Evaluation of the Effect of Mass Transfer on Fixed Bed Electrochemical Reactor for the Treatment of Industrial Produced Water

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Abstract
The removal of heavy metals like copper from industrial effluents is of great importance to both the industries and the ecosystem. The harmful effect of these metals if discharged into the water body results in the high rate of cancer in our society. This experimental research is directed towards the use of electrochemical fixed Bed reactor in the removal of copper ion from sulfate solution. The fixed Bed is in static state using activated carbon as its particle size. The high surface area is expected to give main transfer rate in the system. The variable parameters used in this work are applied current which varies from 2A, 4A and 6A, concentration of the copper in the solution 0.1mol, 0.05mol and 0.01mol. An experiment was conducted using a fixed bed electrochemical reactor filled with activated carbon particles. The over potential in the reactor was measured at different to total applied currents. The effect of concentration of the copper ions on the behaviour of the system was also studied. The experimental results show that increase in the total applied current occasioned negative increase in the over potential in the reactor. Also the result obtained showed that the higher the concentration the higher the deposition rate. Throughout this experiment, it was observed that electrochemical activities are heavily concentrated at the membrane. Only a small fraction of about 60 percent of the reactor was electrochemically active. Liquid flow rate has an effect on percentage removal of copper ion at low flow rate high percent of copper ion is been removed.

Keywords: Electrochemical Reactor, Fixed Bed Reactor, and Produced Water

1. Introduction

It is necessary to separate heavy metals from industrial effluents due to its high negative impact on the environment. Even in very low concentrations heavy metals are highly toxic to both humans and the ecosystem. Conventional methods have been used for the cleaning of these effluents such as: evaporation, absorption by ion-exchange resins, solvent extraction and precipitation. These processes produce lama and could be called dirty technology. Recently, electrochemical processes such as Electrodeposition, Electrooxidation Electrodisinfection, Electrocoagulation, and Electroflotation, are usually used because the technology is "clean". There are more advantages of electrochemical methods over the conventional methods: these includes; high separation efficiency, very easy to construct and operate. The separation process of these techniques uses electrochemical reactors and these reactors are classified as bi-dimensional (two plates) and three-dimensional when they contain conductive particles in electrolyte solution. Electrochemical reactors, particulate permit high rate of mass transfer with high specific area making them useful for treatment even in low current density and dilute solution. When the conductive particles are fluidized it is known as electrochemical fluidized bed reactors; otherwise, they are called electrochemical

fixed bed reactors. In an electrochemical bed reactor, when the electrolyte and current flows are in the same direction it is known as parallel flow while it is perpendicular when the fluid and current flow cross each other at right angle. The perpendicular arrangements are more used than the parallel ones because of the uniform current distribution in the system. It is pertinent to note that fixed bed conducting particles in a stream of electrolyte is more suitable for the design of a number of electrochemical reactor because of it three dimensional electrodes behavior.

Heavy metals such as Sb, Cu, Pb, Zn, Ni etc, present in industrial effluents are highly toxic and dangerous for both the aquatic life and the ecosystem. To avert the effect of these heavy metals on both human and aquatic lives, proper treatment and disposal is recommended. It is of great important to treat these effluents and reduce the concentrations of these heavy metals to acceptable standards before they are disposed of to the environment. Electrochemical techniques, offer more effective methods of treatment with the use of conductive particulate bed reactors in an electrolyte solution. In addition, electrochemical fixed bed reactor has more advantages over the conventional cleaning methods which include but not limited to: Safety, Clean reagent, Environmental compatibility, Versatility, Energy Efficiency and Cost effectiveness. The effective treatment of effluents has poses a challenge, especially for the chemical industry. In order to reduce pollution associated with the discharge of industrial effluents, efforts have been made by improving the process through product recycling and effective treatment of wastes at the production stage (Bernard & Odigure (2013)). In their studies, they concluded that effluents generated during petroleum refining process is within 0.4-1.6 time the amount of crude oil processed. Recently, a total of 33.6 mbpd of effluent is generated globally due to the current production yield of 84 million barrels per day (mbpd) of crude oil Vincenzo et al, (2015) .The discharge of effluents from the oil and gas industries will increase globally from the proposed expected rise of oil demand to 107mbpd since oil will account for over 32% of the world energy supply by 2030. Meanwhile, biofuels are expected to account for 5.9mbpd by 2030 and renewable energy sources will be reduced within 4- 15% Alessandra et al, (2006).

Due to the environmental consequences of discharging produced water to the environment, developed countries have put in place more stringent laws and regulatory standards for discharging PW. Contrary, water-stressed countries are focusing on efficient and cost-effective treatment methods to remove the pollutants for the water to be reused to meet their domestic demand. Research has being made on the new technology in the treatment of produced water. Extensive work on the characteristic and application of newly developed conventional technologies for the treatment of produce water using chemical methods; biological methods and advance oxidation process etc are carried out, Rajkumar and Palanivelu, (2004). In their research shows that oil content and salinity of produced water from both onshore and offshore can be treated using both chemical and physical methods but with high cost associated with them, biological method which is more cost effective can be used for the treatment of both dissolved and suspended compounds in oilfield wastewater. Electrochemical methods of treating petrochemical pollutants have proven to be more effective in recent years, (Farhana et al, (2014); Ahmed et al, (2014); and Andrea et al, (2013).

The process by which catalytic process could be monitor electrode potential which allows the current density is known as electrochemical reaction. Charges could be of finite rate, many models have been developed to determine the extra potential contribution and over potential needed for any current density to pass through the electrode, Ehirim, (2012).

Butter-volmer has given a well acknowledged model in determining the charges transfer kinetics. Electrochemical reaction is also seen to be a reversible first order reaction that has one electrode

This work will be implemented using literature data and an experimental set up of an electrochemical fixed bed reactor. The results from the experimental set and literature data were used to develop a mathematical equation for the electrochemical reactor. The model will aid in predicting the interior of the reactor, distribution of the rate of reaction and over potential distribution of the reactor. The results from the experimental set up were used to validate the model.

2. Mathematical Modeling

The electrochemical fixed bed reactor as shown in the above diagram in a rectangular shape has a high conductivity with non-porous particles. The surface area a_m, with a uniform porosity ε and thickness x. The positively charged ions moves in the same direction with the electric current, the current feeder is at x = L and the counter current at x = 0. The conductivity of both the solid and liquid phase is express as; σ_m and σ_s respectively. Base on the mathematical model formulated by Ehirim, (2012) on the transport equation, the model equation can be applied to solid-liquid state that will give a change in mass balance.

Mass balance solid phase

$$\frac{\partial}{\partial t}\left[(1-\varepsilon)C_{k,m}\right] + div\left[(1-\varepsilon)C_{k,m}\vec{V}_{k,m}\right] = (1-\varepsilon)R_{k,m} \tag{1}$$

Charge balance solid phase

$$div\left[(1-\varepsilon)\vec{\iota}_m\right] = (1-\varepsilon)F\sum_k \frac{zk}{mk}R_{k,m} \tag{2}$$

Mass balance liquid phase

$$\frac{\partial}{\partial t}\left[\varepsilon C_{k,s}\right] + div\left[\varepsilon C_{k,s}\vec{v}_{k,s}\right] = \varepsilon R_{k,s} \tag{3}$$

Charge balance liquid phase

$$div\left[\vec{\varepsilon\iota}_s\right] = \varepsilon F\sum k\,\frac{zk}{Mk}R_{k,s} \tag{4}$$

Chemical reaction rate of specie k, in the electrolyte can be written generally as;

$$R_{k,s} = a_m\frac{(1-\varepsilon)}{\varepsilon}\frac{i^*_{k,s}}{F\frac{zk}{Mk}} \tag{5}$$

Note,

$$i^*_{k,s} = i^*_{k,s}\left(\phi_s, \phi_m, C_{1,s}, C^*_{1,s}, \ldots\ldots\right)$$

Chemical reaction rate of specie k, in the unit volume of the liquid phase are $R_{k,s}$ and $i^*_{k,s}$ respectively, but for charge transferred per unit area of the liquid phase is z_k, molecular mass of chemical specie is M_k and 96500C/mol is the value for F which is the faraday constant.

3. Potential Distribution Equation in the Reactor

The basic assumptions made for the above equation are;

Potential distribution and current density are functions of x.

For concentration change in the bed to be insignificant there should be a high superficial velocity of the electrolytic solution.

Porosity and specific area are constant all through the reaction time.
The process system is isothermal.

Solid phase potential

$$\frac{d^2\phi_m}{dx^2} = \frac{1}{\sigma_m}\frac{\varepsilon}{(1-\varepsilon)}F\frac{z_k}{M_k}R_{k,s} \tag{6}$$

Liquid phase's potential

$$\frac{d^2\phi_s}{dx^2} = -\frac{1}{\sigma_s}F\frac{z_k}{M_k}R_{k,s} \tag{7}$$

Boundary Conditions
For change transfer the conditions are:
All current at the feeder is carried by the liquid phase while the receptor is carried by the metallic phase. Thereby,

$$x = 0; \frac{d\phi_s}{dx} = 0 \text{ And } x = X, \frac{d\phi_m}{dx} = 0 \tag{8}$$

When there is a constant current in the system

$$x = 0; \frac{d\phi_m}{dx} = -\frac{I}{(1-\varepsilon)\sigma_m A} \tag{9}$$

$$x = X, \frac{d\phi_s}{dx} = -\frac{I}{\varepsilon A \sigma_s} \tag{10}$$

I- total current applied and A = A$_L$ = Y.L (t) is the lateral area of the bed.

3.3.2   Kinetic of the System
In the solid phase, the boundary layer of the width σ, and chemical reaction rate of specie k, in liquid phase for electron transfer is:

$$i^*_{k,s} = -F\frac{z_k}{M_k}\frac{D_k}{\delta}\left(C_{k,s} - C^*_{k,s}\right) \tag{11}$$

Substituting Equation (11) into Equation (5), gives

$$R_{k,s} = -a_m\frac{(1-\varepsilon)}{\varepsilon}\frac{D_k}{\delta}\left(C_{k,s} - C^*_{k,s}\right) \tag{12}$$

The intrinsic kinetic that exist at the solid-liquid interface is expressed by Butler-Volmer as;

$$i^*_{k,s} = i_0\left\{\exp\left[-\frac{\alpha nF}{RT}\eta\right] - \exp\left[\frac{(1-\alpha)nF}{RT}\eta\right]\right\} \tag{13}$$

Where,

$$i_o = nFk_oC^*_{k,s}$$

Substituting equations 13 into equation 5 gives.

$$R_{k,s} = -a_m\frac{(1-\varepsilon)}{\varepsilon}\frac{M_k}{Fz_k}i_o\left\{\exp\left[-\frac{\alpha nF}{RT}\eta\right] - \exp\left[\frac{(1-\alpha)}{RT}\eta\right]\right\} \tag{14}$$

for the chemical specie k, D_k is the diffusion coefficient in the reaction, n is the number of electrons in the reaction, i_o is the exchange current density, $C_{k,s}$ and $C_{k,s}^*$ are bulk and superficial concentrations, respectively, δ is the width of the boundary layer, α is the change transfer coefficient, and η is the sustention in the reactor defined by the relation:

$$\eta = \phi_m - \phi_s - \left[E_{eq} + \frac{RT}{nF} \ln\left(C_{k,s}^*\right) \right] \tag{15}$$

When the process is generally controlled by both the intrinsic kinetic and mass transfer $C_{k,s}^*$, can be eliminated in equations 11 and 12 to yield

$$R_{k,s} = -a_m \frac{(1-\varepsilon)}{\varepsilon} C_{k,s} \frac{\Theta}{\left[1 + \frac{\delta}{D_k} \Theta \right]}$$

$$\Theta = \frac{M_k}{z_k} n k_o \left\{ \exp\left[-\frac{\alpha n F}{RT} \eta \right] - \exp\left[\frac{(1-\alpha)nF}{RT} \eta \right] \right\} \tag{16}$$

Since equation 3.17 has limit, therefore,

when $\delta \to 0, then \left[1 + \frac{\delta}{D_k} \Theta \right] \to 1$, equation 16 will becomes

$$R_{k,s} = -a_m \frac{(1-\varepsilon)}{\varepsilon} \Theta C_{k,s} \tag{17}$$

If $\delta \gg 0$ then $\left[1 + \frac{\delta}{D_k} \Theta \right] \to \frac{\delta}{D_k} \Theta$ equation 16 can be reduces to

$$R_{k,s} = -a_m \frac{(1-\varepsilon)}{\varepsilon} \frac{D_k}{\delta} C_{k,s} \tag{18}$$

For an intrinsic reaction, equation 17 is used, while for process controlled by mass transfer equation 18 is used.

Over Potential in the Reactor
The model for distribution of surtension in the reactor can be obtained when equation 6 subtracted from equation 5, and the substituted into equation 12:

$$\frac{d^2\eta}{dx^2} = -a_m \left[\frac{1}{\sigma_m} + \frac{(1-\varepsilon)}{\varepsilon \sigma_s} \right] \frac{D_k}{\delta} F \frac{z_k}{M_k} \left(C_{k,s} \right) \tag{19}$$

The respective boundary conditions are

$$\left(\frac{d\eta}{dx} \right)_{x=0} = -\frac{I}{(1-\varepsilon)\sigma_m A} \tag{20}$$

$$\left(\frac{d\eta}{dx} \right)_{x=x} = \frac{I}{\varepsilon \sigma_s A} \tag{21}$$

3. Materials and Method
3.1   Materials (write in sentence form)
The following materials used for this study were Storage Tank Valves to control both the inlet and outlet flows. Connecting pipes, Electrical instillations (wires, rheostat,18 volt DC cell, wires, ammeter and voltmeter) Copper plate metals Plastic glass as reactor wall Asbestos as diaphragm Activated carbon Copper solution (CuSO4) Circulating Pump.
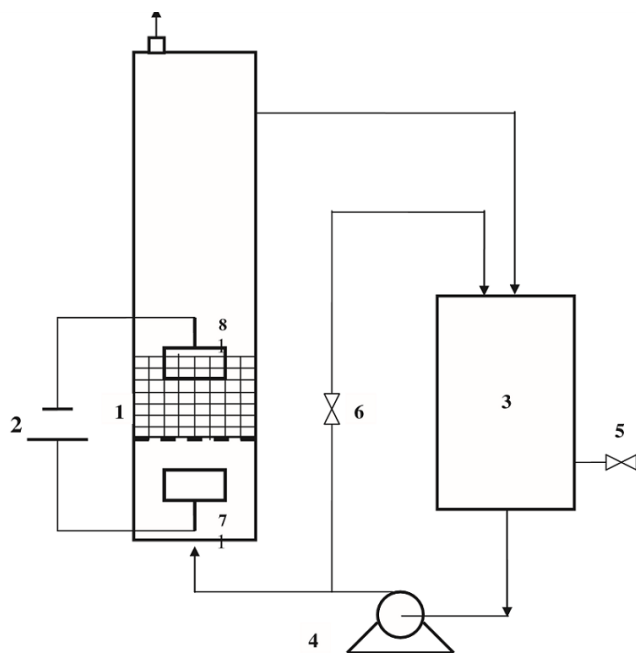
3.2 Experimental set – up and Procedure

Fig 1: Electrochemical Fixed Bed Reactor for Copper Removal Activated carbon bed, 2- DC power supply, 3- Holding Tank, 4- Circulating pump, 5- Sampling point, 6- Flow valve, 7- Current feeder, 8- Current Collector

The set up consist of an electrolytic cell, DC of 18 volt power supply, circulating pump, holding tank in which the solution is contained, flow regulating valve, an ammeter to determine the potential difference in the reactor, a potentiometer to sensor the potential difference in the reactor, a voltmeter, a rheostat, copper solution and activated carbon from coconut shell as particle bed.

The reactor was made of a plastic glass of rectangular shape; thickness was 10'' and diameter of 0.19m with a particle bed height of 0.08825m. The column was separated by a current distribution feeder made of copper plate with 0.2m thickness while the reactor height was 0.3m. The current feeder (anode) was fixed to the left hand side of the reactor and the current collector (cathode) on the right. The solution flow from the holding tank into a reactor through a PVC pipe of 2'' having a valve to regulate the both inlet flow and outlet flow in and out of the reactor, graduated cylinder was used to determine the flow rate of both the inlet and outlet flow and a stop watch and was fixed at 450±50ml/min. The holding tank containing the solution of copper was connected to the reactor while the outlet valve was closed. An electrolytic cell, DC 18 volt was connected in series with the voltmeter, rheostat. The current then passed from the rheostat to the reactor. An ammeter was also connected in series to the reactor and the potentiometer to determine the potential difference across the width of the reactor. The concentration of the solution was varied from 0.1mol, 0.05mol and

0.01mol while the current density also varied from 2A, 4A and 6A. The particle bed used was activated carbon obtained from coconut shell with porosity of 0.36(value obtained from literature). The reaction was initiated with an initial concentration of 0.01mol and current density of 2A. The concentration was kept constant while the current densities changed from 2A, 4A and finally 6A. This was done repeatedly for all the concentration, the concentration was measured using a spectrophometer. This experiment was carried out at room temperature.

Results and Discussion
Over Potential in Fixed Bed Reactor (L) = 0.019m
There is a negative increase of over potential for high applied current in the reactor, which implies that high current density will produce a higher reaction rate. Copper ions in the solution will react with the available electrons is a function of the increase in the density of the current. It was observed that electrochemical activities are confined to the area close to the membrane making the region more favorable to the deposition of copper metal. This result shows that there is a high electrochemical reaction rate associated with fixed bed reactors. The cathodic increases of the over potential at the region closed to the membrane are probably due to the physical impedance imposed by the membrane to the electrons. The over potential distribution shown in fig 4.1 shows that the reactor has an effect on the pore point of the reactor.
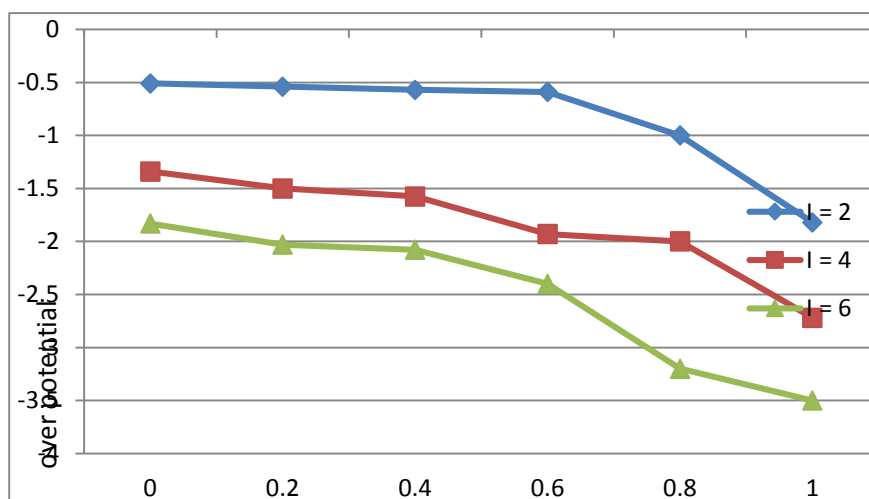

Fig.4.1 Graph of over potential distribution against reactor width

4.3 Validation of Model with Experimental Results
From equation 3.20 the simulated results was validated with experimental data's. Values of the simulated and experimental results are plotted in the graphs below. In this simulation σ_m and σ_s were obtained from German and Goodridge (1975), whose values are 600 ohm $^{-1}m^{-1}$ and 60ohm $^{-1}m^{-1}$ respectively. The reactor has a lateral area (current feeder) of $0.008m^2$ and a width of 0.0192m and porosity of 0.36 and specific area of 600m. The concentration of the copper ion in the electrolyte was 508.361g/m^3 while the current feeder values were 2A, 4A and 6A.
It can be observed from the graph, that the experimental result and model are in agreement.
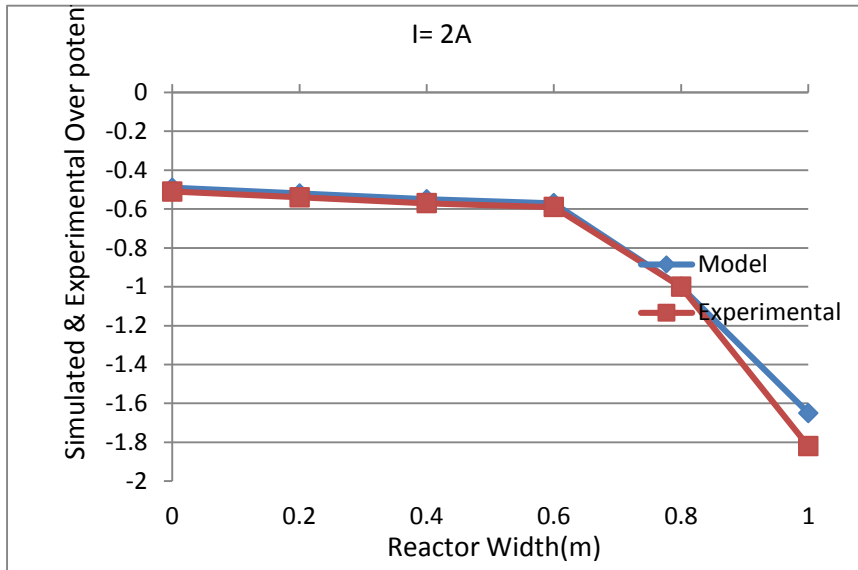The following data's on the table below were used to simulate the equations 20, 21 and 22.

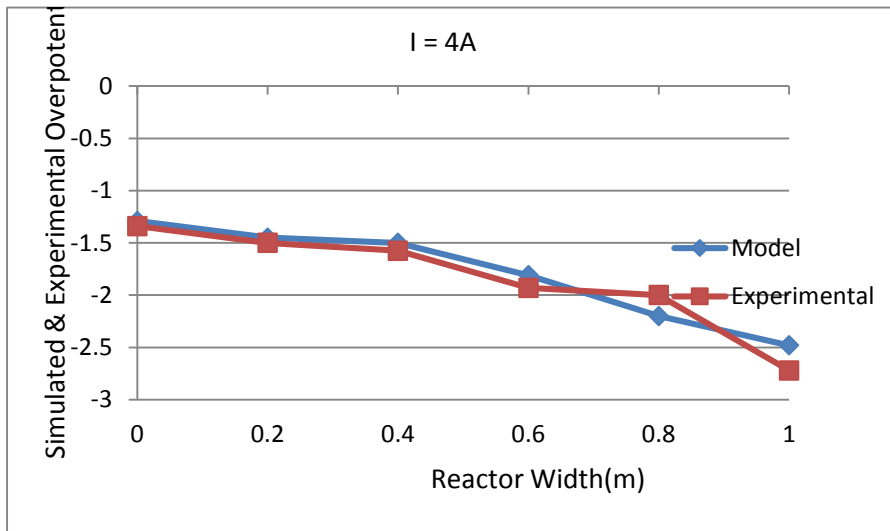**F ig. 4.2:** Graph of Model and Experimental Overpotential Distribution in the reactor

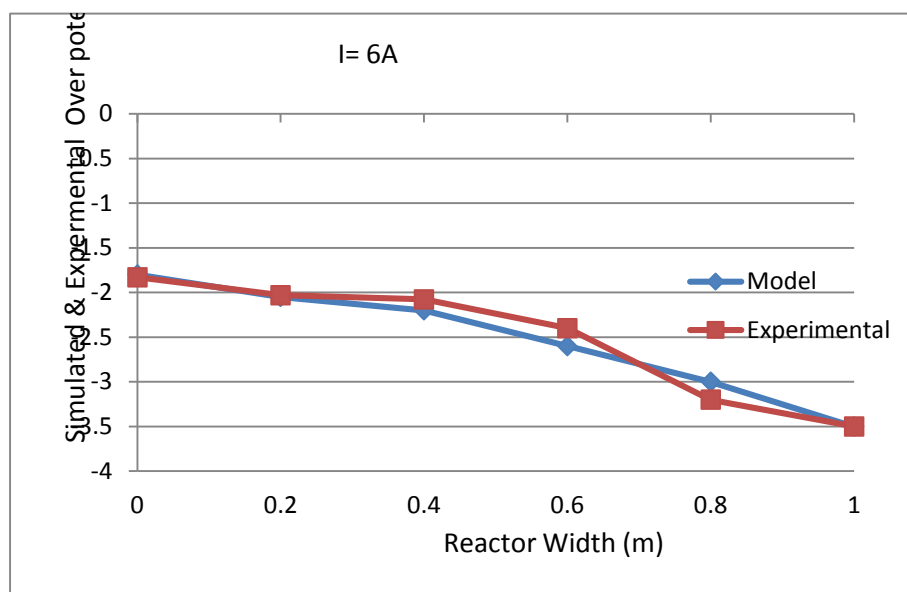**Fig 4.3** Graph of Model and Experimental over Potential for I = 4A

Fig 4.4 Graph of Simulated & Experimental over Potential vs Reactor Width for I = 6A

5. Conclusion

1. A mathematical model on mass transfer was developed for an electrochemical fixed bed reactor. The model developed is in agreement with the experimental results obtained.

2. Over potential in the reactor was measured which shows that electrochemical activities occurs majorly at the region close to the membrane. Only one third of the reactor was electrochemically active. The reactor becomes inactive at the feeder when the pores are completely closed.

3. The rate of reaction in the reactor was calculated and the research shows that there is an increase in the reaction rate with the increase in the concentration of the copper ions in the solution.

4. As the applied current increases, the reaction rate also increases. Thus, the reaction will remain constant if there is no alternation of the applied current throughout the operating time.

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