



Modeling electrowinning process in an expanded bed electrode

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ABSTRACT

A theoretical model has been developed to describe the flow behavior of conducting particles in a fluidized bed electrode for electro winning of metal ions present in the dilute solution. Model equations have been developed for potential and current distributions and mass transfer rates. The influence of operating parameters on particle growth has been critically examined. It has been observed from the present investigation that the particle size increased with electrolysis time. The present model simulations have been compared with the experimental data reported in the literature and observed that the model predictions satisfactorily match with the reported experimental findings.

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1. Introduction

Water contaminated with metals and toxic organics pose a significant threat to human health and the quality of water supply to the aquatic environments. The removal of heavy metals present in the industrial effluent wastewater receiving greater attention among researchers as they not only contaminate the water bodies but also cause series threat to many life forms. Since most of heavy metals are non-degradable, the disposal of heavy metals present in the industrial effluent has becomes a major environmental issue [1]. The increased environmental awareness and the stringent regulations of Pollution Control Board regulations forced the industries to look for an efficient treatment technique.

The heavy metals present in the industrial effluent is conventionally treated with chemical precipitation, adsorption, sedimentation, filtration, biological process and chemical reaction [2–7]. However, these techniques have their own limitations when they are implemented individually. For example, the conventional chemical precipitation technique generates large amount of solid sludge which itself needs further treatment. On the other hand, the biochemical technique is time consuming and some of the heavy metals are resistant to biochemical technique. This forced the scientists/industries to look for an alternative method for effective removal heavy metals present in the industrial effluent.

In recent years, the application of fluidized bed is being extended for the removal of heavy metals present in the industrial effluent [8,9]. Fluidized bed electrodes (FBE) finds extensive applications in chemical process industries as it offers large transfer area, improved heat and mass transfer between the phases, suitability for large scale operation and easy scale up.

2. Fluidized bed electrode

Fluidization is an operation through which fine solids are transformed into a fluid like state through contact with either a gas or a liquid for better heat and mass transfer between the phases. The applications of fluidized beds are being extensively tried for electrochemical processes such as electro synthesis, electro winning, etc. Extensive work has been reported on fluidized bed electrodes for environmental applications. Hadzismajlovic et al. [10] reported the electrochemical behavior of metal particles in spouted, packed and fluidized bed electrodes. LeRoy [11,12] studied the electro winning of copper metal ions present in the dilute solution using fluidized bed electrode and proposed a model for electro winning. Bertrand et al. [13] developed a particle growth mechanism for tin oxide films on Ni particles in Fluidized Bed.

The critical review of the literature shows though good amount of literature on utilization of fluidized bed electrode for environmental applications, the work related to understanding of flow behavior of conducting particle inside the fluidized bed is very limited. The objective of the present work is to develop a theoretical model for to describe the flow behavior of solid particle inside a fluidized bed. A layered growth model has been proposed for particle

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Nomenclature

a	Specific surface area ($\text{m}^2 \text{m}^{-3}$)
C_o	Initial concentration of the effluent (M)
C_{out}	Final concentration of the effluent (M)
d_{pa}	Average particle diameter (μm)
D_s	Diffusivity of solid particle ($\text{m}^2 \text{s}^{-1}$)
E	Equivalent weight of the metal
E_0	Equilibrium potential (V)
F	Faraday constant (96,485 C)
g	Gravitational constant (m s^{-2})
G	Total increase in bed weight (kg)
i	Current density (A m^{-2})
i_l	Electrolyte current density (A m^{-2})
i_m	Electrode current density (A m^{-2})
$\frac{k_m L}{D}$	Sherwood number
K_m	Mass transport coefficient (m s^{-1})
n	Number of electrons involved
N	Number of particles (g^{-1})
ΔP	Total pressure drop (KPa)
S	Surface area of the electrode (cm^2)
t	Electrowinning time (min)
U_l	Electrolyte velocity (m s^{-1})
U_{mf}	Minimum fluidization velocity (m s^{-1})
$\frac{U_l L}{\nu}$	Reynolds number
$\frac{\nu}{D}$	Schmidt number
V_c	Current feeder potential (V)
W_i	Initial bed weight (kg)
x	Thickness of the growth layer (μm)
x_f	Replacement fraction

Greek symbols

ε	Bed voidage
ϕ_l	Electrolyte potential (V)
ϕ_m	Electrode potential (V)
κ_1	Apparent electrolyte conductivity (S m^{-1})
κ_m	Apparent electrode conductivity (S m^{-1})
κ_{10}	Pure electrolyte conductivity (S m^{-1})
κ_{m0}	Pure electrode conductivity (S m^{-1})
μ_1	Viscosity of electrolyte ($\text{kg m}^{-1} \text{s}^{-1}$)
ρ_s	Density of solid particle (kg m^{-3})
ρ_l	Density of electrolyte (kg m^{-3})

Subscripts

a	mean
c	cathode
f	fraction
i	initial
l	Electrolyte component
m	Electrode component
mf	minimum fluidization
p	Solid particles

growth mechanism. Model equations are developed for potential distribution and current distribution and the mass transfer rate. The influence of operating parameters on particle growth has been critically examined.

3. Model development

The schematic diagram of fluidized bed electro winning process is given in the Fig. 1. The bed is charged with fine and known uniform sized particles to have smooth fluidization. The effluent with

Table 1
Parameters used in the simulation

Symbol	Values used
μ_1	0.001
ρ_l	1000
W_i	12.25
η	90
d_p	200
ρ_s	8900
D_s	0.67×10^{-9}
κ_{10}	8
κ_{m0}	600
C_o	0.0005
C_{out}	0.00005
t	30
n	2

metal ions is passed through the bed resulting smooth expansion of bed particles and the bed expansion depends on the particle size and the liquid velocity. When charge is supplied to bed, the suspended metal ions present in the liquid effluent tend to deposit on the surface of the dispersed phase (conducting particles). The particle size increased during the electro winning process and grown particles (heavier particles) tend to settle down to the bottom of the bed. After a period of time, a portion of the grown particles are removed from the bed and an equal amount of fine sized particles are added. Obviously, this kind of one-step operation has several advantages:

- It is a single step process without generation of secondary pollutants.
- The space requirement can be minimized to a large extent.
- Since the heavy metals are coated on the particle surface, no sludge formation occurs.
- The recovered metal ions can be used without any further treatment.

The following assumptions were made while developing the model equations

- The metal ions are distributed uniformly throughout the reactor.
- The metal ions are deposited concentrically around the core of fluidized bed particle.
- The metal ions present in the wastewater are deposited over the fluidized bed particle in an orderly manner.

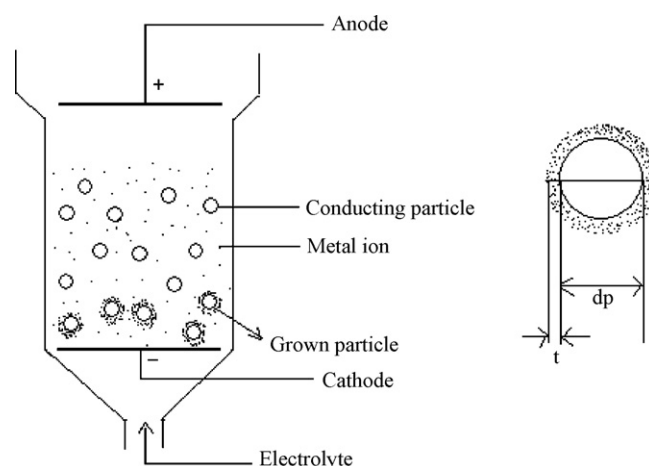


Fig. 1. The schematic diagram of fluidized bed electro winning process.

(iv) The growth of particle size can be assumed to be layered growth.

The growth of particle size during the process can be written as [14]:

$$4x^3 + 6x^2d_p + 3d_p^2x = \frac{\rho_s d_p^3}{2M} \quad (1)$$

where x is the thickness of the growth layer, d_p is the particle diameter and M is the mass of the solid particle. The mean diameter of the coated particles is given as

$$d_a = d_p + 2x \quad (2)$$

where d_a refers the mean particle diameter. The number of particles in the fluidized bed electrode can be estimated using the following equations, i.e.,

$$N = \frac{\text{total volume particle}}{\text{volume of particle diameter}}, \quad \text{i.e. } N = \frac{W/\rho_s}{(\pi/6)d_a^3} \quad (3)$$

The particle surface area can be estimated using the following equation

$$S = N(\pi \times d_a^2) \quad (4)$$

It is assumed that the number of particles in the reactor remains constant during the electro winning process and metal ion removal is reflected in terms of increased bed weight. The constant number of particles in the fluidized bed electrode is maintained with addition of fresh particles whenever the grown particles are withdrawn. The total bed weight can be estimated using the following equation:

$$G = \frac{\eta E}{F} t \quad (5)$$

where G refers total bed weight, η refers the current efficiency, ' E ' refers equivalent weight of the metal, t refers the electrowinning time and F is the Faraday constant. The weight of particles withdrawn from the bed can be given as

$$W_w = G + x_f W_i \quad (6)$$

where W_w is the weight of the particles withdrawn. The number of particles remaining in the bed after the withdrawal of grown particles can be given as

$$N_r = \frac{W_i(1 - x_f)N_0}{W_i + G} \quad (7)$$

where N_r is the number remaining in the bed, W_i is the initial weight of the bed, x_f is the replacement fraction, N_0 is the initial number of particles. The weight of particle added to the system to compensate for the withdrawal can be given as

$$W_{in} = \frac{G + x_f W_i}{W_i + G} W_0 \quad (8)$$

where W_{in} refers the particle weight added to the system. The weight of particles added to the bed [Eq. (8)] compensates for the weight withdrawn from the bed resulting in a constant number of particles during the process. The increase in the bed weight at the beginning of the 2nd cycle [i.e., $(i + 1)$ cycle] can be given as

$$W_{i+1} = \frac{G + x_f W_i}{W_i + G} W_0 + (1 - x_f)W_i \quad (9)$$

The corresponding increase in the bed weight during 1st cycle can be given as

$$\Delta W = \frac{G + x_f W_i}{W_i + G} W_0 - x_f W_i \quad (10)$$

where ΔW refers the increase in the bed weight during 1st cycle. The pressure drop inside the fluidized bed electrode can be estimated using Ergun's equation [15]. The pressure drop across the bed can be given by,

$$\frac{\Delta P}{L} = g(1 - \varepsilon)(\rho_s - \rho_l) \quad (11)$$

where ΔP is the total pressure drop across the bed, L is the bed height, μ is the electrolyte viscosity, d_p is the particle diameter and ρ_l is the electrolyte density. The bed voidage can be written as

$$\frac{\varepsilon^3}{1 - \varepsilon} = \frac{150U_l\mu}{g(\rho_s - \rho_l)d_a^2} \quad (12)$$

The particle minimum fluidization velocity and terminal velocities are estimated using the following equations [16]. The particle minimum fluidization velocity can be given as

$$\frac{\rho_l d_a U_{mf}}{\mu_1} = \left[(33.7)^2 + 0.0408 \frac{d_a^3 \rho_l (\rho_s - \rho_l) g}{\mu_1^2} \right]^{1/2} - 33.7 \quad (13)$$

where U_{mf} refers the particle minimum fluidization velocity, ρ_l is the electrolyte density, ρ_s is the density of solid particle, μ_1 is the electrolyte viscosity and g is the acceleration due to gravity. The particle terminal velocity can be written as

$$U_t = \frac{g(\rho_s - \rho_l)d_a^2}{18\mu_1} \quad Re < 0.4 \quad (14)$$

$$U_t = \left[\frac{4}{225} \frac{(\rho_s - \rho_l)^2 g^2}{\rho_l \mu_1} \right]^{1/3} d_a \quad 0.4 < Re < 500 \quad (15)$$

$$U_t = \left[\frac{3.1(\rho_s - \rho_l)gd_a}{\rho_l} \right]^{1/2} \quad 500 < Re \quad (16)$$

where U_t refers the particle terminal velocity. The model Eqs. (1)–(16) give the particle growth mechanism for a given operating conditions. It is known fact that the electrode reaction can be controlled by the applied current or the electrode potential. Let us consider a simple electrode reaction: $A + ne \rightarrow B$. The electrode reaction can be controlled either by kinetic or mass transfer [17]. The following assumptions are made for the development of model equations to predict the electro winning in the fluidized bed electrode.

- (i) System is one-dimensional (all variables area functions of position in the x -direction only).
- (ii) The operation is under limiting current density.

The limiting current density per unit of electrode surface area is related to the mass transfer coefficient as

$$i_l = nFk_m C \quad (17)$$

The current and potential distributions in a fluidized bed electrode can be given as

$$i_m = -\kappa_m \frac{d\phi_m}{dx} \quad (18)$$

$$i_s = -\kappa_s \frac{d\phi_s}{dz} \quad (19)$$

where κ_s and κ_m represent the conductivity of the electrolyte and the electrode material, respectively. Further more the electrode and electrolyte current can be related to local current density. The electrolyte current density can be written as

$$\frac{di_s}{dz} = -ai \quad (20)$$

where 'a' represents the specific surface area of the electrode, i.e., $a = 6(1 - \varepsilon)/d_p$. Similarly the electrode current density can be written as

$$\frac{di_m}{dz} = ai \tag{21}$$

The following boundary conditions can also be applied for solving the equations.

$$\begin{aligned} i_m &= 0 & \text{at } x &= 0 \\ i_s &= 0 & \text{at } x &= d \\ \varphi_s &= 0 & \text{at } x &= 0 \\ \varphi_m &= V_c & \text{at } x &= d \end{aligned}$$

Considering the above mechanisms along with the boundary conditions, the equations for current and potential distribution for the electrode and electrolyte are given as

The electrolyte current density is written as

$$i_l = U_1 n F C_{out} \left\{ \frac{C_o}{C_{out}} - \exp\left(-\frac{aK_m x}{U_1}\right) \right\} \tag{22}$$

The electrode current density is given as

$$i_m = U_1 n F C_{out} \left\{ \exp\left(-\frac{aK_m x}{U_1}\right) + 1 \right\} \tag{23}$$

The mass transport coefficient K_m can be related to Reynolds and Schmidt numbers as [18]

$$K_m = 0.71 U_1 \left[\frac{U_1 d_a \rho_l}{\mu_l (1 - \varepsilon)} \right]^{-0.33} \left[\frac{\mu_l}{\rho_l D_s} \right]^{-0.67} \tag{24}$$

The conductivity of each phases are related to their pure conductivities as

For electrolyte phase

$$\kappa_l = \kappa_{l0} \frac{2\varepsilon}{3 - \varepsilon} \tag{25}$$

For electrode phase

$$\kappa_m = \kappa_{m0} (1 - \varepsilon)^{1.5} \tag{26}$$

The electrolyte potential φ_l is given as

$$\varphi_l = \frac{U_1^2 n F C_{out}}{a K_m \kappa_s} \left\{ \exp\left(-\frac{a K_m x}{U_1}\right) + \left(\frac{a K_m C_o x}{U_1 C_{out}}\right) + 1 \right\} \tag{27}$$

Similarly the electrode potential φ_m can be given as

$$\varphi_m = V_c - \frac{U_1^2 n F C_{out}}{a K_m \kappa_m} \times \left\{ \exp\left(-\frac{a K_m x}{U_1}\right) - \left(\frac{a K_m (d - x)}{U_1}\right) + \frac{C_o}{C_{out}} \right\} \tag{28}$$

The local over potential η can be calculated from the electrolyte potential, electrode potential and reaction concentration which is given as

$$\eta = \varphi_m - \varphi_l - \left[E_0 + \frac{RT}{nF} \ln\left(\frac{C_o}{C_{out}}\right) \right] \tag{29}$$

The Eqs. (17)–(29) give the theoretical analysis of potential and current distribution in the fluidized bed electrode and the equations can be solved to obtain the current and potential distributions. The system can be considered as convective diffusion controlled process by assuming that there is enough supporting electrolyte to maximize the migration of electro active species. The concentration of metal ion at the surface of electrode is influenced by convective and conductive diffusion metal ion, can be expressed as

$$\frac{\partial C_o}{\partial t} = 0 = D_0 \left(\frac{\partial C_o}{\partial t} \right)_{diff} - U \left(\frac{\partial C_o}{\partial t} \right)_{conv} \tag{30}$$

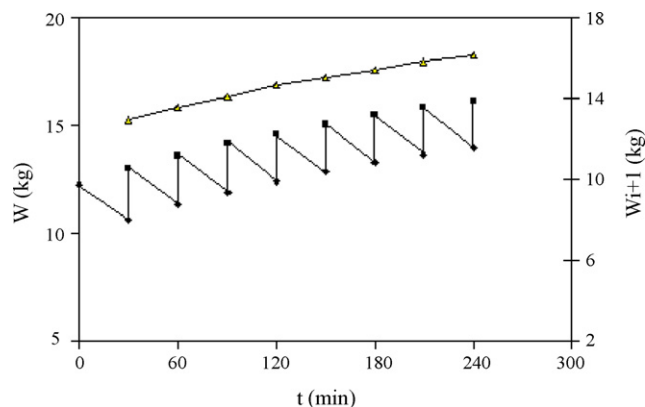


Fig. 2. The rate of increase in the bed weight with process time. d_p : 200 μm , w : 12.25 kg; i : 0.485 mA cm^{-2} .

The above equation can be extended to three dimensions as

$$\frac{\partial C_o}{\partial t} = 0 = D_0 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) C_o - \left(U_x \frac{\partial}{\partial x} + U_y \frac{\partial}{\partial y} + U_z \frac{\partial}{\partial z} \right) C_o \tag{31}$$

where x, y, z are the normal Cartesian coordinates and, U_x, U_y and U_z are the flow velocities corresponding to these coordinates. The relationship between the velocity of the electrolyte and the forces acting upon can be by the Navier–Stoke equation as

$$\left[\left(U_x \frac{\partial}{\partial X} \right) + \left(U_y \frac{\partial}{\partial Y} \right) + \left(U_z \frac{\partial}{\partial Z} \right) \right] U_u = \left(\frac{\nu}{U_0 L} \right) \nabla^2 U_u \tag{32}$$

where X, Y and Z are the Cartesian coordinates while x, y and z divide by the characteristic length for the specific geometry, L ; U refers velocity component ($U = x, y$ or z) divided by the characteristic velocity within the prandtl layer and ν is the kinematic viscosity of the liquid. The Eqs. (30)–(32) are differential equations defined for the system in terms of convective mass transport. The analytical solution can be written in terms of dimensionless numbers. The mass transport process is a function of electrolyte velocity, viscosity, diffusion coefficient, mass-transfer coefficient, and the characteristic length, i.e.,

$$\pi = f(L, k, D, \nu, U_1) \tag{33}$$

The above equation can be written in terms of dimensional numbers as

$$\pi = \left(\frac{k_m L}{D} \right)^a \left(\frac{U_1 L}{\nu} \right)^b \left(\frac{\nu}{D} \right)^{-(b+c)} \tag{34}$$

where a, b and c are the characteristic exponents for each cell arrangement. The mass transfer equation for the present case can written as

$$Sh = 0.29 Sc^{1/3} Re^{3/4} \quad \text{for } 100 \leq Re \leq 5000 \tag{35}$$

The Eqs. (30)–(35) give the mass transfer in the fluidized bed electrode.

4. Results and discussion

The model equations have been solved numerically and the results are presented in Figs. 2–11. The Table 1 gives detail of the parameters used in the simulation. The number of particles in the reactor remains constant during winning process and the removal of metal ion present in the effluent is reflected in terms of increased bed weight. The constant number of particles in the fluidized bed

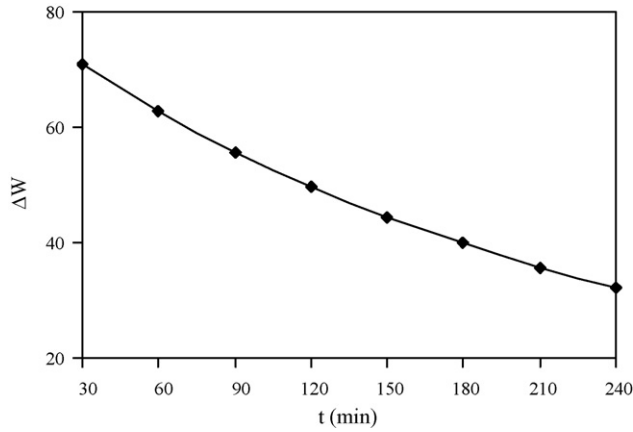


Fig. 3. The percentage of bed weight increase with process time. d_p : 200 μm , w : 12.25 kg; i : 0.485 mA cm^{-2} .

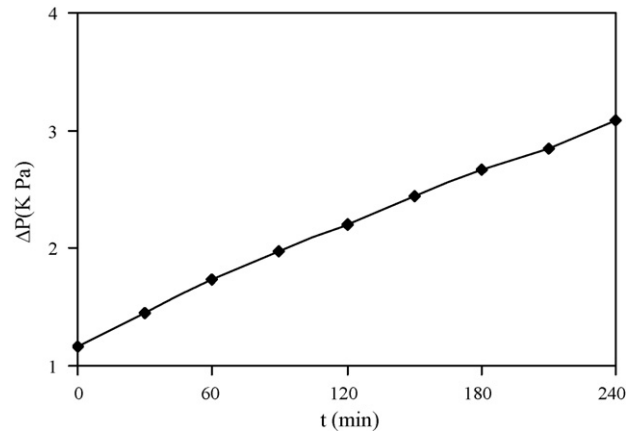


Fig. 6. The variation of pressure drop with electro winning cycle. d_p : 200 μm .

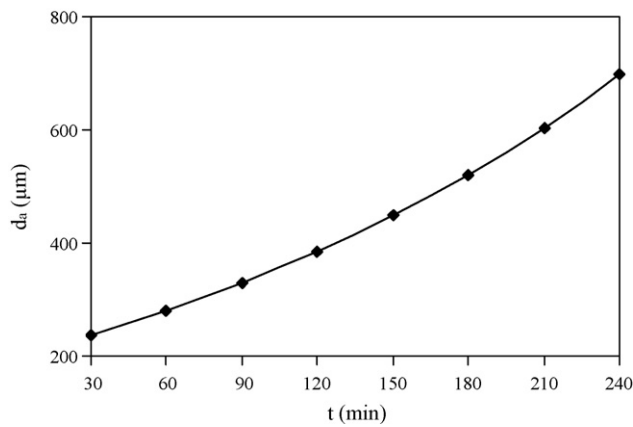


Fig. 4. The variation of particle diameter during electro winning.

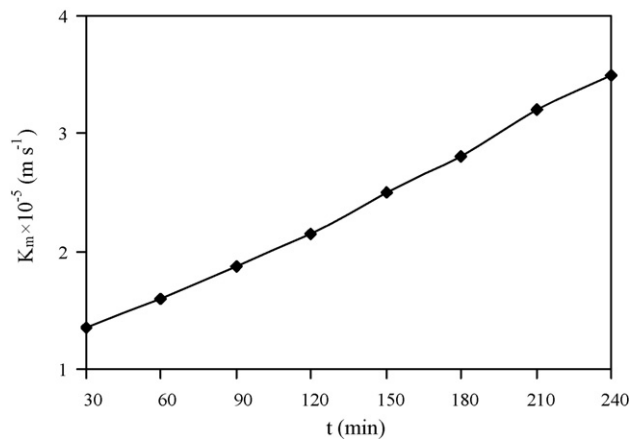


Fig. 7. The variation of mass transport coefficient with electro winning cycle. d_p : 200 μm .

electrode was maintained with addition of fresh particles whenever the grown particles are withdrawn. The distribution of weight inside the fluidized bed during winning process is given in Fig. 2. It can be ascertained from Fig. 2 that the bed weight increased during electro-winning process and decreased at the time of completion of each cycle. It can also be observed that the bed weight increased with the addition of fresh batch of solids during second cycle of operation. Further more it can also be noticed that the bed weight increases with processing time. This can be explained that the process is a constant number of particles and accordingly the bed weight increases.

Fig. 3 shows the percentage of increase in bed weight with each cycle of electrode process. As stated earlier, the increase in bed weight with the addition of fresh material after each cycle is given in Eq. (10). It can be ascertained from Fig. 3 that an increase in the percentage of bed weight decreases with each cycle of operation. It can be explained that the cycle of process is designed for withdrawal at every 30 min cycle and the amount of withdrawal is compensated with the addition of a fresh batch of bed materials.

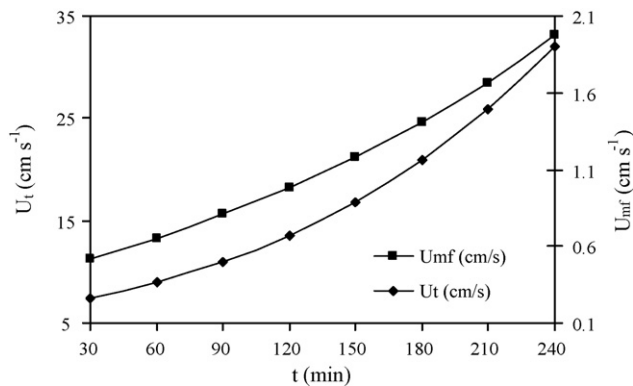


Fig. 5. The rate increase in minimum and terminal particle velocity during the winning process. d_p : 200 μm .

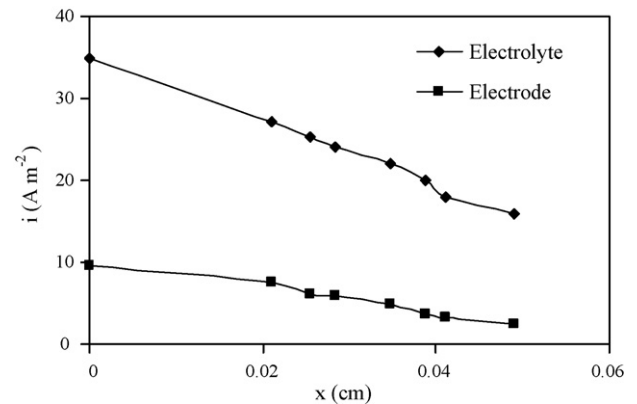


Fig. 8. The rate decrease in electrode and electrolyte current density with process time.

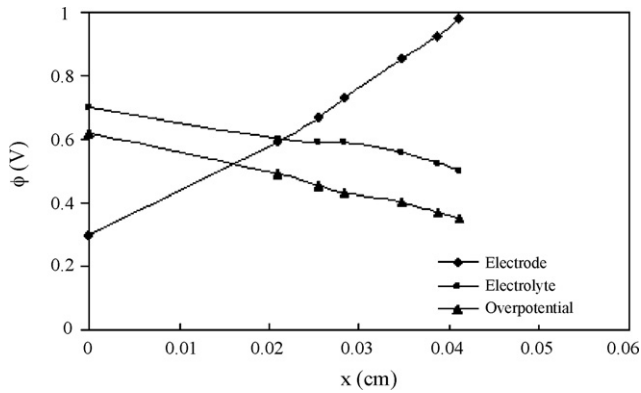


Fig. 9. The potential distribution during the winning process. d_p : 200 μm .

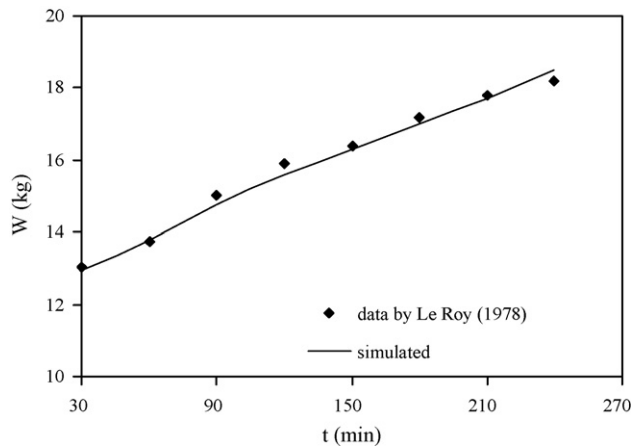


Fig. 10. Comparison of the model simulation for bed weight increase with the experimental data reported due to LeRoy [11,12].

The average diameter of bed particles at the end of each electro-winning cycle was calculated and the size distribution is given in Fig. 4. It can be ascertained from Fig. 4 that the average particles size increased with every cycle of winning process. This may be due to the fact that at the end of each cycle only a fractional amount of grown particles are removed which is compensated by the fresh particles resulting in a increased average particle size.

The minimum fluidization velocity and the terminal velocity of bed particle have been calculated and given in Fig. 5. It can be

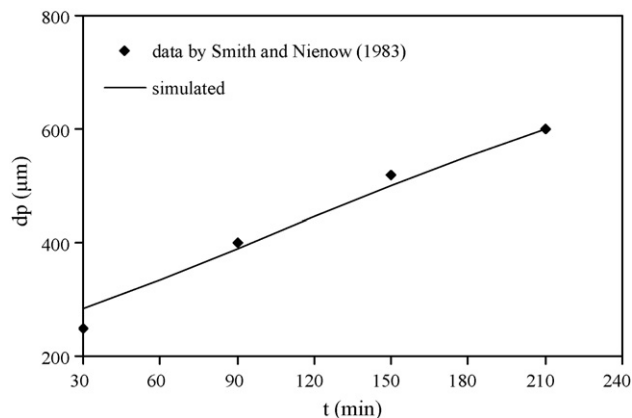


Fig. 11. Comparison of the model simulation for increase in the particle size with the experimental data reported due Smith and Nienow [14].

noticed from the figure the particle minimum fluidization velocity and terminal velocity increased with electro-winning time. It can be explained that the average particle size of bed particles increases and hence the particles minimum fluidization velocity and the terminal velocity. The bed pressure drop during the winning process was estimated using Eq. (12) and given in Fig. 6. It can be noticed from Fig. 6 that during the bed pressure drop increased with an increase in the electrolysis time. This may be due to the fact that the increase in average particle size and decrease in bed voidage with time and hence the total pressure drop.

The mass transfer coefficient of electro winning has been estimated using Eq. (24) and the simulated values are given in Fig. 7. It can be noticed that the mass transfer coefficient is increased with increase in the electrolyte velocity. It is obvious that the mass transfer coefficient is directly related to the electrolyte velocity and an increase in the particle size increases the electrolyte velocity and in turn the mass transfer coefficient.

The current density for the electrolyte and electrode for the given operating condition are estimated using Eqs. (22) and (23) and the simulated results are presented in Fig. 8. It can be ascertained from Fig. 8 that the current densities decreased with increase in the electrode thickness; due to the larger average particle volume in the electrode the current density on the electrode particle is decreases throughout the electro-winning process.

The effective operation of a fluidized bed electrode depends on the potential distribution within the electrode. The electrolyte, electrode and overpotential have been simulated with using Eqs. (27)–(29) and the simulation results are given in Fig. 9. It can be ascertained from the Fig. 9 that the electrode material (with relatively high conductivity) carries a large current from the electrode surface to the current feeder, while the electrolyte (with relatively low conductivity) carries a small current from the current feeder to the electrode surface. At the electrode surface ($x=0$ cm) the overpotential is only 0.62 V and the electrode here is operating under electron transfer control conditions. The overpotential is small and changes very little with electrode thickness.

It is attempted to validate the present model simulations with the data reported in the literature. The Fig. 10 compares the simulation results of the present model of increase in bed weight with the data reported due to LeRoy [11,12]. It can be ascertained from the figure that the model simulation match satisfactorily with the experimental data reported in the literature.

The model simulation for the increase in particle size during electro winning has been compared Fig. 11 with the experimental data reported due to Smith and Nienow [14]. It can be seen from Fig. 11 that the present model simulation on increase in particle size matches satisfactorily with the data reported by Smith and Nienow [14].

5. Conclusions

A layered growth model has been developed to describe the particle growth mechanism in fluidized bed electro winning process. Model equations have been developed for potential distribution, current distribution and mass transfer rate and the influence of operating parameters on particle growth has been critically examined. The following conclusions are made,

- (1) The particle size increases with electrolysis time.
- (2) The electrolyte and electrode potential increases with an increase in the applied potential.
- (3) The weight withdrawal and weight addition at each cycle depends on the increase in the bed weight.

Further more, the present model simulations have been verified with the data reported in the literature and found to match satisfactorily.

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