Design of Fluidized Bed Electrochemical Reactor for the Treatment of Industrial Wastewater

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Abstract

The removal of toxic materials and recovery of heavy metals from industrial wastewater or effluents is done using fluidized bed electrochemical reactors. A design based on the first principles of mass and charge transfer is carried out on fluidized bed electrochemical reactor operating under Current Limit conditions. The design was based on the treatment of 50,000m³ /year of industrial wastewater and the recovery of copper. The reactor volume was calculated to be 1.42m³ while the reactor height was 1.81m. The resident time was 736 second, and the space velocity was 0.0014 sec-1 , while the corresponding volumetric flow rate was 0.00193m³ /s at 95% conversion. The minimum fluidization velocity was 0.03 m/s, fluidization velocity was 0.07m/s and terminal velocity was 1.53m/s. The sphericity of the particles was 0.6 and the voidage (porosity) was 0.5. The flow regime was turbulent with pressure drop of 272.23N/m² . The over potential of the system was 0.70V, while the required power was 0.5254Nm/s and the mass of catalyst (Zeolite A) was 61.07kg respectively. These results can be used for Engineering scale-up of this type of process.

Keyword: Design, Fluidized Bed Electrochemical Reactor, Fluidization, Industrial Wastewater

1.0 Introduction

A chemical processing industry operates in such a way that in all of its activities, there is the tendency that the industrial wastewater is cared for. This wastewater is noted to emanate from the source in which the industry channels its purge. Wastewater containing heavy metal ions is generated in large quantities from the mining, ore processing, microelectronics, metal finishing and photographic industries (Abo-Ghander, *et al*., 2005). The quantum of wastewater generated is increased proportionately with industrial revolution and day-to-day human activities. Industries such as textile, refineries, chemical, plastic and food-processing plants share major portion of wastewaters generated in chemical process industries (Kumar *et al*., 2008).

The wastewater generally contains toxic materials which are pollutants in the environment. Chemical wastes often contain both organic and inorganic materials in different degrees of concentrations. Industrial waste or effluent contains acids, bases, suspended solids, etc. These effluents cannot be left or disposed of without passing the proper stages of treatment to reduce its pollutant concentration. Conventionally industrial effluents containing organics are treated with adsorption, biological oxidation, coagulation, etc., (Kumar *et al*., 2008). It is important to use an appropriate method to treat industrial wastewater so that adequate result can be achieved. The adequate result is that the treated wastewater must be minimally toxic (less pollutant). Electrochemical engineering techniques use reactors called electrochemical reactors for the process of cleaning and recovery of heavy metals from industrial wastewaters (Ehirim, 2014). In fluidized bed reactor, the solids particles are supported by an upward flow of fluidizing fluid. The conversion of fluidized bed reactor electrochemically, makes it more efficient in the treatment process. It becomes more convenient, safer, less time-consuming and cheaper among other appreciable characteristics. Electrochemical cleaning technology offers an efficient means of controlling pollution as it provides removal of transition and heavy metals by redox reactions without the disadvantages of conventional treatment (Denise *et al*., 2005).

Electrochemical process can provide valuable contributions to the protection of the environment through implementation of effluent treatment and production-integrated processes for the minimization of waste and toxic compounds (Juttner, 1999). Electrochemical Engineering process offer alternative efficient mechanisms for the prevention, control and remedy of environmental pollution problems, particularly in the cleaning processes of industrial effluents and recovery of heavy metals present in the industrial reservoirs or effluents. With the ever increasing standard of drinking water supply and the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades (Gouhua, 2004). The removal of toxic materials and recovery of heavy metals from industrial effluents are done using porous or tridimensional electrochemical reactors. Particulate electrodes in general and particularly fluidized beds stimulate considerable interests in organic electro synthesis, cleaning of industrial effluents and electro separation or electrode position of heavy metals (Ehirim, 2012).

2.0 Development of Design Equations (Fluidized Bed)

The design equations are developed for the computation of the functional parameters of Fluidized bed electrochemical reactor for the treatment of industrial wastewater and recovery of copper using Zeolite A as the bed particles and as catalyst.

For the development of the design equation, the following considerations were made.

- **1.** Only one component $k = 1$ reacts in the system.
- **2.** There is no accumulation of the chemical specie(s) in the liquid phase.
- **3.** Hydrodynamic and electrochemical operating conditions are maintained constant.
- **4.** There are no concentration and temperature gradients in the reactor.
- **5.** The reactor operates as a CSTR.

2.1 Material Balance

 ${Rate of inf low} = {Rate of outflow} + {Rate of Disappearance} + {Accumulation}(2.1)$ Rate of Inflow $= F_{A0}$ (2.2)

Rate of Outflow =
$$
F_A
$$
 = F_{A0} (1-X_A) (2.3)

Rate of disappearance =
$$
(-r_A)V_R
$$
 (2.4)

Rate of accumulation =
$$
\frac{dN_A}{dt}
$$
 (2.5)

Substituting equations (2.2) through (2.5) into equation (2.1)

$$
F_{A0} = F_A + (-r_A)V_R + \frac{dN_A}{dt}
$$
 (2.6)

But the rate of accumulation for CSTR, $\frac{uv_A}{v} = 0$ *dt dNA*

Hence,

$$
F_{A0} - F_A = (-r_A)V_R
$$
 (2.7)

But

$$
F_A = F_{A0}(I - X_A)
$$
 (2.8)

Substitution of equation (2.8) in equation (2.7) gives:

$$
F_{A0}X_A = (-r_A)V_R \tag{2.9}
$$

$$
V_R = \frac{F_{A0} X_A}{-r_A} \tag{2.10}
$$

But the rate term in equation (2.10) can be compared to equation (1.13) . That is

$$
-r_A = -R_{k,s} = a_m \frac{(1-\varepsilon)}{\varepsilon} \frac{D_K}{\delta} (C_{k,s} - C_{k,s}^*)
$$

Hence,
$$
V_R = \frac{F_{A0} X_A}{a_m \frac{(1-\varepsilon)}{\varepsilon} \frac{D_K}{\delta} (C_{k,s} - C_{k,s}^*)}
$$

$$
C_{k,s}^* = C_{k,s} (1 - X_A)
$$

$$
V_R = \frac{F_{A0}X_A}{a_m \frac{(1-\varepsilon)}{\varepsilon} \frac{D_K}{\delta} (C_{k,s} - C_{k,s}(1 - X_A))}
$$
(2.11)

2.1 The design Equations for other Functional Parameters of the reactor.

i) **Reactor Height**.

The height of cylindrical shaped reactor is given as

$$
H_R = \frac{4V_R}{\pi d^2} \tag{2.12}
$$

$$
\overline{\text{or}}
$$

$$
H_R = \frac{4F_{A0}X_A}{\pi d^2 a_m \frac{(1-\varepsilon)}{\varepsilon} \frac{D_K}{\delta} (C_{k,s} - C_{k,s}(1 - X_A))}
$$
(2.13)

ii). Space Time (
$$
\tau
$$
)
\n
$$
\tau = \frac{V}{V_o}
$$
\n(2.14)

iii) Space Velocity (S_V) $=\frac{v_0}{1} = \tau^{-1}$ *V V Sv* (2.15)

iv) Mass of Catalyst (M)

The mass of catalyst can be determined using the equation stated by Brown and Fogler (2008). **(**2.16)

v) Pressure Drop (ΔP)

The pressure drop along fluidized bed reactor in terms of both laminar and turbulent flows are expressed using Ergun equation (Idris *et al*, 2007) as stated below:

Laminar or Streamline Flow

$$
\Delta P = \left[150 \frac{\left(1 - \varepsilon\right)^2}{\varepsilon^3} \frac{\mu u}{d_p^2} + 1.75 \frac{\left(1 - \varepsilon\right)}{\varepsilon^3} \frac{u \rho_f}{d_p} \right] \times h \tag{2.17}
$$

Turbulent Flow

$$
\Delta P = [(\rho_s - \rho_f)(1 - \varepsilon)g] \times h \tag{2.18}
$$

vi) Minimum Fluidized Velocity (Umf)

General Equation for the Fluid, Solid and Bed

$$
u_{mf}^{2} + \frac{150(1 - \varepsilon_{mf})\mu_{f}}{1.75\rho_{f}d_{p}^{1}}u_{mf} - \frac{g(\rho_{p} - \rho_{f})\varepsilon_{mf}^{3}d_{p}^{1}}{1.75\rho_{f}} = 0
$$
\n(2.19)

vii) Relatively Small Particle Size and Small Reynolds Number

For both relatively small particle size as well as small Reynolds number and relatively large particle size as well as large Reynolds number, the minimum fluidization velocity is expressed by Roland *et al* (1999) as:

$$
u_{\rm mf} = \frac{8(\rho_p - \rho_f)(d_p^1)^2}{150(1 - \varepsilon_{\rm mf})/\varepsilon_{\rm mf}^3}
$$
(2.20)

viii) Relatively Large Particle Size and Large Reynolds Number

$$
u_{mf} = \left[\frac{g(\rho_p - \rho_f) \varepsilon_{mf}^3 d_p^1}{1.75 \rho_f} \right]^{1/2}
$$
 (2.21)

ix) Reynolds Number

$$
\text{Re} = \frac{\rho_f d_t u_f}{\mu} \tag{2.22}
$$

x) **Fluidized Velovity (** U_f **)**

This is the velocity at which fluidization occurs. It can be expressed using Kozeny-Carmen equation as stated under:

$$
u_f = \frac{(\rho_p - \rho_f)gd_p^2}{150\mu} \frac{\varepsilon^3}{1-\varepsilon}
$$
 (2.23)

xi) Terminal Velocity (U*t***)**

Terminal velocity can be assessed by application of the Richardson–Zaki equation (Richardson & Zaki (1954)), which describes expansion of the fluidized bed as: $U = U_t \varepsilon^n$ (2.24)

xii) Sphericity

It can be expressed using Narsimhan's correlation as stated below.

$$
\left(\frac{1-\varepsilon}{\varphi_s}\right) = 0.231 \log d_{psm} + 1.417
$$
\n
$$
\varphi_s = \frac{1-\varepsilon}{0.231 \log d_{psm} + 1.417}
$$
\n(2.25)

xiii) Power Requirement

It is represented by the equation below according to Suleiman *et al.,* (2013). $P = \Delta P * V_0$ (2.26)

2.2 Design Calculations

The basis of this design was on the treatment of $50,000m^3$ /year of industrial wastewater vis-àvis recoveryof copper. The prime calculations are shown in Appendix A.

Table 2.1 Data for the determination of the process parameters

3.0 Results and Discussion

Table 3.1 Calculated Values of some of the Functional Parameters for $50,000\text{m}^3/\text{year}$ waste treatment using Electrochemical (Fluidized bed) Reactor.

Table 3.1 shows the design values of the functional parameters for the treatment of a 50,000m³/year of wastewater. These values are in close agreement with those found in literatures(Gouhua, 2004).

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3.1 Results

Figure 3.1: Effect of Reactor Volume on Conversion Figure 3.2: Effect of Reactor height on Conversion

Figure 3.3: Effect of Catalyst Mass on Bed Voidage Figure 3.4: Effect of Pressure Drop on Bed Voidage

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Figure 3.5: Effect of Fluidized Velocity on Bed Voidage Figure 3.6: Effect of Concentration of Treated Water on over potential

3.2 Discussion

The relationship between conversion and the reactor volume as well as the height is shown in figures 3.1 and 3.2. They both show the same trend indicating that the reactor volume and height increase as the conversion does.

In figure 3.3, the relationship between mass of catalyst and voidage shows that when the mass of catalyst is increasing then the interstitial spaces (voidage) reduces until there will be no space, but subsequent reduction in mass increases the voidage.

Figure 3.4 shows the effect of voidage on pressure drop. It indicates that increase in pressure drop is as a result of decrease in the voidage. When the voidage is high, the fluid flows freely without experiencing pressure drop, but as the voidage decreases, definitely, pressure drop is noticed in the fluidizing system.

The relationship between fluidized velocity and voidage is shown in figure 3.5 where the loglog plot of the parameters against each other is plotted, showing a linear relationship among them.

Figure 3.6 shows the inverse relationship between the system overpotential and the concentration of the treated wastewater. As the concentration of the treated wastewater increases, the overpotential decreases and vice-versa.

4.0 Conclusion

The fluidized bed electrochemical reactor was designed for the treatment of 50,000 m^3/year of industrial waste water and recovery of copper as the identified heavy metal. The reactor volume is calculated to be $1.42m³$ while the reactor height is 1.81m at 95% conversion. The resident time is 736 second, and the space velocity is 0.0014 sec^{-1} , while the corresponding volumetric flow rate is $0.00193m³/s$. The minimum fluidization, fluidization and terminal velocities are 0.03, 0.07 and 1.53m/s at voidage value of 0.5. The pressure drop is 272.23 N/m² in the turbulent flow regime. The overpotential of the system is 0.70V by calculation. The mass of catalyst is calculated as 61.07kg. The design calculations can be used for Engineering Scale-up.

Nomenclature

 a_m Specific superficial area of the solid (m^{-1}) $C_{k,s}$ Concentration of chemical specie k in the liquid phase (g/m^3)

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APPENDIX A

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2.2.1 Volumetric Flowrate

The treatment of $50,000\,\text{m}^3/\text{year}$ was based on 300 days out of 365 days in the year. This is because routine maintenance and other operational factors were taken into account. Thus, the reactor volumetric flowrate required for the treatment was obtained as stated below:

0.00193 m^3 / sec 60sec 1min 1440min 1 300 $50,000 m^3$ $1 day$ $1 min$ $-0.00103 m^3$ $\frac{50,000m^3}{200M} \times \frac{1 day}{1440 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ min}} = 0.00193m$ *days* $V_0 = \frac{50,000m^3}{2000 \text{ J}} \times \frac{1 \text{day}}{1440 \text{ J}} \times \frac{1 \text{min}}{100 \text{ J}} =$ Input Mass flow rate, $m = Density$, $\rho \times Volumetric$ *flow rate*, *V o o* Density of aqueous $CuSO_4 = 3600000 \text{g/m}^3$ Molar mass of aqueous $CuSO_4 = 159.609$ g/mol \int_{m}^{∞} *m* = 3600000g / m^3 × 0.00193 m^3 / s = 6948g / s Input Mole flow rate, $F_{A0} = \frac{m\alpha s s J\omega w r \alpha t}{r} = \frac{6346}{150,600} = 43.53 \text{mol/s}$ *Molar mass* $\frac{Mass \, flow \, rate}{150 \, sec}$ = 43.53 *mol* 159.609 $=\frac{6948}{150-100}=$ Input Mass flow rate, F_{A0} = Input Mole flow rate X Molar mass $= 43.53$ X 159.609 $= 6948$ g/s $F_A = F_{A0} (1-X_A)$ Where: F_A = Output Mole flow rate (mol/s) X_A = Conversion (fraction) = 95% = 0.95 $F_A = 43.53$ (1-0.95) = 2.1765 mol/s Output Mass flow rate $=$ Output Mole flow rate X Molar mass $F_A = 2.1765 \text{ X } 159.609 = 347.40 \text{ g/s}$ $C_A = C_{A0} (1 - X_A)$ Where: $C_{A0} = C_{k,s} = 508.358$ g/m³ $C_A = C_{k,s}^* = 508.358$ (1-0.95) = 25.42 g/m³

Data Feed

 $F_{A0} = 43.53$ mol/s = 6948 g/s $V_0 = 0.00193$ m³/s $C_{A0} = C_{k,s} = 508.358$ g/m³ Conversion, $X_A = 0.95 = 95\%$

2.2.2 Reactor Volume

The reactor volume was calculated using the general formula below according to equation 2.11:

$$
V_R = \frac{F_{A0}X_A}{a_m \left(1 - \varepsilon\right) D_K \left(C_{k,s} - C_{k,s}(1 - X_A)\right)}
$$

Where:
F_{A0} = 6948g/s
X_A = 0.95
a_m = 6000 m⁻¹
\varepsilon = 0.5
D_k = 1.6 x 10⁻⁷ m²/s
\delta = 0.1 x 10⁻³ m

$$
C_{k,s} = 508.358g/m^{3}
$$

\n
$$
C_{k,s}^{*} = 25.42g/m^{3}
$$

\n
$$
V_{R} = \frac{F_{A0}X_{A}}{a_{m} \frac{(1-\varepsilon)D_{K}}{\varepsilon} (C_{k,s} - C_{k,s}(1 - X_{A}))}
$$

\n
$$
V_{R} = \frac{6948 \times 0.95}{6000 \frac{(1-0.5)}{0.5} \frac{1.6 \times 10^{-7}}{0.1 \times 10^{-3}} (508.358 - 508.358(1 - 0.95))} = 1.42m^{3}
$$

2.2.3 Reactor Height

The reactor height was calculated according to equation 2.13

C_{k,x} = 508.358g/m³
\nC_{k,x} = 25.42g/m³
\nV_R =
$$
\frac{F_{.00}X_A}{a_m \frac{(1 - \mathcal{E}) D_K}{\mathcal{E}} (C_{k,x} - C_{k,x}(1 - X_A))}
$$

\nV_R = $\frac{6948 \times 0.95}{6000 \frac{(1 - 0.5) 1.6 \times 10^{-7}}{0.5} (508.358 - 508.358(1 - 0.95))} = 1.42m^3$
\n2.2.3 **Reactor Height**
\nThe reactor height was calculated according to equation 2.13
\nH_R = $\frac{4F_{.00}X_A}{m^3 a_m \frac{(1 - \mathcal{E}) D_K}{\mathcal{E}} (C_{k,x} - C_{k,x}(1 - X_A))}$
\nWhere:
\nV_R = 1.42 m
\nd = 1 m
\nF_{A00} = 6948g/s
\nX_A = 0.95
\nD_k = 1.6x 10⁷ m²/s
\n $C_{k,x}$ = 508.358g/m³
\n $C_{k,x}$ = 508.358g/m³
\n $C_{k,x}$ = 25.42g/m³
\n $C_{k,x}$ = 25.42g/m³
\n3.142 × 1² × 6000 $\frac{(1 - 0.5) 1.6 \times 10^{-7}}{0.1 \times 10^{-3}} (508.358 - 508.358(1 - 0.95))$
\n2.2.4 **Residence Time (t)**
\nThe residence time was calculated according to equation 2.14
\n $\tau = \frac{V}{V_0}$
\nWhere:
\n $V_R = 1.42$ m³
\nW₀ = 0.00193 m³/sec
\n $\tau = \frac{V}{V_0} = \frac{1.42}{0.$

2.2.4 Residence Time (τ)

The residence time was calculated according to equation 2.14

$$
\tau = \frac{V}{V_0}
$$

Where:

$$
V_R = 1.42 \text{ m}^3
$$

\n
$$
V_0 = 0.00193 \text{ m}^3/\text{sec}
$$

\n
$$
\tau = \frac{V}{V_0} = \frac{1.42}{0.00193} = 736 \text{ sec}
$$

2.2.5 Space Velocity (Sv)

Space very was calculated using equation 2.15 as:

$$
S_{v} = \frac{V_0}{V} = \tau^{-1} = 736^{-1} = 0.0014 \text{ sec}^{-1}
$$

2.2.6 Catalyst Mass (M)

From equation 3.16, the catalyst mass was calculated thus:

Where: *Wc*= mass of catalyst(kg) *ε*= 0.5 ρ_c = density of the catalyst = 1555kg/m³ A_c = Column cross-section area (m) $h =$ Height of the bed = 0.10m But, $d =$ Bed diameter = 1.0m $A_c = 3.142 \times (0.5)^2 = 0.7855 m^2$ $W_c = \rho_c A_c h (1 - \varepsilon)$ $W_c = 1555 \times 0.7855 \times 0.10(1 - 0.5) = 61.07kg$ $W_c = \rho_c A_c h(1 - \varepsilon)$

Where:
 W_c = mass of catalyst(kg)
 ε = 0.5
 ρ_c = density of the catalyst = 1555kg/m³
 A_c = Column cross-section area (m)
 h = Height of the bed = 0.10m

But,
 $A_c = \pi r^2$
 $r = 0.5d$
 d $W_c = \rho_c A_c h (1 - \varepsilon)$ $r = 0.5d$ $A_c = \pi r^2$

2.2.7 Calculation of Minimum Fluidized Velocity (*umf***)**

The minimum velocity was calculated using equation 2.21

$$
u_{mf} = \left[\frac{g(\rho_p - \rho_f) \varepsilon_{mf}^3 d_p}{1.75 \rho_f} \right]^{1/2}
$$

$$
u_{mf} = \left[\frac{9.81 \times (1555 - 1000) \times (0.5)^3 \times 2.5 \times 10^{-3}}{1.75 \times 1000} \right]^{1/2} = 0.03 m/s
$$

2.2.8 Calculation of fluidized velocity (u_f)

From equation 3.23, the fluidized velocity was calculated thus:

$$
u_f = \frac{(\rho_p - \rho_f)gd_p^2}{150\mu} \frac{\varepsilon^3}{1-\varepsilon}
$$

$$
u_f = \frac{(1555 - 1000) \times 9.81 \times (2.5 \times 10^{-3})^2}{150 \times 7.65 \times 10^{-4}} \frac{(0.5)^3}{(1-0.5)} = 0.07 m/s
$$

2.2.9 Terminal Velocity

This can be calculated by using equation 2.24: $U = U_t \varepsilon^n$

$$
Log U = Log U_t + Log \varepsilon^n
$$

$$
Log U = Log U_t + nLog \varepsilon
$$

From figure 6, the equation of the straight line which is analogous to $Log U = Log U_t + nLog \varepsilon$ is $y = 3.8775x + 0.1845$

From this relationship, it can be seen that:

n = 3.8775

 $Log U_f = 0.1845$

 $U_t = 10^{0.1845} = 1.53$ m/s

2.2.10 Sphericity

The sphericity of the particles was calculated using equation 2.25 as stated below.

$$
\varphi_s = \frac{1 - \varepsilon}{0.231 \log d_{psm} + 1.417}
$$

$$
\varphi_s = \frac{1 - 0.5}{0.231 \log(2 \times 10^{-3}) + 1.417}
$$

$$
\varphi_s = \frac{0.5}{0.8159} = 0.6
$$

2.2.11 Reynolds Number (Re)

The Reynolds number is calculated using equation 2.22 as stated below.

$$
\text{Re} = \frac{\rho_f d_t u_f}{\mu}
$$

Where:

 ρ_f = Fluid density = 1000kg/m³ d_f = Column diameter = 1m U_f = Fluidized velocity = 0.07m/s $\mu = 7.65 \times 10^{-4}$ Kg/m.s 91503.27 $\text{Re} = \frac{1000 \times 1 \times 0.07}{7.65 \times 10^{-4}}$ \times $=\frac{1000\times1\times0.5}{7.65\times10^{-7}}$

2.2.12 Pressure Drop (ΔP)

Assuming laminar flow and calculating according to equation 2.17:

$$
\Delta P = \left[150 \frac{(1 - 0.5)^2}{(0.5)^3} \frac{7.65 \times 10^{-4} \times 0.07}{(2.5 \times 10^{-3})^2} + 1.75 \frac{(1 - 0.5)}{(0.5)^3} \frac{0.5 \times 1000}{2.5 \times 10^{-3}} \right] \times 0.1 = 19856.04 N/m^2
$$

Assuming turbulent flow and calculating according to equation 3.18: $\Delta P = [(1555 - 1000)(1 - 0.5) \times 9.81] \times 0.1 = 272.23N/m^2$

2.2.13 Power Requirement

The required operational power was calculated using equation 2.26. $P = \Delta P * V_0$ Considering turbulent flow which has a lower pressure drop, $P = 272.23 \times 0.00193 = 0.5254$ *Nm*/sec Considering laminar flow which has a higher pressure drop, $P = 19857.04 \times 0.00193 = 38.3241$ *Nm*/sec

2.2.14 Overpotential(η)

The system overpotential was calculated using equation 1.18,

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

$$
\eta = 3 - 1.5 - \left[0.76 + \frac{8.314 \times 303}{2 \times 96500} \ln(25.42) \right] = 0.70V
$$