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ELECTROREDUCTION OF p-NITROSOPHENOL TO p-AMINOPHENOL USING TITANIUM OXIDE COATED TITANIUM ELECTRODE

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Electroreduction of p-nitrosophenol to p-aminophenol was carried out at different cathode materials like copper, lead and TiO_2/Ti. It was observed that TiO_2/Ti gave better current efficiency and yield than other electrodes. Using a divided cell the effects of current density, acid concentration, temperature etc. were studied to optimise the conditions for maximum yield. Rotation of the cathode was found to improve the yield as well as current efficiency.

Key words: Electroreduction, p-nitrosophenol, titanium oxide coated titanium electrode, p-aminophenol

INTRODUCTION

p-aminophenol (PAP) finds use as an intermediate in the manufacture of paracetamol and is chemically prepared from p-nitrophenol by reduction with iron and HCl [1]. From the point of view of the environmental pollution, this method creates a problem for the disposal of iron oxide. Electrochemical methods are normally clean and yield is superior to chemical method. There are 3 routes for the manufacture of p-aminophenol by electrochemical method viz. (i) p-nitrophenol is reduced to p-aminophenol which involves 6F/mole [2] (ii) Nitrobenzene is reduced to p-aminophenol which involves 4F/mole [3] and (iii) p-nitrosophenol is reduced to p-aminophenol which also involves 4F/mole [4].

In view of high cost of raw material and more quantity of electricity needed for the first method, it is not economically viable. As p-nitrophenol is made from p-chloronitrobenzene, it is likely to contaminate p-acetamol. In the second method, the acid concentration is high and aniline is the coproduct and thus becomes costlier than the third one. The cost of phenol is comparatively lower than that of p-nitrophenol. Hence the conversion of phenol to p-nitrosophenol by chemical method and its electroreduction to p-aminophenol makes the process economically viable. Some work on the electroreduction of p-nitrosophenol has already been reported [4, 5] with a maximum yield of 85% involving the addition of p-nitrosophenol in small quantities at regular intervals so as not to exceed the concentration of equivalent quantity of titanous sulphate in the catholyte. Some improvements were made in these experiments by fixing the Ti^{3+}/Ti^{4+} on the electrode itself by ceramic method [6]. The new technique has improved the yield also. Cyclic voltammetric work has established that the number of electrons involved are four [7]. Industrial feasibility can be assessed only after establishing that the electrode can withstand several runs. TiO_2/Ti electrode was used for the reduction of p-nitrophenol to p-aminophenol with an yield and current efficiency of 97% and 98% respectively [8] and p-nitrobenzene to p-aminophenol with an yield and current efficiency of 90% and 94.5% respectively [9].

EXPERIMENTAL

Titanium sheet was etched in 50% HCl at 363K for about an hour, as the etching improves the adherence of oxide coating. A solution of 0.05M titanyl acetyl acetonate in isopropanol was prepared. The etched titanium sheet was dipped in the above solution and dried in an oven at 373-383K, and heated in a muffle furnace at 573K for 25 minutes. The above process was repeated 5 times. The coating of TiO_2 over titanium was strongly adherent.

p-nitrosophenol (PNP) was prepared by the method mentioned in the literature [10], using laboratory reagent grade chemicals to obtain an yield of 89%. The purity of p-nitrosophenol was determined by reduction with zinc dust and HCl and estimating the resulting amine with standard sodium nitrite using starch indicator. The purity of the freshly prepared dry p-nitrosophenol was 99%.

A 600ml capacity glass beaker was used as the electrolytic cell. 400ml of 10% by volume H_2SO_4 was taken as catholyte and 50ml of 10% (v/v) H_2SO_4 as anolyte. PNP was added to the catholyte. Anolyte and catholyte were separated by a porous pot. Lead strip of area 0.5 dm^2 was used as anode. TiO_2/Ti of area 0.55 dm^2 was the cathode. A constant inter electrode gap of 5cm was maintained. 4F of electricity was passed per mole of p-nitrosophenol.

After electrolysis, the catholyte was treated with ammonia or ammonium carbonate to liberate the free base, which was isolated by ether extraction. The product was identified as p-aminophenol by qualitative tests [11] as well as melting point determination of the free base and its acetyl derivative.

RESULTS AND DISCUSSION

Effect of cathode material

Reduction of PNP was done using different cathode materials viz. TiO_2/Ti, copper and lead. Among the three materials, TiO_2/Ti gives the best yield and current efficiency. Results are given in Table-I.

TABLE-I: Effect of various cathode materials on the yield and current efficiency of PAP

Surface area of cathode 0.3dm^2; Cathode current density:3.3 $A.dm^{-2}$

Cathode material used	Weight of PNP (g)	Weight of PAP obtained (g)	Yield of PAP (%)	Current efficiency (%)
TiO_2/Ti	4.4	3.1	78.2	60.4
Copper	4.5	2.3	57.2	45.2
Lead	21.8	0.8	3.6	3.2

Effect of process conditions

After confirming that the yield of PAP on TiO_2/Ti electrode is the highest, studies were conducted with TiO_2/Ti stationary electrode at different current densities, acid concentrations and temperatures. Studies were also carried out on TiO_2/Ti rotating electrode (800 rpm) at various current densities. The results are given in Table-II.

TABLE-II: Effect of operating conditions (C.d., acid concentration, temperature) on yield and current efficiency of PAP
Cathode: TiO_2/Ti

No.	Catholyte conc. aq.H_2SO_4 (%)	PNP content (g)	Current density (A. dm^{-2})	Temperature (K)	Wt. of PAP obtained (g)	Yield (%)	C.E. (%)	* Nature of cathode
1	10	7.0	1.8	303–308	5.10	82.5	76.0	S
2	10	7.0	3.3	303–308	4.80	78.2	59.0	S
3	10	7.0	7.3	303–308	2.20	36.0	26.2	S
4	10	12.0	2.8	303–308	8.40	79.0	64.4	S
5	20	12.0	2.8	303–308	7.76	73.0	64.0	S
6	30	12.0	2.8	303–308	6.94	65.3	64.0	S
7	10	16.5	2.2	303–308	11.40	78.2	60.4	S
8	10	16.5	2.2	313–323	6.63	45.4	40.0	S
9	10	16.5	2.2	323–333	5.20	35.6	32.4	S
10	10	23.0	2.0	303–308	20.00	98.0	90.5	R
11	10	23.0	3.0	303–308	16.50	80.8	79.2	R
12	10	23.0	4.9	303–308	14.70	72.4	50.3	R

* S - Stationary; R - Rotating;

As the current density increases, the yield as well as current efficiency decreases. It is observed that at a current density 1.8 A.dm^{-2}, the yield (82.5%) and current efficiency (76.0%) are maximum. At higher current densities, the lowering of current efficiency may be due to hydrogen evolution. The yield and current efficiency decrease with increase of the acid concentration. At the lowest acid concentration, i.e. 10% H_2SO_4, the yield and current efficiency are maximum, viz. 79% and 64.4% respectively. With the increase in temperature, the yield and current efficiency decrease. The yield and current efficiency are maximum at room temperature (303–308K). The decrease in yield at higher temperatures may be due to side reactions.

With rotating TiO_2/Ti electrode, the lowest current density viz. 2.0 A.dm^{-2} gave maximum yield and current efficiency. For nearly the same current density, rotating cathode gives maximum yield (98%) and current efficiency (90.5%) compared to the stationary cathode. Yield and current efficiency fall with increase in current density probably due to hydrogen evolution. Even though PNP contents are different for various parameters, the amount of electricity passed, however, is proportional to the PNP content added.

CONCLUSION

For the electroreduction of p-nitrosophenol, TiO_2/Ti cathode was found to be the best among the materials studied. Yield as well as current efficiency were maximum at low current density (1.8 A.dm^{-2}), low sulphuric acid concentration (10% by volume), and at low temperature (303–308K). Further, rotation of the cathode significantly improves the yield and current efficiency.

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