SCALE-UP OF ELECTROCHEMICAL REACTORS

Abbas H. Sulaymon, Qasim M. Slaiman*, **and Ali H. Abbar**
Chemical Engineering Department - College of Engineering - University of Baghdad - Iraq
* Chemical Engineering Department - Collage of Engineering - University of Saddam - Iraq

ABSTRACT

The design and scale-up of the electrochemical reactor plays an important role in the development of industrial electrochemical processes. The selected system used for studying the scale-up of electrochemical reactors is the reaction of nitrobenzene to p-aminophenol. A flow through porous electrode type was adapted in the present work since it is more convenient for the theoretical treatment of scale-up process.

The polarization curves that describe the reduction of nitrobenzene to p-aminophenol were obtained experimentally for different conditions: electrode type, concentration, electrolyte type and temperature. An effectiveness criterion (K_n), which is the similarity criterion for scaling-up, was used to calculate the potential distribution based on data extracted from experimental polarization curves.

INTRODUCTION

Industrial electrochemical processes provide a variety of products used by modern society: aluminum, magnesium, sodium, chlorine, sodium hydroxide, chlorates, perchlorates, tetra alkyl lead and electrorefined metals to mention a few. The most important item in these processes is the electrochemical reactor which is more familiarly known as "Electrolyser", "Electrolytic Cell" or "Electrochemical Cell". The most important tool in scale-up of systems is the principle of similarity. Consequently, similarity between systems can be specified in terms of intrinsic ratio of measurements; force, resistance or rates within each system. These intrinsic ratios are called the similarity criteria which must be the same in laboratory and industrial scales to be similar. These are dimensionless groups and can be determined by dimensional analysis and/or mathematical modeling [1].

Typical engineering problems are encountered on expanding the scale of a set-up from laboratory size to industrial dimensions, especially problems of mass transfer and current and potential distribution. The case of potential distribution is the most important problem in the electro-chemical reactor; the yield of products, energy consumption and quality of products are closely related factors.

In recent years, the need for improved reactor design to accomplished high rate electrolysis has led to the development of new reactor configuration, as well as methods for scale-up and prediction of performance. Therefore, porous electrodes were devised to increase the space time yield of the electrochemical reactors. They have the major advantage of large area available for reaction per unit volume of the reactor in comparison with the more conventional plane electrodes, in addition to a higher mass transfer coefficient.

Two principle configurations for mixed bed electrodes have been developed, the flow-through porous electrode, (FTPE) where fluid flow and current are parallel, and flow-by porous electrode (FBPE) where the fluid flows perpendicularly to the current. The current and potential distribution in the first configuration is one-dimensional (the electrode potential varies in the direction of current flow), while the second type involving a two-dimensional problem (the electrode potential varies in the direction parallel to and perpendicular to current flow), which is inherently more complex), than in the first type [2].

The present work is conducted for studying experimentally the electrochemical reduction of nitrobenzene in acidic medium to p-aminophenol and the scale-up principle of such system. The reason behind this work is the need for p-aminophenol in many industrial applications, as an intermediate in the synthesis of pharmaceuticals, as a drying agent for feathers and fur, as a wood stain imparting roselike color to timber and as photographic developer.

THEORY

The study of the behavior of fixed bed electrode falls within the scope of electrochemical engineering considered to be the application of the principle of analysis and design of the chemical engineering discipline to electrochemical processes[1]. Fixed bed electrodes do not normally operator with a uniform reaction rate and potential, because of ohmic voltage losses within their structure and consequently the specific area is not used to the full. On the other hand, from a practical point of view, it is desirable to utilize most of the internal surface area of the electrode[2].

The estimation of the utilized specific area is therefore of great importance in design and scale-up of these electrodes and approach is by analogy of the chemical engineering analysis of heterogeneous reactions such as gas-solid catalytic reaction and gas-liquid absorption with chemical reaction, extended to the electrochemical case. Therefore, an effectiveness or effectiveness factor is introduced to account for the fraction of bed thickness electrochemically reactive. This effectiveness (ε) is defined as follows:

$$\varepsilon = \frac{\text{Observed Electrolytic Current}}{\begin{array}{c}\text{Current Obtained with an Electrode}\\\text{whose Overpotential is the same}\\\text{at every Po int}\end{array}} \quad (1)$$

In essence the value of (ε) determines the distance the reaction penetrates the electrode. As a rough guide to the operation of fixed bed electrodes, the effectiveness should have a minimum value of about 0.05 if they are to be considered worth while alternative to plate electrode cell.

Coeuret et al. In several papers[3, 4, 5] were the first in the studying and analyzing the current and potential distribution in fixed by using a mathematical approach similar to that proposed by the chemical engineering discipline for heterogeneous reaction. In their analysis, the following hypotheses are made:

1. The hydrodynamical and electrochemical operating conditions are steady.
2. The electrical potential and the current density within the electrode depend only on the x-direction, see Fig. (1), i.e. one-dimensional mode.
3. The continuous phase (electrolyte) in the electrode can be considered as a continuous medium whose electrical conductivity γ is depending on γ_0 and the tortousity of the current lines by the following relation[6].
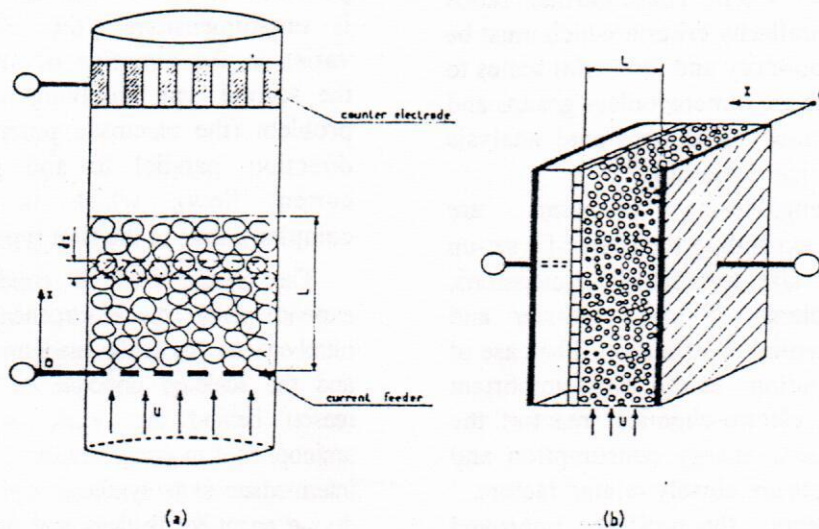

(a)   (b)

Fig. (1) Porous Electrode Configuration

$$\gamma = \gamma_o \frac{2\,\epsilon}{3-\epsilon} \qquad (2)$$

4. The velocity (u_{av}) of the electrolyte is sufficiently high to ensure that the concentration change of the electrolyte through bed thickness is negligible.
5. The electrical potential ϕ_2 of the dispersed phase is considered as constant.
6. The conduction through the continuous phase, whose electrical potential is $\phi_1(x)$ obeys Ohm's law.
7. Double layer and migration effects are negligible.
8. Pore structure and porosity distribution are uniform.
9. The operation is isothermal.

Firstly, they[3] considered the linear polarization condition and solved the one-dimensional model with the following boundary condition:

$$\eta_{(x)} = \eta_{(L)} \qquad \text{at } x = L \qquad (3.a)$$

$$\frac{\partial \eta}{\partial x} = 0 \qquad \text{at } x = 0 \qquad (3.b)$$

Then they represent the current and potential distribution by the following dimensionless relationship:

$$\frac{\eta_{(x)} - \eta_{(0)}}{\eta_{(L)} - \eta_{(0)}} = \frac{\cosh\left(k_1 \dfrac{x}{L}\right) - 1}{\cosh(k_1) - 1} \qquad (4)$$

$$k_1 = \left[i_o \frac{z\,F}{R\,T} \frac{a}{\gamma} L^2\right]^{1/2} \qquad (5)$$

where, k_1 is a dimensionless number which appears as an effectiveness factor by the following relation:

$$\varepsilon_1 = \frac{\tanh k_1}{k_1} \qquad (6)$$

Equation (6) has the same mathematical form as that known for the effectiveness of a catalytic reactor with first order chemical reaction[7]. Also they represented the relation between the over potential at the front of the bed and that at the back of bed as follows:

$$\frac{\eta_{(L)}}{\eta_{(0)}} = \cosh k_1 \qquad (7)$$

In addition to that, they found the current density of a fixed bed electrode based on the cross-section area as follows:

$$I = \frac{\eta_{(0)}}{L} \gamma\, k_1 \sinh k_1 \qquad (8)$$

Secondly, they[4] consider the Tafel polarization condition by expressing the experimental current $\{i = f(\eta)\}$ to a power function of η as follows:

$$i = i_o \frac{z\,F}{R\,T} \alpha^{1-n} \eta^n \qquad (9)$$

in which n would be a positive exponent lower than one α is a dimensionless coefficient.

They then solved the one-dimensional model with the same previously given boundary conditions. And expressed the potential distribution in a similar fashion as follows:

$$\frac{\eta_{(x)} - \eta_{(0)}}{\eta_{(L)} - \eta_{(0)}} = \frac{\cosh\left(k_n \dfrac{x}{L}\right) - 1}{\cosh(k_n) - 1} \qquad (10)$$

$$k_n = \left[\frac{n+1}{2} i_o \frac{z\,F}{R\,T} \frac{a L^2}{\gamma} \left(\frac{\alpha}{\eta_{(L)}}\right)\right]^{1/2} \qquad (11)$$

In this case, k_n is an effectiveness criterion for fixed bed electrode operating under Tafel polarization regime. Its value determines the effectiveness factor by the following relation:

$$\varepsilon_n = \frac{\tanh k_n}{k_n} \qquad (12)$$

where, ε_n is the effectiveness factor for packed bed electrode under Tafel regime. Similarly:

$$\frac{\eta_{(L)}}{\eta_{(0)}} = \cosh(k_n) \qquad (13)$$

and

$$I = \frac{\eta(0)}{L} \gamma k_n \sinh k_n \qquad (14)$$

Figure (2) shows the influence of k_n on the overpotential distribution.

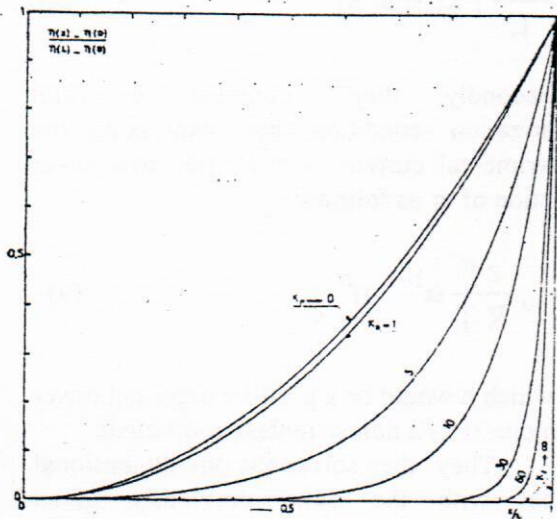Fig. (2) Influence of k_n on the Overpotential Distribution

Where $k_n \to 0$, $\varepsilon_n \to 1$ (entirely three dimensional electrode). $k_n \to \infty$, $\varepsilon_n \to 0$ (two-dimensional electrode, the top of the bed in $x = L$ only been reactive). $0 < k_n < \infty$, $1 > \varepsilon_n > 0$ (the electrochemical reaction takes place in a slab whose thickness decreases with increasing value of k_n).

These analysis were checked experimentally by using different types of reaction systems and different types of bed (granular and stackes of metal screens or nets).

Later, Coeuret et al[5]. analyzed the current distribution in a fixed bed electrode opening under limiting current condition in a similar fashion of the previous works[1]. They solved the one-dimensional model and represented the potential distribution by the following dimensionless relationship.

$$Y = \frac{\eta(x) - \eta(0)}{\eta(L) - \eta(0)} = \frac{(1-R_o)^{-x/L} + \frac{x}{L}\ln(1-R_o) - 1}{(1-R_o)^{-1} + \ln(1-R_o) - 1} \qquad (15)$$

which is only dependent on the overall efficiency R_o, and expressed as follows:

$$R_o = \frac{|I_L|}{zFU_{av}C_\infty} \qquad (16)$$

EXPERIMENTAL WORK

The experiments were performed in a rectangular electrolytic cell consisting of the following parts, [as shown in Fig. (3)].

1. **Cathode Chamber:** It was made of perespex with an outer dimensions (150 x 100 x 50 mm) and having internal compartment with dimensions (80 x 30 x 30 mm). This compartment was divided into three sections: the first was for the distribution of catholyte at inlet, the second was for installing a calming section and the cathode electrode, the third was for collecting the catholyte solution for output.

2. **Cathode Electrode:** The cathode was a rectangular screen with dimension (40x25x0.5 mm) and having a specific surface area equal to 86.125 cm^{-1}.

3. **Calming Section:** Calming section was used to reduce the entrance effect. It consisted of a stack of polytetraflouroethylene net (40x25x10 mm).

4. **Anode Chamber:** It was made of perspex with outer dimensions (150x100x50 mm) and having internal dimensions (80x30x30 mm). It was provided with opening for input and output of anolyte solution.

5. **Anode Electrode:** It was made of pure lead in a rectangular box shape, with dimensions (70x25x10 mm) and threaded at for fixing inside anode chamber.

6. **Membrane:** The membrane was anionic ion-exchange membrane (MA-3475).

Experimental procedure

The cathodic specimen was fitted inside the cathode chamber, and the two chambers (cathodic and anodic) were bolted together after placing the ion-exchange membrane between them, then the electrolytic cell was connected to the flow system.

Before starting each run, 750 ml of supporting electrolyte (i.e. 1 M H_2SO_4) was added to the catholyte and anolyte reservoirs, the pumps were switched on and the catholyte and anolyte started to flow in the system
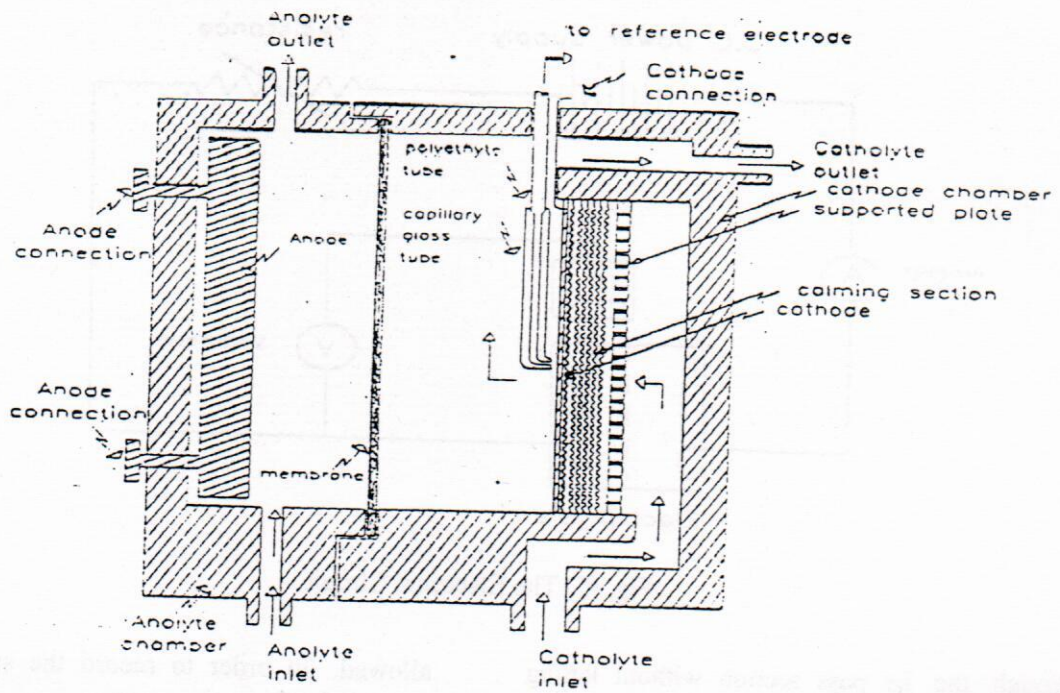
Fig. (3) A Sketch Showing the Components off Electrochemical Reactor (electrolysis cell)
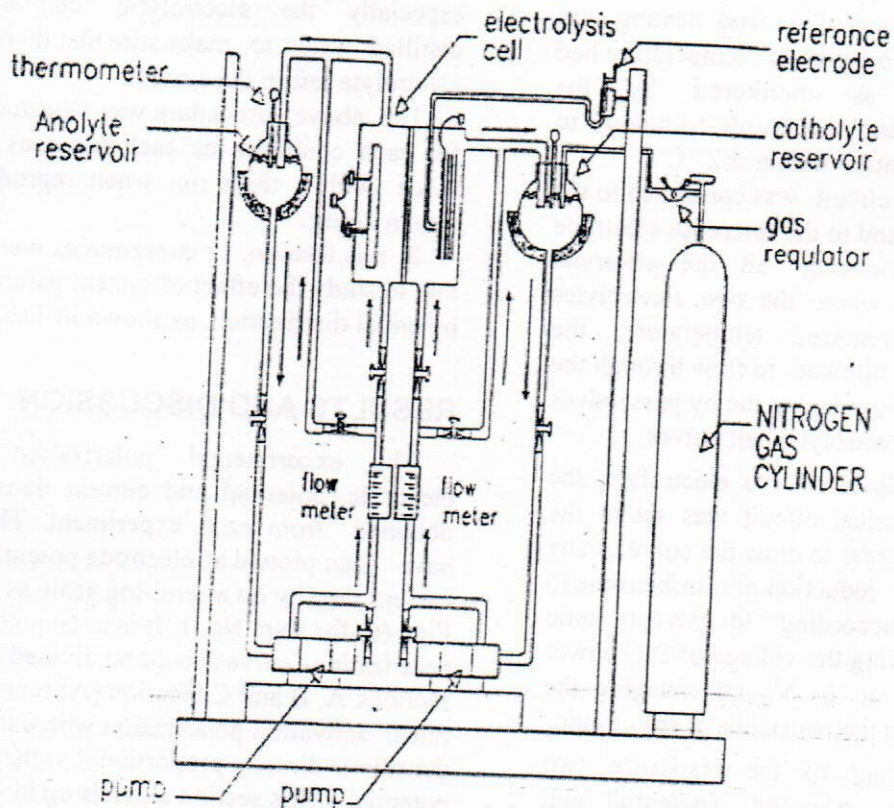

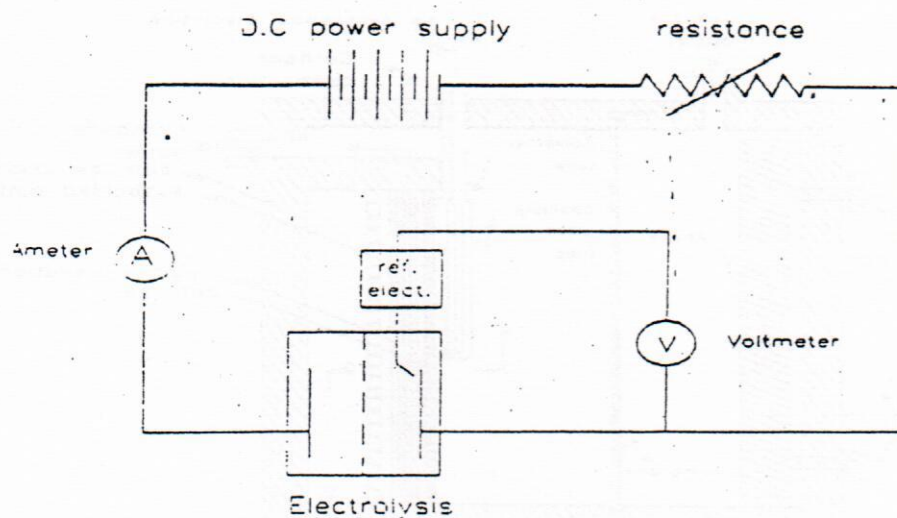Fig. (4) A Simple Sketch Showing the Details of the Flow System

Fig. (5) The Electrical Circuit

through the by pass section without letting them to flow through the electrolytic cell, then the nitrobenzene was added to the catholyte with appropriate concentration. This was followed by bubbling nitrogen gas through the catholyte for 1 hr. after that the heating mantels were switched on and heating was continued until the level of temperature had been reached as monitored by the thermometers using the on/off technique to control the temperature within $\pm 2\,^{\circ}C$.

The electrical circuit was connected to the electrolytic cell and to the reference electrode (SCE). After checking all the electrical connections and when the two electrolytes were at the required temperature, the electrolytes were allowed to flow through the electrolytic cell by closing the by pass valves and opening the electrolytic cell valves.

During the flow of the electrolyte, the polarization electrical circuit was set to the (ON) position in order to draw the curve of any condition for the reduction of nitrobenzene to p-aminophenol, according to galvano static technique by making the voltage of D.C power supply constant at 8 V and changing the current by altering the resistance of the circuit.

At each setting of the resistance two parameters were recorded (potential and current) by the voltmeter and the ammeter respectively, i.e. to determine the cathodic polarization curve. Two minutes at least were

allowed in order to record the steady state values of polarization process.

At the end of each run the power supply was switched off, then the drain valves, were opened in order to drain the used electrolytes. The system was then washed entirely and especially the electrolytic cell by using distilled water to make sure that there was no electrolyte left in the system.

The above procedure was repeated exactly for each condition as each run was repeated twice with a third run when reproducibility was in doubt.

In this fashion, 11 experiments were carried out to study the effect of system parameters on potential distribution, as shown in Table (1).

RESULTS AND DISCUSSION

The experimental polarization data of electrode potential and current density were obtained from each experiment. These data have been plotted as electrode potential versus current density on a semi-log scale as shown in Fig. (6) for Exp. No. 1. It is to be noted that all polarization curves could be divided into three sections A, B and C. Section (A) represents the linear activation polarization where the current density is directly proportional to the electrode potential. This section extends up to -150 mV. Beyond this value section (B) begins where Tafel activation polarization occurs. In this case the relation between the current density

Table (1) The Experiments

| Exp. | Cathode Material | Catholyte | | | Redox System | | Temp. (°C) |
| | | Supporting Electrolyte | | Reactant Conc. (g/l) | Type | Conc. (g/l) | |
		Type	Conc. (M)				
1	B	H	1	2	-	-	80
2	=	=	=	5	-	-	=
3	=	=	=	7	-	-	=
4	=	=	=	=	Sn^{+4}/Sn^{+2}	1	=
5	AB	=	=	=	-	-	=
6	B	HE	-	8	-	-	25
7	=	=	-	=	Sn^{+4}/Sn^{+2}	1	=
8	AB	=	-	=	-	-	=
9	B	A	4	7	-	-	80
10	=	=	=	=	Sn^{+4}/Sn^{+2}	1	=
11	AB	=	=	=	-	-	=

B = Brass, AB = Amalgamated brass, H = Sulfuric acid, HE = 60:40 water (1 M H_2SO_4)-ethanol [by weight] and A = Acetic acid.

and electrode potential takes an exponential form extending from approximately −150 mV to about −500 mV whereby section (C) begins.

In section (C), a mass transfer effects takes place characterized by the occurrence of a limiting current plateau, the later extends typically over at least a hundred mV, and is terminated by the onset of another electrode reaction at more negative potential.

The polarization equation was obtained by plotting the absolute value of potential versus the current density on log-log scale as shown in Fig. (7).
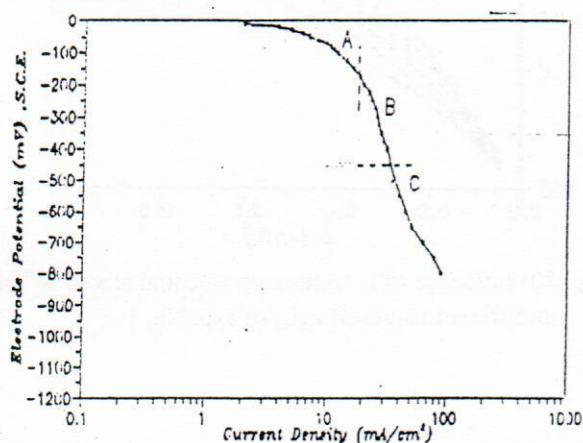

Fig. (6) Polarization curve of experiment No. 1

As a special case, for experiment, the effectiveness criterion was plotted against the thickness of electrode (L) at different values of η_L as shown in Fig. (8) for Exp. No. 1. it can

be seen that k_n increases as thickness of electrode bed increases and η_L decreases.

In a similar fashion, the effectiveness factor, ε_n was plotted against L and η_L as shown in Fig. (9) for Exp. No. 1. It can be seen that ε_n increases as L decreases and η_L increases, therefore a higher fraction of the height electrochemically reactive can be obtained either at lower thickness or higher value of η_L.
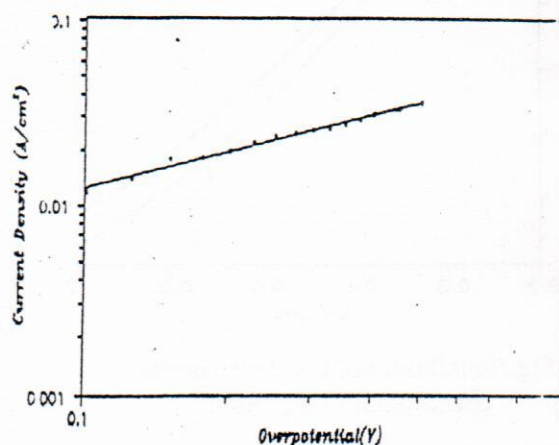

Fig. (7) Best fit of power function polarization curve of experiment No. 1

Also, the overpotential at electrode back (η_L) was plotted against L and η_L as shown in Fig. (10) for Exp. No. 1. It can be seen that $\eta_{(0)}$ decreases with thickness increasing and η_L decreasing.

Finally, the current density (I) was plotted against $L\eta_L$ as shown in Fig. (11) for Exp. No. 1. It can be seen that (I) increases as the thickness (L) increases at constant η_L until a certain value of (L) where the current density is approximately constant.
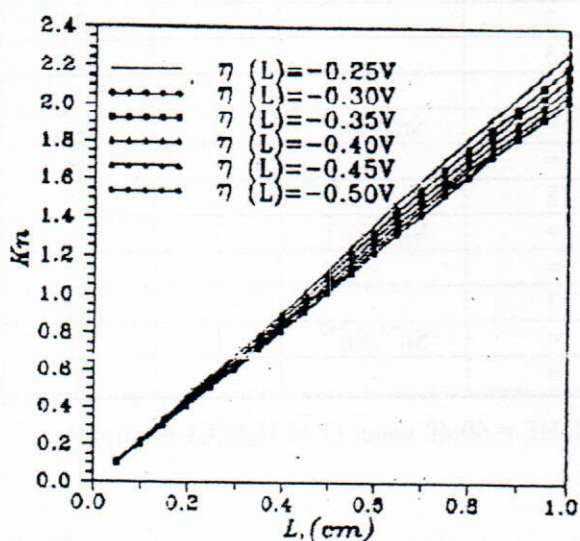

Fig. (8) Influence of L and $\eta(L)$ on the effectiveness of exp. No. 1
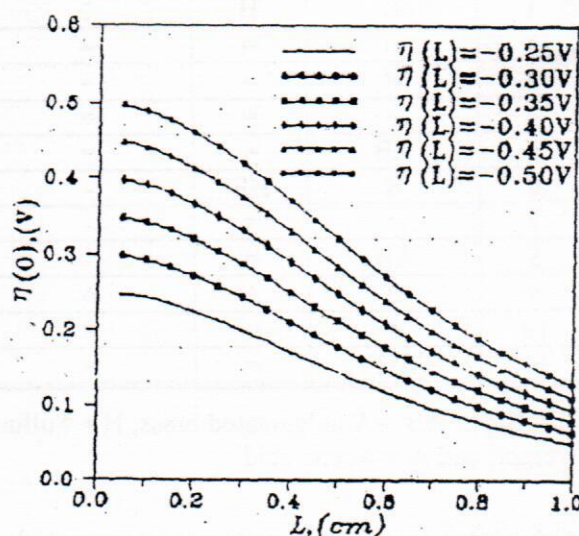

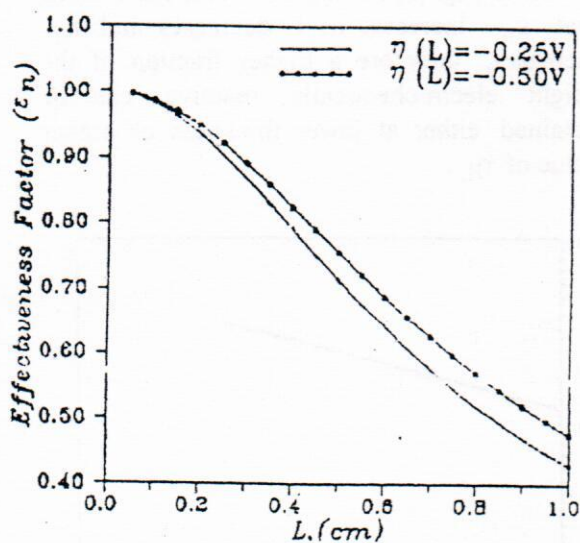Fig. (10) Influence of L on the overpotential at x=0 at different values of $\eta(L)$ of exp. No. 1

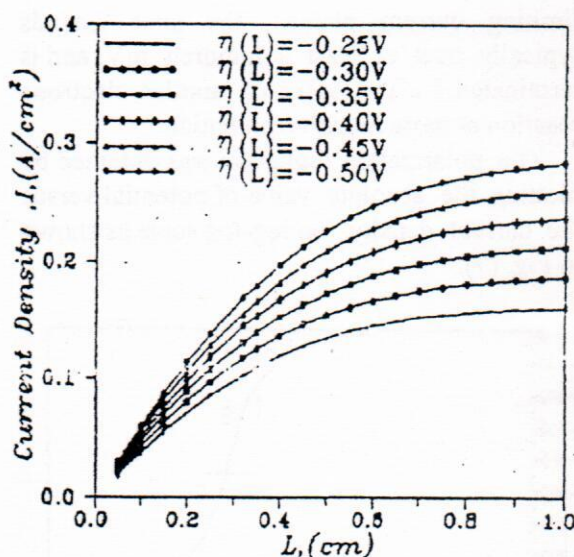Fig. (9) Influence of L and $\eta(L)$ on the effectiveness of exp. No. 1

Fig. (10) Influence of L on the overpotential at x=0 at different values of $\eta(L)$ of exp. No. 1

CONCLUSIONS

From the present investigation, the following conclusions are drawn:

1. It has been found experimentally that amalgamated brass screen electrode is more suitable than brass screen electrode for reduction of nitrobenzene.

2. It has been found theoretically that the lower the value of k_n the higher penetration depth in bed is. This is found by using polarization parameters obtained experimentally.

3. It has been found that k_n is small if: (I) The original bed thickness is small. (II) The

overpotential η_L has a high value. (III) The electrical conductivity of electrolyte is high.

4. It has been found that current density based on cross section area of bed increases as thickness of bed increases until a certain thickness where it reaches nearly a constant value.

REFERENCES

1. Pickett, "Electrochemical Reactor Design", Elsevier, New York, 1977.
2. Newman, J. S. & Tiedemann, W., "Flow Through Porous Electrodes", in C. W. Tobias (ed.), "Advances in Electrochemistry & Electrochemical Engineering", vol. 11, Electrochemical Engineering, John Wiley & Sons, P. 353, N. Y. 1978.
3. Coeuret, F., Hutin, D. and Gaunand, A., J. Appl. Electrochem., vol. 6, P. 417, 1976.
4. Paulin, M., Hutin, D. and Coeuret, F., J. Electrochem. Soc., vol. 124, No. 2, 180-186, 1977.
5. Coeuret, F., Hutin, D. and Gaunand, A., Electrochem. Acta, vol. 22, P. 93, 1977.
6. Neal, G. H. & Nader, W. K., AIChE. J., vol. 19, P. 112, 1973.
7. Peterson, E. E., "Chemical Reaction Analysis", Prentice-Hall, New Jersey, 1965.
8. Abbar, A. H., "Scale-Up of Electrochemical Reactors", M. Sc. Thesis, University of Baghdad, 1997.