]	2.5	2.7	50.9	48.1	54.1
5	6[d]	2.5	2.9	54.5	45.5	57.9
6	30	2.5	14.4	81.3	13.3	81.2
7	40	5.0	24.4	68.9	5.1	69.0
8	56.2	7.5	28.2	56.5	2.8	57.0
(b) With rotating cathode						
9	10.5	2.5	6.3	68.8	30.6	18.9
10	31.0	7.5	22.8	81.2	17.4	81.2
11	55.1	12.5	45.8	93.8	5.2	93.8

[a] Temp. 60–70° C.
[b] Temp. 70–80° C.
[c] 30% H_2SO_4 as catholyte.
[d] 40% H_2SO_4 as catholyte.

depolarizer). For the rotating amalgamated copper cathode the yield (or c.e.) for p-aminophenol increases with increase in current density with simultaneous decrease in aniline percentage (Table 2 with variation of nitrobenzene as depolarizer).

4. Conclusion

It is concluded that the TiO_2/Ti electrode under rotating conditions, when used as cathode in a divided cell with 50% H_2SO_4 as electrolyte using a lead anode at a temperature of 80–85° C and a c.d. 12.5 $A\,dm^{-2}$, can give maximum yield/c.e. of p-aminophenol, viz. 93.8%, with simultaneous aniline formation of 5.2%. At a stationary electrode, under identical conditions and at a c.d. of 2.5 $A\,dm^{-2}$, the yield and c.e. for p-aminophenol were 90% and 94.5%, respectively with simultaneous aniline formation of 5.5%.

For a rotating amalgamated copper under identical conditions and at a c.d. of 12.5 $A\,dm^{-2}$, the yield for p-aminophenol was 89.5% with simultaneous aniline formation of 8.3%. Here nitrobenzene was added in various amounts to save time for the low c.d. experiments.

Table 2. Electroreduction of nitrobenzene to p-aminophenol (PAP) using a rotating amalgamated copper cathode. Conditions same as in Table 1; rotating cathode

No.	*Nitrobenzene taken* (g)	*C.d.* ($A\,dm^{-2}$)	*Wt of PAP estimated* (g)	*Yield of PAP* (%)	*Yield of aniline* (%)
1	9	2.5	4.4	57.8	38.2
2	23	7.5	13.8	67.7	31.8
3	45	12.5	33.9	89.5	8.3

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