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Anodic oxidation of aniline for waste water treatment

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The electro-oxidation of dilute aqueous solutions of aniline was studied on a lead dioxide packed bed anode. The anolyte consisted of 400 ml of 5.5 mM aniline in dilute sulphuric acid. The anolyte was recirculated through a packed bed electrochemical reactor with an anode compartment volume of 5.0, at various flowrates. The concentrations of aniline, benzoquinone, maleic acid and carbon dioxide were measured against time for experiments ranging from 0.5 to 5.0 h in duration. The effects of applied current, pH, flowrate and initial aniline concentration on the percentage of aniline oxidized and carbon dioxide produced are discussed. Aniline in the solution oxidized readily, but further oxidation of intermediates to carbon dioxide was more difficult. The percentage of aniline oxidized increased with increasing current density, while it decreased with increasing initial aniline concentration and pH. Current efficiencies ranged from 15 to 40% for complete oxidation of aniline to CO_2.

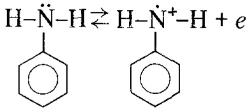
1. Introduction

Aromatic amines, such as aniline, *m*-nitroaniline and benzedine, belong to one of the few highly toxic chemical groups that can react readily in the blood to convert haemoglobin to methamoglobin, thereby preventing oxygen uptake. These aromatic amines are commonly produced as byproducts of the petroleum, pulp and paper, coal and chemical industries. Because of the toxicity of these species, the study of their degradation by oxidation is very important.

The determination of aniline and its derivatives in water using gas chromatography (GC) was reported by Kulikova, Kirichenko and Pashkevich [1]. The compounds were determined from benzene extraction followed by conversion into trifluoromethoxytetrafluoropropionanilides prior to gas chromatographic analysis. High pressure liquid chromatography (HPLC) also has been used to supplement GC/MS (mass spectroscopic) analysis in studies to determine the nature and composition of pollutants in industrial wastewater [2].

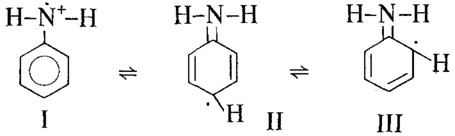
There are several methods of treating industrial wastes [3] including recovery, incineration, adsorption, biological treatment and chemical or electrochemical oxidation. The choice of treatment depends on economics as well as ease of control, reliability and treatment efficiency. The electrochemical method for wastewater treatment has attracted a great deal of attention recently [4], mainly because of the ease of control and the increased efficiencies provided by the high surface areas of three dimensional electrodes.

Preliminary studies of electro-oxidation of aniline were performed by Lord and Rogers [5]. Adams, McClure and Morris [6] determined the formal potential over a wide pH range. From these works the following one-electron oxidation process has been indicated:



(1)

which has the principal resonance structures of



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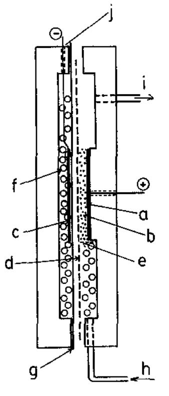

Fig. 1. Electrochemical reactor: a – lead anode, b – packed bed of 1 mm lead particles, c – stainless steel cathode, d – Nafion 427 cationic membrane, e – stainless steel retaining screen, f – glass beads, g – gasket, h – inlet, i – outlet, j – cathode gas vent.

Once formed, the resonance structures I and II undergo rapid oxidation to produce dimeric and polymeric products. It has been shown that bulk electrolysis of acidic aniline solutions generates a dark green precipitate (emeraldine) at the anode [7]. However, in other work *p*-aminodiphenylamine and benzidine were found to be the predominate products of aniline oxidation from pH 0 to 6.5 during the time scale of cyclic voltametry [8].

In general little interest has been shown in the further anodic oxidation of intermediate products to carbon dioxide. The present work describes the main products formed during the anodic oxidation of aniline for wastewater treatment application at lead dioxide electrodes in a fixed bed reactor. This research follows the work of Smith de Sucre and Watkinson [4] on phenol oxidation. In addition, the effects of applied current, pH, flowrate and initial aniline concentration on the percentage of aniline oxidized and carbon dioxide produced are discussed.

2. Experimental details

Fig. 1 shows the cross-section of the experimental reactor, which contained a packed bed of 1 mm spherical lead pellets in contact with a pure lead anode collector plate. The electrode bed was 19 mm wide, 66 mm high and 9 mm deep. The initial geometric surface area was approximately 225 cm^2. Before an experiment was started, the reactor was run for 1 h with sulphuric acid (pH = 2) at a current density of 300 A m^{-2} in order to oxidize the lead surface to lead dioxide. A stainless steel 1 mm thick plate was used as the cathode current feeder. The anode and cathode chambers were separated by a Nafion 427 cationic exchange membrane. The reactor volume was approximately 5.0 ml. A schematic drawing of the experimental apparatus is shown in Fig. 2. The anolyte was pumped through the reactor powered by a dc power supply and then returned to the anolyte tank for recycle. The anolyte consisted of 5.5×10^{-3} M aniline in sulphuric acid (pH = 2) with a total volume of 400 ml, while the catholyte

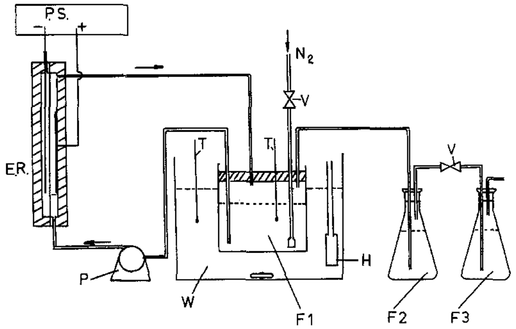

Fig. 2. Apparatus schematic: E.R. – electrochemical reactor, P.S. – dc power supply, V – values, P – peristaltic pump, T – thermometer, W – water bath, H – heater, F_1 – anolyte reservoir, F_2, F_3 – CO_2 scrubbers.

was sulphuric acid of pH = 2. Reagent grade chemicals and doubly-distilled water were used throughout the work. The temperature of the electrolyte was maintained at 24–25° C. After each run the cell was washed thoroughly with doubly-distilled water.

The benzoquinone concentration was determined by iodiometry [9], while carbon dioxide, purged from the acidic solution by nitrogen, was measured by absorption in barium hydroxide solution followed by back titration with standardized HCl. In alkaline solutions carbon dioxide was measured both by absorption in barium hydroxide solution and by gravimetric analysis of the reservoir electrolyte, and the results combined to obtain the net amount of carbon dioxide in each experimental run. A Polargraphic Analyser (PAR) Model 384 with a digital plotter Model RE0082 was used to determine aniline and maleic acid concentrations during various stages of the electrolysis. A PAR static mercury drop electrode Model 303 was employed to measure the maleic acid concentration, while the aniline concentration was determined at a glassy carbon electrode (PAR Model 9333). Differential pulse polarography with a pulse height of 0.05 V was employed in all measurements. A blank and several standard solutions were run prior to the determination of aniline or maleic acid concentrations.

3. Results and discussion

3.1. *Process chemistry*

The experimental results indicate that the anodic oxidation of aniline in sulphuric acid can proceed via the following reactions:

$$\underset{\text{Aniline}}{C_6H_7N} + 2\,H_2O \longrightarrow \underset{\text{Benzoquinone}}{C_6H_4O_2} + 3\,H^+ + 4\,e + NH_4^+ \qquad (2)$$

$$\underset{\text{Benzoquinone}}{C_6H_4O_2} + 6\,H_2O \longrightarrow \underset{\text{Maleic Acid}}{C_4H_4O_4} + 12\,H^+ + 2\,CO_2 + 12\,e \qquad (3)$$

$$\underset{\text{Maleic Acid}}{C_4H_4O_4} + 4\,H_2O \longrightarrow 12\,H^+ + 4\,CO_2 + 12\,e \qquad (4)$$

$$2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e \qquad (5)$$

According to this oxidation pathway, aniline is oxidized to benzoquinone, which then undergoes further oxidation to maleic acid and carbon dioxide. The major competing reaction is that of oxygen evolution by Reaction 5. However, this reaction can be partially suppressed by the use of lead dioxide electrodes which have a high oxygen overpotential.

3.2. *Aniline oxidation*

Fig. 3a shows the number of moles of aniline, benzoquinone, maleic acid and carbon dioxide that were present during various stages of the electrolysis of 400 ml of a 5.5×10^{-3} M aniline solution at a total current of 2 A. It can be seen that the number of moles of benzoquinone and maleic acid increase to a maximum and then decrease as further oxidation takes place. The maximum benzoquinone concentration follows the loss of aniline from the solution and in turn is followed by a maximum in the maleic acid concentration as benzoquinone is lost. Carbon dioxide, the final oxidation product, continuously increases with time. Thus the reaction sequence of Equations 2–4 appears to be followed.

Depending on the conditions, aniline may oxidize to form benzoquinone, maleic acid or other byproducts, or may oxidize completely to carbon dioxide. The relative extent of each process can be expressed in terms of the amount of each species formed (or lost) as a percentage of the initial quantity of aniline present. For aniline, benzoquinone and maleic acid this is given by:

$$\frac{\text{moles of species}}{\text{initial moles of aniline}} \times 100\% \qquad (6)$$

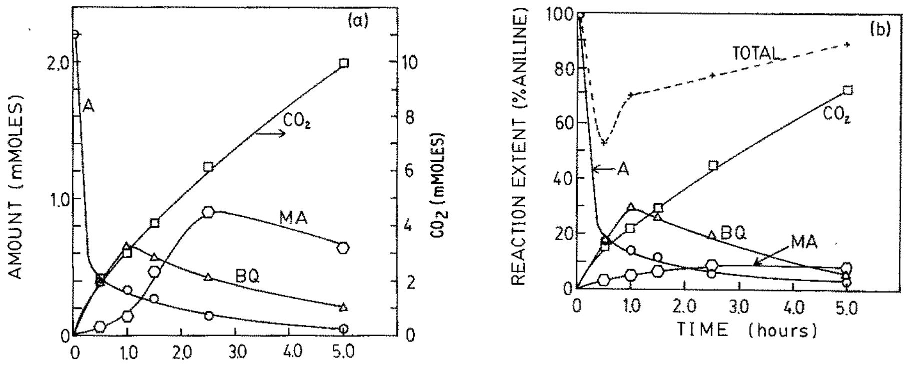

Fig. 3. Electrochemical oxidation of aniline. Aniline initial concentration = 5.5 mM; intial pH = 2.0; cell current = 2.0 A; electrolyte volume = 400 ml. (a) millimoles of species; A – aniline, BQ – benzoquinone, MA – maleic acid; (b) extent of reaction based on aniline conversion to that species; A – aniline, BQ – benzoquinine, MA – maleic acid, total = A + BQ + MA + CO_2.

In the case of complete oxidation to CO_2, the formation of CO_2 by both Reactions 3 and 4 must be taken into consideration so that the percentage of aniline that reacts completely to carbon dioxide is given by:

$$\frac{1/6\,[(\text{total moles } CO_2) - 2\,(\text{moles of maleic acid})]}{\text{initial moles of aniline}} \times 100\% \tag{7}$$

These data are plotted in Fig. 3b and show that about 97.5% of the aniline has been converted to byproducts and 72.5% has been completely converted to carbon dioxide after 5 h.

Since the percentages shown in Fig. 3b are based on aniline conversion the sum of the percentages of maleic acid, benzoquinone, carbon dioxide and residual aniline represents a mass balance for aniline. The sum is plotted in Fig. 3b and demonstrates that at 5 h 89% of the aniline is accounted for by residual aniline and the byproducts benzoquinone, maleic acid and carbon dioxide. At short electrolysis times ($t = 30$ min) only 52.5% of the aniline is accounted for by these species. Thus it is clear that there must be additional byproducts formed in the initial stages of the oxidation reaction. Since the amount not accounted for decreases with time (for $t > 30$ min) its appears that these byproducts are also subject to oxidation. The initial rate of oxidation of aniline is very rapid. Greater than 80% of the initial aniline is oxidized within 30 min. Further oxidation of aniline proceeds at much lower rates, probably due to competition with byproduct oxidation.

3.3. *Initial aniline concentration*

The effect of the initial concentration of aniline is shown in Fig. 4a–c. The percentage of aniline converted completely to CO_2 is presented in Fig. 4a. With an increase in initial aniline concentration, a smaller percentage is converted completely to CO_2 under the same processing conditions. In Fig. 4b the percentage of aniline oxidized is plotted. Although the percentage of aniline oxidized is smaller for higher initial aniline concentration, the difference is not as significant as in the percentage of CO_2 formed (Fig. 4a). For electrolysis times greater than 1.5 h, 90% of the aniline has been oxidized despite the difference in initial concentrations. However, the percentage of aniline converted completely to CO_2 is very dependent upon the initial concentration. The ratio of the amount of aniline oxidized to the amount of aniline completely converted to CO_2 is shown in Fig. 4c. It is clear from the figure that greater initial concentrations of aniline result in much higher proportions of byproduct formation. At sufficiently long times the ratios should approach 1.0 provided that all the byproducts can be oxidized. It is interesting to note that the extrapolation of the ratios to the value of 1.0 indicates that the oxi-

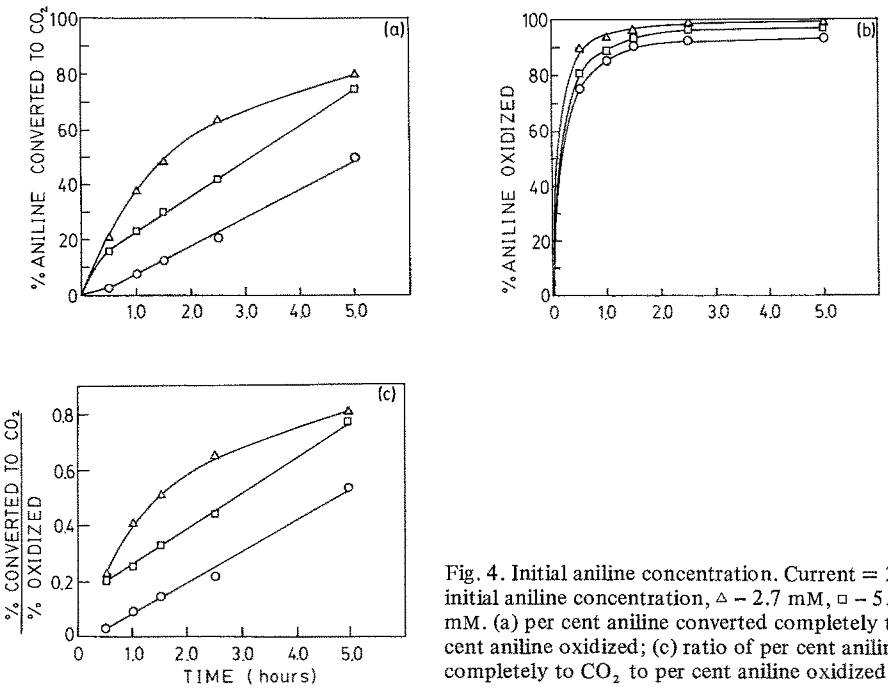

Fig. 4. Initial aniline concentration. Current = 2.0 A, pH = 2.0, initial aniline concentration, △ – 2.7 mM, □ – 5.5 mM, ○ – 11.0 mM. (a) per cent aniline converted completely to CO_2; (b) per cent aniline oxidized; (c) ratio of per cent aniline converted completely to CO_2 to per cent aniline oxidized.

dation would be complete within 9 to 13 h. Since the solution is recirculated through the cell to the reservoir and the cell has a volume of 5 ml, these times represent effective cell residence times of 7 to 10 min.

3.4. *Effect of applied current*

Figs. 5a and b show the effect of the applied current on the percentage of aniline converted completely to carbon dioxide and the percentage of aniline oxidized as a function of time. From Figs. 5a and b it is clear that higher currents oxidize more aniline and generate more carbon dioxide. The ratio of the percentage of aniline converted completely to CO_2 to the percentage of aniline oxidized is shown in Fig. 5c and demonstrates that higher currents produce less byproduct. The current efficiency for complete oxidation of aniline to CO_2 for a 5 h run changes from 13.0 to 12.0 to 9.0% for 1, 2 and 3 A, respectively. The lower current efficiency at higher currents results from greater oxygen evolution which also may contribute to the reduced byproduct formation. In addition, greater evolution of oxygen on the electrode surface may cause improved mass transfer rates, which could affect the byproduct formation. If the current efficiency for complete oxidation to carbon dioxide is measured for a 90% conversion of initial aniline concentration then the values are 13.0, 16.5 and 21.5% for 1, 2 and 3 A, respectively. The improved current efficiency with applied current is a consequence of the shorter time required to achieve a 90% conversion for the higher currents.

3.5. *Effect of pH*

The initial pH of the supporting electrolyte was set at 2.0, 8.0 and 11.0 to determine the effect of pH on the oxidation reactions. The results of these measurements are shown in Figs. 6a and b for a 2 A current and 5.5 mM initial aniline concentration. The percentage of aniline converted completely to

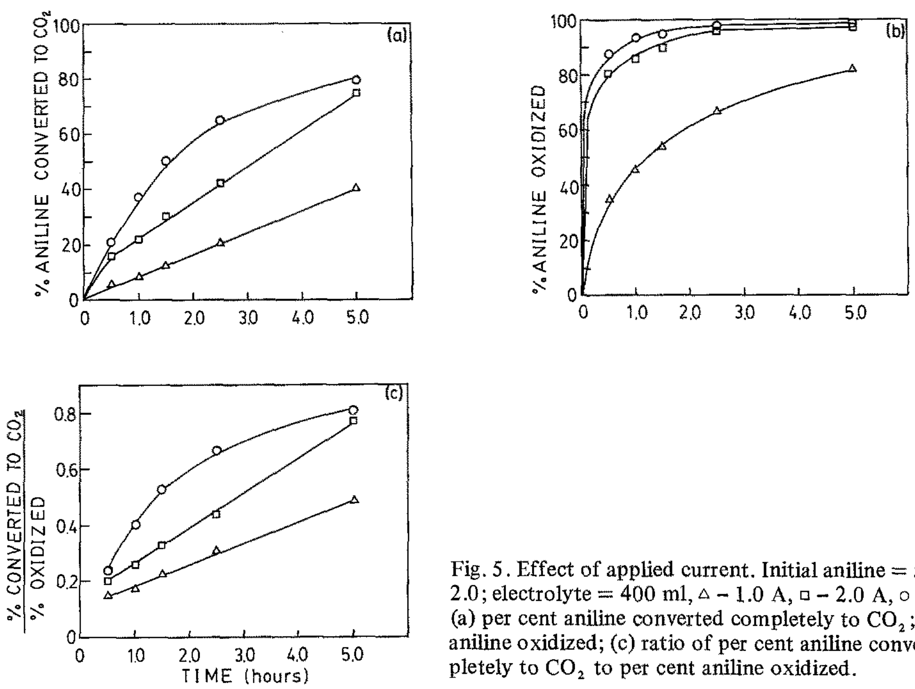

Fig. 5. Effect of applied current. Initial aniline = 5.5 mM; pH = 2.0; electrolyte = 400 ml, △ – 1.0 A, □ – 2.0 A, ○ – 3.0 A. (a) per cent aniline converted completely to CO_2; (b) per cent aniline oxidized; (c) ratio of per cent aniline converted completely to CO_2 to per cent aniline oxidized.

CO_2 increases with increasing initial pH. However, the percentage of aniline oxidized decreased with increase in initial pH.

The ratio of the percentage of aniline consumed to the percentage of aniline converted completely to carbon dioxide, shown in Fig. 6c, indicates that complete oxidation is favoured at high initial pH values. The reaction sequence of Equations 2–4 is consistent with these observations since each step results in hydrogen ion production and an increase in pH would improve the driving force for each step. These effects also are reflected in the current efficiencies for complete oxidation of aniline to carbon dioxide which are plotted in Fig. 6d. The best current efficiency (39.5%) is found at short times (0.5 h) for the highest initial pH value (pH = 11). With time, current efficiency decreases as did pH for the alkaline runs. It is interesting to note that despite the improved conversion of aniline to carbon dioxide and improved current efficiency at higher initial pH, more aniline is consumed under acidic conditions as shown in Fig. 6b. This indicates that the rate determining step must not involve the production of hydrogen ions. In Fig. 6d, it is clear that while the initial current efficiency for complete oxidation of aniline to CO_2 is better at high initial pH values, the current efficiency decreases with time and at 5 h approximately the same current efficiency is found for any of the initial pH values. Since the cell was operated in a batch operation no control of pH was maintained during the runs, and the pH fell rapidly as hydrogen ions were produced by the anodic reactions (Equations 2–5). The pH values at 5.0 h were 2.2, 2.2 and 2.0 for runs with initial pH values of 11.0, 8.0 and 2.0, respectively. The final pH values were achieved within 1 h of the cell operation. Since the pH did not drop below 2.0, some acid neutralization was achieved by hydrogen ion transport through the Nafion membrane to the cathodic compartment. The results suggest that control of alkalinity could be used to improve current efficiency.

3.6. *Effect of flow rate*

In Fig. 7 the effect of flow rate is shown for the operation of the cell in a single pass mode. Although more aniline is oxidized for very slow flow rates (0.05 m s^{-1}), the percentage of aniline oxidized tends to level off at about 18% for higher flow rates because of the very rapid initial oxidation rate. The

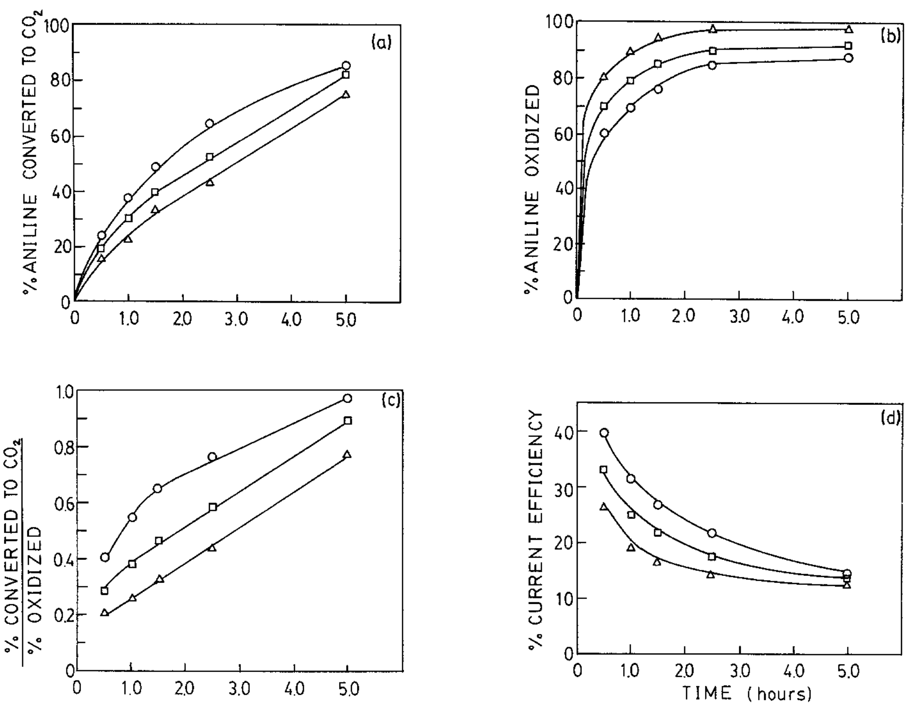

Fig. 6. Effect of initial pH. Initial aniline = 5.5 mM, current = 2.0 A, electrolyte = 400 ml. △ – pH = 2.0, □ – pH = 8.0, ○ – pH = 11.0. (a) per cent aniline converted completely to CO_2; (b) percent aniline oxidized; (c) ratio of per cent aniline converted to CO_2 to per cent aniline oxidized.

current efficiency shown in Fig. 7 for the complete oxidation of aniline initially increases with flow rate and then tends to level off at about 41%. One might expect the current efficiency to increase with flow rate since more aniline is oxidized per unit time. However, although the percentage of aniline oxidized remains at about 17.5% with higher flow rates there is less time for complete oxidation to CO_2 and thus the rise in current efficiency is not observed.

4. Conclusions

1. The electrochemical oxidation of aniline in aqueous solutions to CO_2 occurs through the formation of benzoquinone and maleic acid. A large proportion of other byproducts form at short electrolysis times.
2. The initial rate of aniline oxidation is rapid with greater than 90% of the initial aniline being

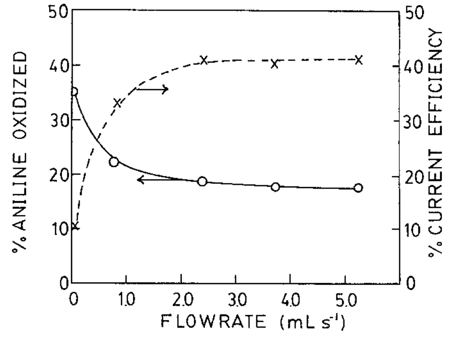

Fig. 7. Effect of flow rate on aniline oxidation with no recycle. Initial aniline = 5.5 mM, initial pH = 2.0, current = 2.0 A. Current efficiency based on complete oxidation of aniline to CO_2.

oxidized within 1 h for an initial concentration of 2.7 mM aniline at a pH of 2.0 and an applied current of 2 A.

3. The percentage of aniline oxidized increases with acidity but the current efficiency, based on complete oxidation of aniline to CO_2, increases with alkalinity.

4. The latter stages of the oxidation of aniline to benzoquinone, maleic acid and CO_2 are pH-dependent and slow relative to the initial oxidation of aniline.

5. Electrolysis can be used to remove aniline from aqueous solutions with current efficiencies ranging from 15 to 40%.

Acknowledgements

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