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Design and Development of Packed Bed Electrochemical Reactors (PBER's) Using Scrap Lead Dioxide as Novel Electrodes

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Abstract

The present work focuses on the effective utilization of discarded Lead dioxide particles as particulate electrodes in a carefully designed packed bed electrolyser. It is known that particulate electrodes provide a large electrode area in proportion to conventional flat electrode configuration. Consequently, this packed bed electrolyser, will be exceptionally useful when dealing with slow reactions. This design entirely avoids the necessity of expensive valve metals as substrates and associated noble metal oxide undercoating. In the present study, an optimized design of a packed bed electrochemical reactor setup using peeled off electro deposited Lead dioxide particles was carried out. The above electrolyser was used for studying its effectiveness in the electrochemical oxidation of Sodium Chlorate to Sodium Perchlorate, which is the starting raw material for the manufacture of rocket propellant oxidizers. Effect of certain parameters like electrolyte flow rates, current density and thickness in the desired current efficiencies for the formation of perchlorates were estimated. Results indicate that this electrolyser proves to be a potential method for improving the reaction rates of slow reactions like perchlorate formation, utilizing cheaper discarded Lead dioxide particles.

Keywords: Lead dioxide; Packed bed electrolyser; Particulate electrodes; Perchlorate reaction; Scrap lead dioxide; Hazardous solid waste; Effluent treatment of organics

Introduction

Lead dioxide is used as one of the insoluble anodes in the electrochemical industries due to their significant stability, better electronic conductivity and inherently low cost [1]. However, their relatively weak mechanical strength necessitates the use of conductive support such as expensive titanium metals. The use of conductive supports, leads to a problem of adhesion between the metal substrate and Lead dioxide coating due to the formation of insulating oxides. This calls for the need of a careful under coating of highly expensive noble metal oxides over the valve metal for making the surface conductive. In spite of this, occasional peeling of Lead dioxide crystals due to the difference in thermal expansion coefficients during electrolysis is a serious problem faced by allied electrochemical industries. Moreover, decisive removal of Lead dioxide particles from the conductive substrate (after definite lapse of service life) and recoating with fresh Lead dioxide crystals, for want of higher energy efficiencies, is a common procedure adopted in many similar electrochemical industries.

Generally, Lead dioxide anodes coated over conductive Titanium substrates are commercially manufactured through electrodeposition techniques from Lead containing salts like Nitrates, Acetates, Methane Sulphonates, etc. Long term stability is always a critical issue when lead dioxide anodes are considered because corrosion of the coating must lead to contamination of the product/effluent with toxic Lead (II) [2]. In a typical Perchlorate manufacturing unit, these electrodes are dipped in electrolytes like Sodium Chlorate solution, which will be subsequently electrochemically oxidized to Sodium Perchlorate, a major intermediate for any type of Perchlorate manufacture. Though these electrodes are sufficiently inert and falls in the class of DSA (Dimensionally Stable Anodes) under these oxidizing environments, PbO_2 slowly loses its adherence from its substrate resulting in its peeling out after completing a definite period of its service life. Consequently, the performance of these electrolysers comes down necessitating the removal of such substrates for want of another layer of coating. Above

detached PbO_2 particles, generally seems to be 'relently useless', still retains all its chemical features other than loss of its adherence from the parent substrate.

Moreover, such Lead dioxide flakes which are removed from the substrate metal, becomes a solid hazardous waste, if allowed to accumulate. Its known from the literatures that Lead compounds interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys, and reproductive and nervous systems. It interferes with the development of the nervous system and is therefore particularly toxic to children, causing potentially permanent learning and behavior disorders. Symptoms include abdominal pain, confusion, headache, anemia, irritability, and in severe cases seizures, coma, and death. Hence safe disposal of discarded lead compounds is one of the major challenges in the recent era [3].

The present work focuses on the effective utilization of above generated discarded or peeled off Lead dioxide particles as particulate electrodes in a carefully designed packed bed electrolyser. It is known that particulate electrodes provide a large electrode area in proportion to conventional flat electrode configuration [4-7]. Consequently, this packed bed electrolyser, will be exceptionally useful when dealing with low reactant concentrations or slow reactions. This "substrateless" design entirely avoids the necessity of expensive valve metals as substrates and

associated noble metal oxide undercoating. Additionally, the service life of such electrodes is also found to be remarkably higher. In the present study, an optimized design of a packed bed electrolyser setup using peeled off electro deposited Lead dioxide particles was carried out for proper current and voltage distribution. The above electrolyser was used for studying its effectiveness in the electrochemical oxidation of Sodium Chlorate to Sodium Perchlorate, which is the starting raw material for the manufacture of rocket propellant oxidisers. Effect of critical cell parameters such as current load, electrolyte flow rate and temperature was also carried out in the present study. An attempt for corroborating above results in a known Concentration - time model was also carried out.

Experimental Details

Experiments were carried out in the packed bed electrochemical reactor schematically presented in Figure 1. The cell was of cylindrical geometry and was made of High Density Polyethylene (HDPE), the overall dimensions were 17.78 cm (ID) × 30 cm (H). Scrapped Lead dioxide particles (about 3.5 Kg) were thoroughly cleaned using DI water and closely packed in the electrolyser upto 5 cm height. Perforated Poly propylene supports (which also serves as distributor) with nylon mesh filter were used at both ends for ensuring rigid and leak proof packing. Particle size distribution of these particles obtained using sieve analysis and its image analysis using Zoom Stereoscopic Microscope are mentioned in Tables 1 and 2 respectively. Since particles collected were widely varying in size and shape, particles belonging to fine, medium and coarse were individually taken for image analysis. The hydraulic flow circuits consisted of centrifugal pump, valves and tanks for feeding and overflow electrolyte collection. Electrolyte was introduced to the cell through the inlet opening at the bottom, leaving the cell by overflows at the top, pumped to the feed tank and got returned to the cell by gravity. The tanks were filled with about 11.5 liters of Sodium Chlorate solution having an initial concentration of 669 gm/litre (gpl). A conductive (Noble metal oxides containing Ti, Ru and Pd) coated Titanium tube was used as a current feeder while the counter electrode was SS 316 L. A DC Rectifier having 200 A, 60 V specifications was used for providing DC current to the electrolyser. Isothermal conditions were maintained in the overflow collection tank by providing it with a cooling water circulation system through cooling coils and an electric heater. Both electric heater as well as solenoid valve in the cooling water feeding line was interlocked with temperature sensor kept in the over flow tank as shown in Figure 2.

Results and Discussion

Optimization of design configuration

Different design configurations in the mode of packing of particulate electrodes were attempted as shown in Figure 3a, 3b and 3c. Central aim of this sub study was to conduct a broader screening while choosing the optimized packed bed electrolyser design configuration for perchlorate conversion study. Configuration I and II basically suits for a batch operation whereas configuration III allows a continuous mode of operation. Sodium Chlorate solution of known concentration was filled in cell configuration I and II whereas same solution was allowed to over flow in Configuration III as explained in Figure 1. All these cells were operated under similar conditions for about 3 days and average current efficiency (CE) for perchlorate formation was determined as shown in Figure 4. Method of calculation of current efficiency is mentioned in Appendix A.1.

From the above graph, it is clear that annular design shown in Configuration I having PbO_2 particles filled in the inner cylinder

exhibited least performance. Poor current distribution through the electrode bed owing to low resistance path between the cylinder regions had resulted in meager conversion. Significant improvement in current distribution and hence in CE was noticed in Configuration II when the anode feeder rod was inserted in to the bed of anode particulates. But the exact benefits from the inherent nature of Lead dioxide particulates were obtained in configuration III when there is a continuous circulation of electrolyte through the bed. Better current distribution coupled with uniform distribution of flow across the electrode bed had resulted in its improved CE. Resistance due to diffusion layer generated in the other two configurations was completely eliminated in configuration III owing to continuous regeneration of surface of electrode particles with fresh feed of unconverted Chlorate ions. This design resembles 'Flow through electrode design" mentioned in ref. [8]. Configuration III was selected for further studies based on the above performance results.

Influence of current density

Influence of current density on the performance of PBER was studied at various current load by keeping other parameters like temperature and flow rate constant. Figure 5 shows the variation of CE for each current load. Dependence of current load on initial current efficiency is given in Figure 6.

As expected, current efficiency increases steadily with current density in the electron transfer control regime where higher over potential ensures better charge transfer reaction kinetics. A peak at 80 A exhibits the limiting current region (I_L) where reaction rate reaches sufficiently high for given operating conditions where after mass transfer control region prevails. As the current load is still increased, reaction will be sufficiently mass transfer controlled resulting in slight drooping down of current efficiency owing to depletion of reactant radicals at the electrode surface. Another significant finding is the systematic reduction of current efficiency with the depletion in concentration of $NaClO_3$ as shown in Figure 7. This may probably be due to the dependence of limiting current density on the concentration of reactant radicals as per following equation given by Walker and Wagg in ref. [9].

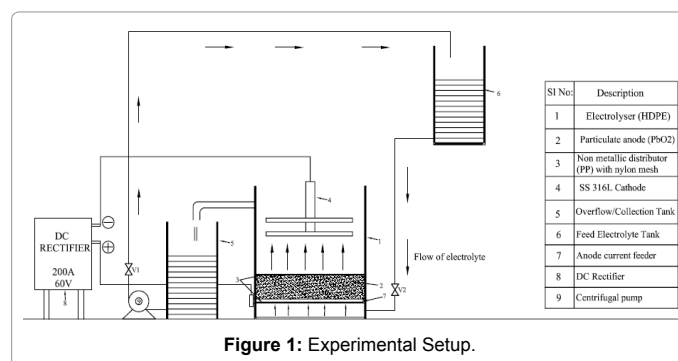$$I_L(t) = nFQC_i\left[1 - \exp(-KAaL/Q)\right]\left\{\exp(-t/\tau)\left[1 - \exp(-KAaL/Q)\right]\right\} \quad (1)$$

Figure 1: Experimental Setup.

Particle Size Distribution	
Size range	**Weight %**
>710 µ	87.53
500-710 µ	9.46
355-500 µ	2.28
300-355 µ	0.27
<300 µ	0.46

Table 1: Sieve analysis and its image analysis using Zoom Stereoscopic Microscope.

| S No | Sample Ref. | Size in Microns | |
		Min	Max
1	Fine PbO_2 -1	721.8	1756.6
2	Fine PbO_2 -2	485	837.4
3	Medium PbO_2 -2	1029.3	1245.4
4	Medium PbO_2 -2	1182.8	3285.7
5	Coarse PbO_2 -1	767.7	3341.9
6	Coarse PbO_2 -2	482.9	9439.4

Table 2: Sieve analysis and its image analysis using Zoom Stereoscopic Microscope.
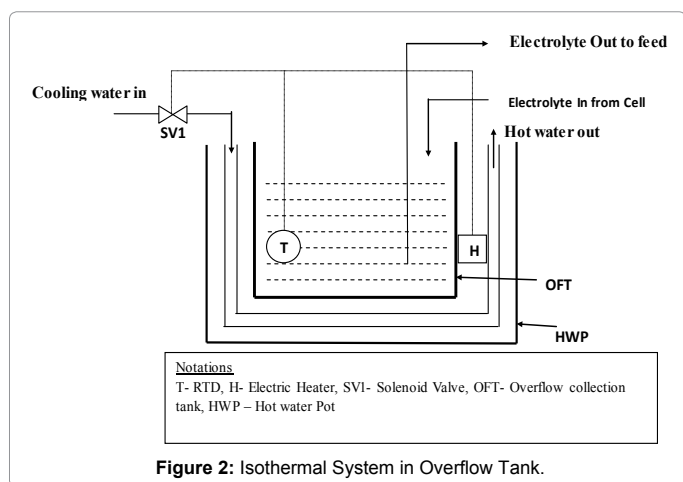
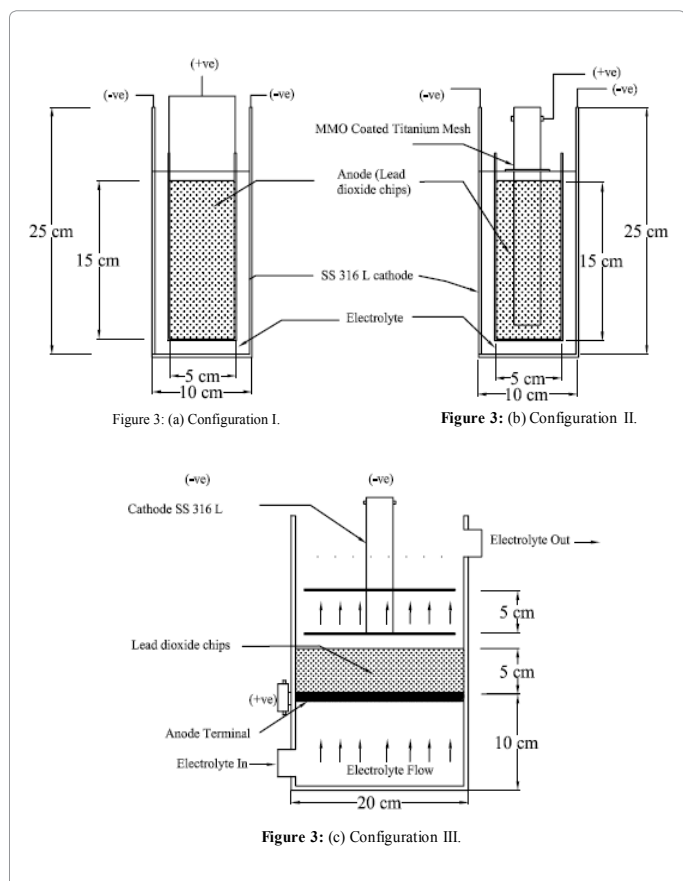**Figure 2:** Isothermal System in Overflow Tank.

Notations
T- RTD, H- Electric Heater, SVl- Solenoid Valve, OFT- Overflow collection tank, HWP – Hot water Pot

Figure 3: (a) Configuration I.

Figure 3: (b) Configuration II.

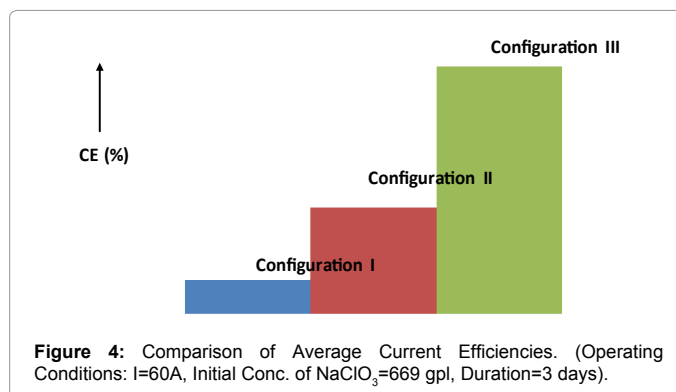**Figure 3:** (c) Configuration III.

Figure 4: Comparison of Average Current Efficiencies. (Operating Conditions: I=60A, Initial Conc. of $NaClO_3$=669 gpl, Duration=3 days).
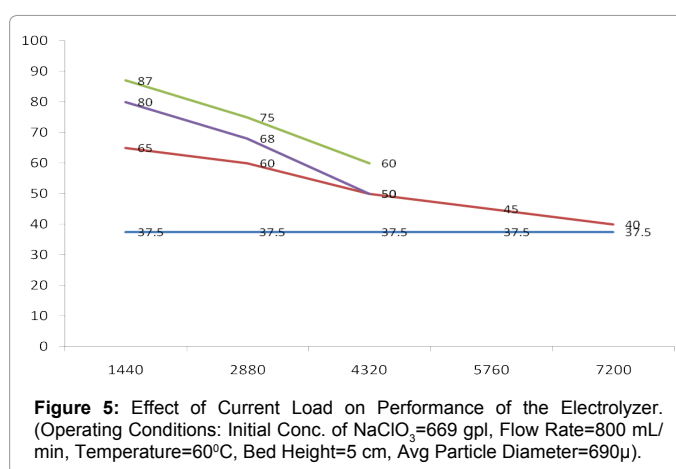

Figure 5: Effect of Current Load on Performance of the Electrolyzer. (Operating Conditions: Initial Conc. of $NaClO_3$=669 gpl, Flow Rate=800 mL/min, Temperature=60^{0}C, Bed Height=5 cm, Avg Particle Diameter=690μ).
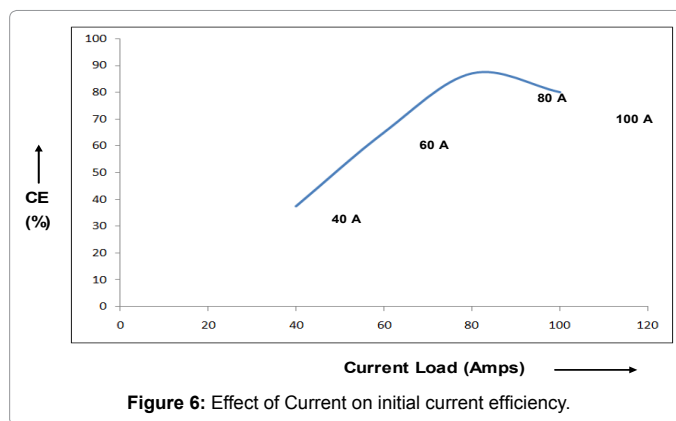

Figure 6: Effect of Current on initial current efficiency.

As per above equation, Limiting current value (I_L) also gets reduced as the concentration of Sodium Chlorate (C_i) decreases with time. Thus, maintaining electrolyser at I_L (optimized for higher C_i) during the lagging phase of electrolysis (lower C_i) clearly sets up a mass transfer control regime and thereby a progressive reduction in efficiency.

Influence of electrolyte flow rate

Figures 8 and 9 depicts the effect of electrolyte flow rate on the performance of electrolyser. Though not as influential as current density, an optimum flow rate of 800 mL/min was obtained when other parameters were kept unvaried. As the flow rate is significantly increased beyond this value, residence time distribution of the reacting radicals becomes poorer resulting in substantial reduction in CE. Another finding from the graph is that CE gets slightly improved
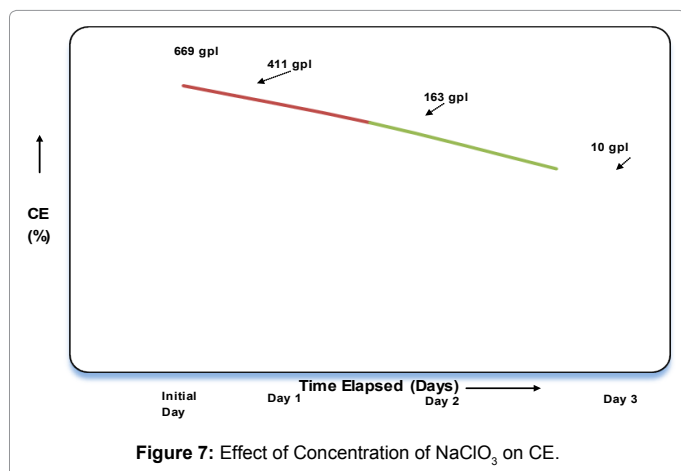
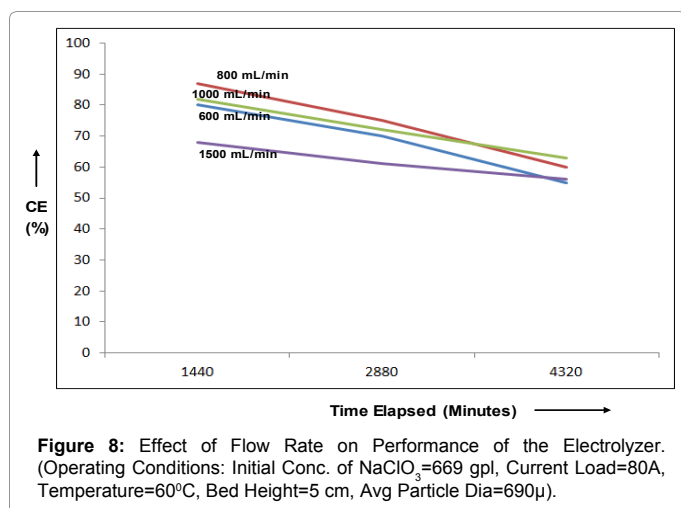**Figure 7:** Effect of Concentration of NaClO$_3$ on CE.

Figure 8: Effect of Flow Rate on Performance of the Electrolyzer. (Operating Conditions: Initial Conc. of NaClO$_3$=669 gpl, Current Load=80A, Temperature=60°C, Bed Height=5 cm, Avg Particle Dia=690μ).
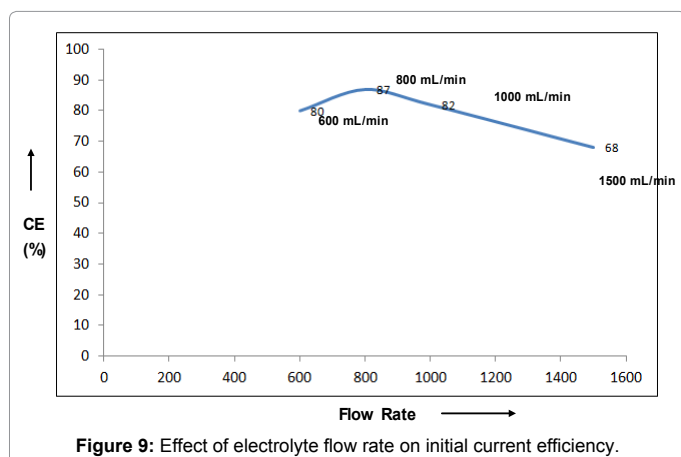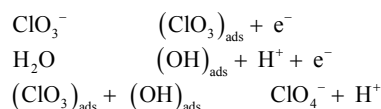

Figure 9: Effect of electrolyte flow rate on initial current efficiency.

towards the lagging phase of electrochemical oxidation for higher flow rates (1000 mL/min & 1500 mL/min). This may probably be due to better availability of unconverted radicals at the electrode surface at limiting current conditions thereby slightly overcoming the mass transfer resistance.

Influence of temperature

Three different electrolyte temperatures viz. 50°C, 60°C and

70°C were selected to study its influence on the performance of electrolyser. Results are shown in Figures 10 and 11. Surprisingly, a peak performance was observed at 60°C, beyond which CE sags down. This could be explained as follows. Basic electrochemical mechanism for perchlorate formation is reproduced from ref. [10] as follows.

$$ClO_3^- \qquad \left(ClO_3\right)_{ads} + e^-$$
$$H_2O \qquad \left(OH\right)_{ads} + H^+ + e^-$$
$$\left(ClO_3\right)_{ads} + \left(OH\right)_{ads} \qquad ClO_4^- + H^+$$

Perchlorate formation is a complex heterogeneous reaction proceeding through intermediate steps as shown above. Formation of hydroxyl ions by splitting of water molecule through one electron transfer step and its subsequent adsorption on Lead dioxide surface forms the slowest among all. Charge transfer rate coupled with the net availability of hydroxyl ions on the electrode surface are the two complimentary requisites for the enhancement in net reaction rate and hence in CE. With temperature, though charge transfer rate could be improved due to the higher solution conductivity, there could be a reduction in net availability of hydroxyl ions on the electrode surface owing to higher desorption rate. This could be a most probable reason for above drop in CE at higher temperature.

Concentration-Time model

Inorder to assess the theoretical behavior of the above PBER at limiting conditions, imminence with already established concentration-time (C-t) model in ref. [8] was checked. For ideal plug flow assumption at limiting current conditions in a recirculation system, C-t relationship is reproduced as follows.

$$C_i\left(t\right) = C_i \exp \left\{ -t/\tau \left[1- \exp \left(-KAaL/Q\right)\right]\right\} \qquad (2)$$

where $C_i(t)$ - Concentration of reactant ions in the electrolyte (here Sodium Chlorate)

C_i° –initial concentration of reactant ions. All other terms are conventional and have usual meanings. Table 3 shows list of parameters considered in the model. Details are given in Appendix A.2. After inserting above parameters, equation can be written as follows.

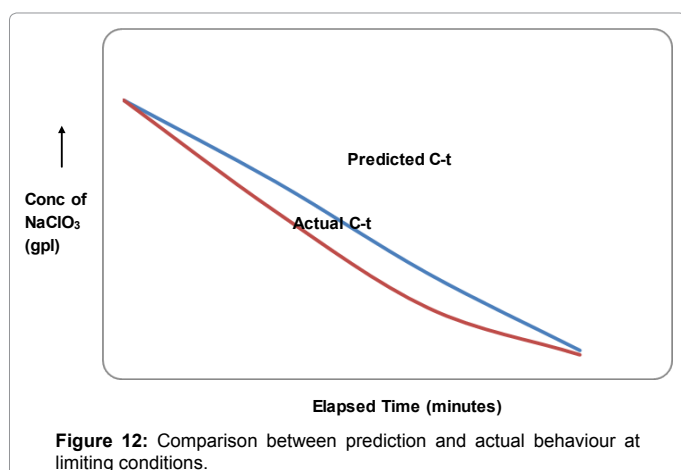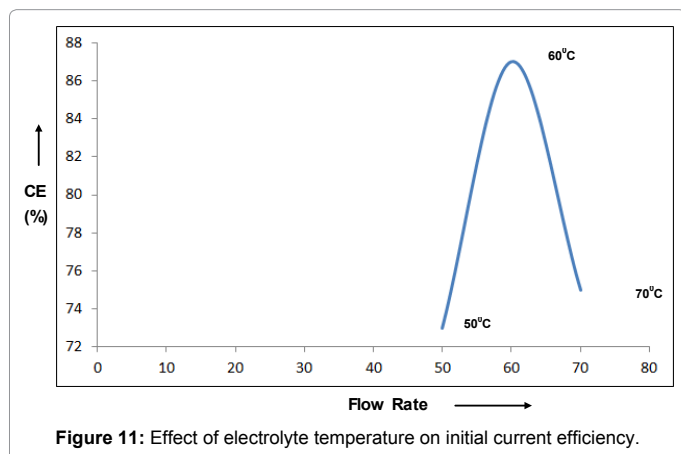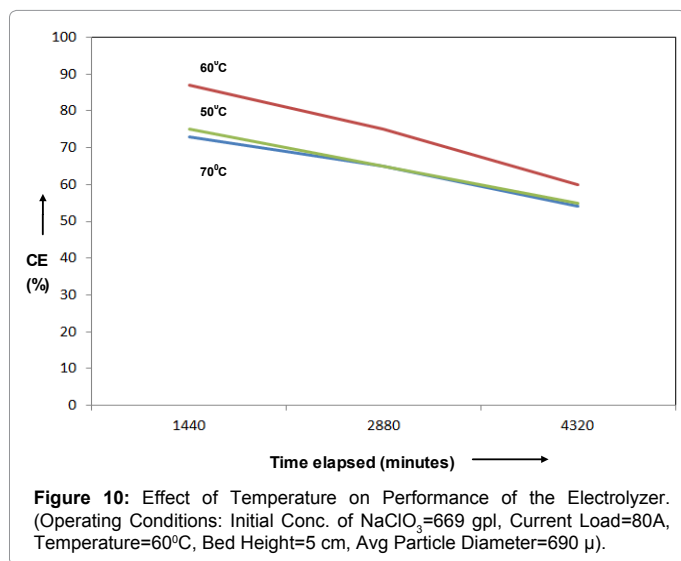$$C_i = 669 \times \exp \left(-t/12.5 \, x \, \left(1 - \exp \left(-2.54/C\right)\right)\right) \qquad (3)$$

Figure 12 gives the comparison between the actual behavior and theoretical model. Slight deviation between the predicted and actual behavior can be attributed to the erroneous and non uniform velocity distribution of electrolyte through the bed of non spherical and irregular Lead dioxide particles. Another reason may be the inadequacy of ideal plug flow assumption in the development of the above model.

Conclusion

An optimized flow- through packed bed electrochemical reactor using discarded Lead dioxide particles was made for energy efficient production of Sodium perchlorate. Systematic studies were conducted

Parameters	Value
Space time, τ	12.5 min
Cross sectional area of electrolyser, A	248.16 cm^2
Length of bed, L	5 cm
Specific surface area, a	368.83 cm^2/g
Initial concentration, C_i^0	669 gpl
Mass transfer coeff., K	6.44 × 10^{-3}/C cm^2/sec (C: Conc. of NaClO$_3$ in gpl)

Table 3: List of parameters considered in the model.

Figure 10: Effect of Temperature on Performance of the Electrolyzer. (Operating Conditions: Initial Conc. of $NaClO_3$=669 gpl, Current Load=80A, Temperature=60^0C, Bed Height=5 cm, Avg Particle Diameter=690 µ).

Figure 11: Effect of electrolyte temperature on initial current efficiency.

Figure 12: Comparison between prediction and actual behaviour at limiting conditions.

to understand the influence of various critical parameters like current, temperature and flow rate on the performance of electrochemical reactor. This electrolyser outperforms the conventional parallel plate design owing to higher contact surface available. Another added feature of above design is the complete elimination of expensive inert substrate and noble metal oxide under- coating required in parallel plate design. Though not recorded in the study, the service life of these

particulate electrodes will be extensively higher, since the life of TSLA's (Titanium Substrate Lead dioxide coated anode) is defined till Lead dioxide gets adhered to the substrate. Thus it excludes the necessity of labour intensive repeated Lead dioxide coating procedures adopted in several electrochemical industries.

It also opens up the possibility of a cheaper way of adding similar types of electrolysers in series using Lead dioxide particulates for continuous manufacture of Sodium perchlorate. This is because any attempt in converting the conventional batch type parallel plate Lead dioxide coated electrolysers to continuous mode would result in premature peeling of Lead dioxide owing to forced circulation of electrolyte. Another promising element regarding this design is the flexibility in leveraging its application in other industries where electrochemical oxidation is preferred like oxidation of effluents containing traces of organics like Phenol etc. [11,12].

Acknowledgements

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