Research Article

Simultaneous Recovery of Hydrogen and Chlorine from Industrial Waste Dilute Hydrochloric Acid

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Recovery of chlorine from byproduct HCl has inevitable commercial importance in industries lately because of insufficient purity or too low concentration to recycle it. Instead it is being neutralized in industries before disposing to meet stringent environmental conditions. Although recovery through catalytic oxidation processes is studied since the 19th century, their high operating conditions combined with sluggish reaction kinetics and low single pass conversions make electrolysis a better alternative. The present motive of this work is to develop a novel electrolysis process which in contrast to traditional processes effectively recovers both hydrogen and chlorine from dilute HCl. For this, an electrolytic cell with an Anionic Exchange Membrane has been designed which only allows the passage of chlorine anions from catholyte to anolyte separating the gasses in a single step. The catholyte can be as low as 3.59 wt% because of fixed anolyte concentration of 1.99 wt% which minimizes oxygen formation. Preliminary results show that the simultaneous recovery of hydrogen and chlorine is possible with high conversion up to 98%. The maximum current density value for 4.96 cm² membrane surface area (70% active surface area) is 2.54 kAm⁻², which is comparable with reported commercial processes. This study is expected to be useful for process intensification of the same in a continuous process environment.

1. Introduction

Industrially generated hydrochloric acid/hydrogen chloride is often byproduct of chlorine consuming process such as chlorination of organic compounds. Around 90% of HCl produced in US is byproduct of chlorination [1]. The open market of HCl is very less and most of the HCl produced is either productively used by the producer or put to local use (domestic, local industry). The industrially produced HCl is generally up to 38 wt% concentration; higher concentrations are expected to cause vapour losses. The byproduct HCl produced has many uses depending upon concentration; all the uses are summarized in Scheme 1. But this byproduct HCl needs to be treated for trace amounts of impurities before it is put to use which increases operational costs. It is not always possible to locate use for dilute HCl produced and shipping it to over large distances is not an economically lucrative option. In general, market for HCl is saturated and does not grow as necessary [2] and open market for HCl as said earlier is very less. So the excess dilute HCl is traditionally neutralized

before disposing without its effective utilization; it is quite comprehensible to note the expense of neutralization which in turn increases the quantity of waste and also large amount of potential chemicals is lost. The quantity of HCl, which was neutralized in Germany in 1995 because no option for reuse was available, is 230,000 ton HCl [3]. The option of evaporating may look as a feasible alternative for producing concentrated HCl from dilute, but with evaporation the HCl concentration cannot be increased more than a certain value because of HCl boiling point being very less in comparison to water. Through distillation high purity HCl can be recovered from water, but the major problem would be high energy demand and need to use exorbitant metals when using concentrated HCl at high temperatures.

Chlorine is no doubt one of the most important base chemicals in industry to produce many useful products. Being a halogen group element, it is a very strong oxidizing agent. Hydrogen on the other hand has many uses; it is the richest fuel in terms of calorific value and its demand increasing from day to day especially in developing countries as the

SCHEME 1: Uses of HCl recovered as byproduct [4–6].

demand for energy increases makes hydrogen important. It is also said that hydrogen being a clean fuel will be the source of energy in future. So recovery of hydrogen and chlorine is being inevitably important industrially as time progresses.

The market price of HCl can be under pressure because the expansion in demand for vinyl chloride monomers (main raw material is HCl) is smaller [7]. Additionally, since chloralkali is the main route for producing chlorine industrially and the expansion of the demand for chlorine (annual production of Cl_2 globally is 58 MMT [8] and has an expected demand growth of 4.4% per year since 2010 [9]) is greater than that of the demand for the caustic soda (NaOH), main product of chloralkali process, there is a danger that the demand balance between Cl_2 and NaOH will collapse [7]. So it is important to develop technologies for recovering chlorine and hydrogen from HCl and reutilizing it, which can decrease the amount of excess HCl expected in market and also will balance the demand of chlorine in market.

Initially many processes are developed to recover chlorine, like electrolysis (UHDE ODC) and catalytic oxidation (MT-Chlor). Although the recovery of chlorine from HCl is being studied for more than 100 years, the recovery of both hydrogen and chlorine is nevertheless studied less in comparison. With this in background, current study reports simultaneous recovery of chlorine and hydrogen from industrial waste, using batch electrolysis process. An attempt has been made to study the effect of various parameters which affect the conversion significantly. The results and discussion are mainly focused on 2 N (7.08 wt%) and 4 N (13.73 wt%) because the industrial waste HCl generally is up to 20 wt% [10].

The recovery of hydrogen and chlorine if developed will have much scope for application industrially. One such example is phosgene mediated isocyanate production of Toluene Diisocyanate (TDI); the reactions shown below depict the process:

For every 1 mole of TDI 4 moles of HCl is produced as byproduct. Approximately half of the Cl_2 produced annually is estimated to end up as HCl byproduct generated in the way described above, or as various other chlorides [7]. So HCl either is a direct byproduct or is also produced when chlorine is removed in order to obtain chlorine-free products.

Considering the concerns mentioned above with treating industrially waste dilute HCl, it is a motivation to work on recovery of both hydrogen and chlorine from waste dilute HCl from industries using electrolysis. One of the main advantages of electrolysis is that it is a low temperature and pressure process and it can be monitored easily compared to oxidation processes.

Different industrial recovery processes are explained in Table 1. Table 1 mainly summarizes two processes: catalytic oxidation and ion exchange electrolysis. The catalytic oxidation processes are Deacon, Kel-Chlor, Shell-Chlor, MT-Chlor, and Sumitomo; none of these processes recover hydrogen (it is lost as water). Out of these, Kel-Chlor and Shell-Chlor are said to be commercialized, but they are not operational now; only MT-Chlor and Sumitomo processes are commercially being used at present. Even though catalytic oxidation processes are said to consume less energy, the main disadvantage is that they operate above 250°C and product purification involves multiple steps if feed conversions are less (even assuming 66% conversion the effluent has only 33% Cl_2). In contrast, electrolysis is low temperature operation and it is possible in few configurations (UHDE diaphragm and DuPont gas phase electrolysis) to recover both hydrogen and chlorine. UHDE ODC is very much being licensed because of low energy consumption. Table 2 summarizes research studies on recovering chlorine from HCl. As can be seen, the literature also reports similar electrolytic processes; however studies on simultaneous recovery of both chlorine and hydrogen have not been many. Moreover, reported studies have been carried out for several hours of operation, which do not seem to be economical. Hence, it is thought desirable to work on the effect of different parameters affecting the electrolytic process. However, the other advantages of recovering hydrogen and chlorine also include making the plant economics independent of both hydrogen and chlorine

TABLE 1: Industrial processes of chlorine recovery.

Author	Process	Reaction	Methodology	Conclusions	Remarks
Benson and Hisham [11] (1992).	Deacon process developed by Henry Deacon in 1868 [11].	$4\text{HCl} + \text{O}_2 \rightarrow 2\text{Cl}_2 + 2\text{H}_2\text{O}$	(i) Direct oxidation around 425 to 475 °C [11] in presence of copper catalyst. (ii) Exothermic process has intermediate reactions resulting in sluggish reaction kinetics.	(i) Lower yields because of low conversion and catalyst activity [12]. (ii) Construction is expensive due to highly corrosive [11] intermediates.	(i) Single pass conversions around 60% to 80%. (ii) Catalyst activity decreases above 402 °C because of volatilization [9]. (iii) Never been put to commercial use [12, 13].
Ando et al. [7] (2010).	Kel-Chlor by Kellogg in the 1960s [14].	$4\text{HCl} + \text{O}_2 \rightarrow 2\text{Cl}_2 + 2\text{H}_2\text{O}$	(i) Oxidation using nitrogen oxides as the catalyst and sulphuric acid as circulating medium [7].	(i) Needs expensive plant design and safety features because of many intermediate reaction steps [7, 11], making it only possible for large-scale plants.	(i) Needs extensive downstream processing to get pure chlorine. (ii) DuPont started 200,000 ton/year plant in 1974, but it is not operating at present [7].
Engeland Wattimena [15] (1965).	Shell-Chlor by Shell patented in 1965 [15].	$4\text{HCl} + \text{O}_2 \rightarrow 2\text{Cl}_2 + 2\text{H}_2\text{O}$	(i) Oxidation in fluidized bed process at 300 to 425 °C. (ii) Catalyst is composed of copper, chloride, rare earth materials, and others at determined ratio [15].	(i) High catalyst activity because of low volatilization. (ii) Corrosion is also less [15].	(i) Conversion of 80% can be achieved [15]. (ii) Shell operated a facility of 30,000 t/yr in the 1970s [13], but operation was eventually shut down.
ThyssenKrupp [2].	UHDE diaphragm process developed by Bayer Material Science & Uhdenora.	Anode: $2\text{Cl}^- \rightarrow 2\text{Cl}_2 + 2\text{e}^-$ Cathode: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	(i) Aqueous electrolysis process using PVC/PVDF diaphragm at 65 to 70 °C [2]. (ii) Graphite electrodes are used. Water transfer (osmotic drag) is present.	(i) Gas purity is limited because the diaphragm cannot impede gas diffusion completely [3]. (ii) Minimum HCl concentrations should be maintained to avoid oxygen evolution [3].	(i) The conversion is 25% (23 to 17 wt%). (ii) Power consumption is 1670 kWh ⁻¹ Cl ₂ at 5 kAm ⁻² [2]. (iii) In Germany in 1995 20% of the HCl produced was recycled this way [3].
Itoh et al. [16] (1989).	MT-Chlor by Mitsui Toatsu patented in 1989 [16].	$4\text{HCl} + \text{O}_2 \rightarrow 2\text{Cl}_2 + 2\text{H}_2\text{O}$	(i) Oxidation in fluidized bed process using Cr ₂ O ₃ ·SiO ₂ catalyst [7] in presence of pure oxygen [16] at 300°–500 °C.	(i) Unlike Deacon here catalyst operates without melting, so the stability of the catalyst is greatly improved [7].	(i) Conversions up to 80% can be achieved [16]. (ii) Omuta since 1988 has 60,000 t/y capacity plant operating successfully [7].
Trainham et al. [17] (1995).	DuPont gas phase electrolysis by DuPont de Nemours patented in 1995 [17].	Anode: $2\text{HCl}(\text{g}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^-$ Cathode: $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	(i) Similar to CEM electrolysis process but occurs in gas phase through gas diffusion type membranes. (ii) The electrolyser is operated at 450–550 kPa and 70–90 °C.	(i) No HCl absorption step. (ii) Simple downstream process is sufficient for purification because feed is anhydrous [14]. (iii) Water transport (osmotic drag) is present.	(i) HCl conversion ratio up to 85% [7] can be achieved because of high diffusion coefficients (gas phase) [14]. (ii) Power consumption at 5 kAm ⁻² is roughly 1120 kWh/tCl ₂ [14].

TABLE I: Continued.

Author	Process	Reaction	Methodology	Conclusions	Remarks
Iwanaga et al. [13] (2004).	Sumitomo process by Sumitomo Chemical Co., Ltd. developed in 2000 [13].	$4\text{HCl} + \text{O}_2 \rightarrow 2\text{Cl}_2 + 2\text{H}_2\text{O}$	(i) Oxidation process in fixed bed reactor using $\text{RuO}_2/\text{TiO}_2$ (rutile) catalyst. Can be operated as low as 250°C . (ii) This process has higher conversions because of fixed bed reactor.	(i) This catalyst has higher activity and thermal stability than the ones discussed above [13]. (ii) Since 2003 a plant having production capacity of 100,000 t/y is operating smoothly.	(i) Conversions up to 95% are possible [13]. (ii) Power consumption is $165 \text{ kWh}^{-1} \text{ Cl}_2$ [13] which is very less in comparison to Bayer-DE Nora Process, but no comparisons for capital costs are reported.
ThyssenKrupp [2].	UHDE ODC process developed by Bayer Material Science & Uhdenor.	Anode: $4\text{HCl}(\text{aq}) \rightarrow 4\text{H}^+ + 4\text{e}^- + 2\text{Cl}_2$ Cathode: $4\text{H}^+ + 4\text{e}^- + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$	(i) Similar to CEM electrolysis process, but hydrogen generation is suppressed by water formation resulting in 30% savings in electric consumption and voltage less than 1 V [2].	(i) Water transport is present from anode to cathode. (ii) Many plants lately licensing this technology; for example, Bayer started operating a commercial plant of 215,000 t/yr [7].	(i) The power consumption is $1070 \text{ kWh}^{-1} \text{ Cl}_2$ at 5 kA m^{-2} that is less than diaphragm process, but the capital costs for the same are not reported.

TABLE 2: Research studies on chlorine recovery.

Author	Methodology	Main parameters' effects discussed	Conclusions	Remarks
Johnson and Winnick [18] (1999).	(i) An AEM process is developed for recovery of chlorine from gaseous HCl, but here chloride ions migrate across the molten salt electrolyte saturated membrane.	(i) In free electrolyte (no membrane) trials, conversion and current efficiency were determined as a function of current density, required cell voltage, and feed gas flow rate. (ii) At single-cell membrane, cross cell potentials at different feed rates are studied.	(i) This study shows that electrochemical membrane separation is a feasible alternative for the removal of chlorine from HCl at reasonable voltages, high conversion.	(i) This paper is more of a feasibility study. (ii) Nothing in regard to power consumption or process economics is said.
Vidakovic-Koch et al. [10] (2012).	(i) Polymer electrolyte membranes have broad applications; in this review emphasis is upon the application of Nafion membranes for chlorine recycling.	(i) The Nafion membrane has role of a separator and a solid electrolyte. (ii) Proton transport, mechanical stability of membrane, and influence of dispersion medium and its relevance for formation of ion conducting network are studied.	(i) Nafion performance is studied in the range of 18 wt% to 20 wt% HCl. (ii) Nafion performance is important for reactor optimization.	(i) This review study only considers Nafion membranes performance and no reference is made to process economics.
Barmashenko and Jörissen [3] (2005).	(i) An AEM process is developed for recovery of hydrogen and chlorine from dilute HCl to overcome the limitations of CEM process. (ii) The results are shown with alternative designs to overcome its limitations (EOD).	(i) Parameters like selectivity of membrane and current efficiencies with respect to CaCl_2 concentration and cell voltage are discussed. (ii) Voltage drop versus current density and water transfer through membrane is also considered. (iii) A possible design for an AEM with empty (gas filled) anode chamber is presented.	(i) This paper reviewed almost all electrolysis processes developed till 2005. (ii) They were able to perform AEM process with cathode concentration as low as 3.2 wt%.	(i) The energy requirement is 1740 kWh at 4 kAm^{-2} and cell voltage of 2.3 V. (ii) Effects of membrane surface area, electrode surface area, and temperature of the system are not considered. Process economics is not studied in detail.
Mazloomi et al. [19] (2012).	(i) This paper tries to study parameters which affect electrical efficiency of KOH electrolysis to optimize electricity expense which is a majority in electrolysis.	(i) Total electrical efficiency is divided into three separate factors: electrical resistance, electrolysis, and thermal efficiency. (ii) Temperature, pressure, and resistance of electrolyte, alignment of electrodes, electrode material, and applied voltage waveform are studied.	(i) This paper does not exactly deal with AEM electrolysis, but the nature of the parameters might remain the same to some extent in all electrolysis processes.	(i) Almost all of the parameters studied are only on KOH electrolysis. (ii) This study only focused on electrical efficacy.
Koter and Warszawski [20] (2000).	(i) Electrodialysis, electro-electrodialysis, and membrane electrolysis are discussed along with their applications to reduce environmental impact.	(i) A great deal regarding ion exchange membranes is discussed like application of membranes in fuel cells. Membranes (Nafion) properties are also discussed.	(i) Concludes that ion exchange processes are more sustainable and cleaner technologies in comparison to other recovery processes.	(i) This paper is more of a review study for membrane electrolysis. (ii) Economic aspects are not discussed in detail.

TABLE 2: Continued.

Author	Methodology	Main parameters' effects discussed	Conclusions	Remarks
Ando et al. [7] (2010).	(i) This R&D report of Sumitomo Chemical Co., Ltd. mainly deals with newly developed rutile-type catalyst for oxidation of dilute HCl and also considers energy economics.	(i) Performance of rutile catalyst is determined in comparison to other catalysts based on conversion, corrosion resistance, and stability. (ii) Complete overview of the process is presented.	(i) Rutile-type catalysts consume very less energy compared to UHDE ODC process. (ii) The paper also reviews all recovery processes in the literature.	(i) Although it says that rutile based catalytic oxidation is better than electrolysis, it does not recover hydrogen. (ii) Direct comparison of capital and operating costs with UHDE is not reported.

market prices. As is well known, transportation of hydrogen has always been an expensive operational cost.

With this in the background and motivation, the objective of the current work has been to simultaneously recover hydrogen and chlorine from industrially waste HCl and study the effect of parameters such as time of operation, conversion, electrode distance, current density, feed concentration, and current efficiency which are presented in the following sections.

2. Materials and Methods

Considering the wide scope of work in this field, as initial stage, current work has been confined to batch process. Schematic of the experimental setup can be viewed in Figure 1. The system consists of cathode and anode chambers separated by an Anionic Exchange Membrane (AEM) typically used for gas separation. AEM is chosen over CEM (Cationic Exchange Membrane) because in case of CEM the conversion is observed to be less and CEM membranes are generally more expensive [3].

Both cathode and anode chambers have a capacity of 30 mL separated by AEM. Catholyte comprised feed solution of HCl, while the anolyte is fixed to very dilute 0.55 N (1.99 wt%) HCl with added salt in order to aid as an electrolyte in ion movement. Different electrodes such as tin, titanium, and stainless steel have been attempted, but since they yielded to corrosion due to the presence of HCl/chlorine, platinum wire electrodes were used. It is to note that in spite of using these electrodes for more than 200 total experimental hours no corrosion was observed. The membrane surface area for all the experiments has been 7.068 cm².

All samples have been analysed based on standard acid-base titration methods. Hydrogen is collected based on the downward displacement of water technique, by passing through an inverted measuring cylinder filled completely with water. Mass balances have been established for all the inflow and outflow materials. Chlorine is bubbled into a bubbler filled with potassium iodide (KI in water) solution and analysed using iodometry, one of the best known

analytical methods for estimating chlorine. Iodometry uses sodium thiosulphate as titrant. Chlorine determination using iodometry involves two steps; firstly, the chlorine is bubbled through potassium iodide solution displacing iodine and forming potassium chloride. Now the liberated iodine forms a complex with potassium iodide which is dark brown in colour; it was made sure that the solution contained excess KI such that chlorine losses are minimized. As is well known, the following reactions take place:

The standardization of sodium thiosulphate and titration of KI₃ should be conducted at certain predetermined procedure to avoid errors and unwanted reactions. Iodometry is a well-known procedure for determining chlorine quantity and many open sources are available; it has some limitations regarding the molar concentrations of chlorine and these are also reported in the literature. While establishing material balances, additionally simultaneous water electrolysis and water transport through the membrane are also taken into account. All experiments are performed at ambient conditions.

3. Results and Discussions

As per the procedure explained in previous section, experiments were carried out for simultaneous recovery of chlorine and hydrogen. Most of the analysis presented here is explained in terms of the conversion (from here onwards termed as CE) and charge generated, as these are the most important objectives of this entire research work. Further, experiments were carried out at different conditions by varying each parameter at a time keeping the others unchanged. The parameters considered for the study of CE and total charge generated are feed catholyte concentration, electrode potential, time of operation, electrode distance (ED), and current efficiency.

FIGURE 1: Schematic of the experimental setup used for batch electrolytic process of hydrochloric acid.

Conversion simply put forward is the percentage of feed electrolysed and it is determined by estimating the final concentration of catholyte after the electrolysis; estimated based on titrimetry, it is to note that the conversion is simply the percentage of feed HCl that got electrolysed. Thus,

Conversion

$$= 100 \times \left(1 - \left(\frac{\text{Final Catholyte Concentration}}{\text{Initial Catholyte Concentration}} \right) \right). \quad (5)$$

The term total charge generated is the total amount of current that passed through the solution due to the ion movement caused by the electrolytic process or the total amount of current that is generated by the solution when subjected to a certain voltage. Total charge values are mentioned in ampere hours:

$$\text{Total charge} = \sum \text{Charge generated} * \text{Time}. \quad (6)$$

Total charge value is a quantitative measure of ions passing through anion exchange membrane, so if more numbers of ions are passing, it implies that more of the feed is electrolysed, so we can say that CE and total charge are directly proportional, although the exact relation depends on other parameters (such as electrode distance, time of operation, electrode potential, and ionic movements of the solution). Figure 2 depicts a graph of total charge generated against CE for 4 N and 2 N (here "N" refers to normality = equivalents/m³) initial feed concentrations at electrode potential of 16 V. It can be seen that the curve is linear with total charge increasing with increase in CE.

3.1. Chlorine Recovery. Chlorine is estimated quantitatively using iodometry. Chlorine solubility in water is estimated based on Figure 3 [21]; it can also be calculated from [22] at the temperature during experimentation. The free iodine solubility in water is very less; hence, as soon as iodine

FIGURE 2: Conversion percent (—) versus total charge (ampere hour).

is displaced by chlorine, it forms the complex. Chlorine recovery percentage is calculated based on

Chlorine recovery

$$= \frac{\text{Amount of Chlorine captured}}{\text{Chlorine amount to be captured}} * 100. \quad (7)$$

Figure 4 depicts typical recoveries at different feed catholyte concentrations. Recoveries greater than 100% can be observed because the ambient temperature, during the course of the electrolysis, reached as high as 48°C for few days such that the solubility of chlorine in water could

FIGURE 3: Chlorine solubility in water.

FIGURE 4: Chlorine recovery percent (—) versus feed catholyte concentration (normality).

have been even less than 4.4 kg/m^3 . This smaller change in solubility alters the recovery up to a range of 20%.

Chlorine material balance has been established, in order to calculate the amount of chlorine recovered. Herein, the amount of chlorine to be captured refers to the decrease in the amount of chlorine present within catholyte (in the form of HCl). Total amount of chlorine captured comprises chlorine determined from the iodometry of bubbler solution, chlorine from solubility of chlorine in bubbler solution, and finally chlorine residual in anolyte which is determined using iodometry by adding small amount of KI.

FIGURE 5: Hydrogen recovery percent (—) versus feed catholyte concentration (normality).

3.2. *Hydrogen Recovery.* Hydrogen recovery is calculated as

$$\text{Hydrogen Recovery} = \frac{\text{amount of Hydrogen captured}}{\text{Hydrogen amount to be captured}} * 100. \quad (8)$$

The hydrogen is collected using downward displacement of water. Figure 5 shows the % recovery of hydrogen at different feed concentrations. Though downward displacement of water technique is very accurate because it does not involve any reactions and no titrations are required to estimate it, the volume of electrolysis cell chambers is only 20 mL; hence even 0.1 mL error attributes to around 5% difference in hydrogen recovery values. These values are only approximations with errors up to 5%.

Before detailing on hydrogen material balance, two important phenomena are to be discussed: simultaneous water electrolysis and electroosmotic drag that occur during the electrolysis process. Water electrolysis is quite possible because the minimum voltage required for water electrolysis is 1.23 V theoretically, around 1.85 V with overpotential resistances [23]. Since the current work has been carried out, around 16 V water electrolysis is expected, so the amount of hydrogen captured was always observed to be greater than the amount of hydrogen decrease in catholyte. The other phenomenon is electroosmotic drag [3] (from here onwards termed as EOD). As chlorine anions pass through the membrane, water molecules surrounding the anion also try to pass through the membrane and water transport is additionally supported by diffusion due to higher water concentration in the catholyte compared with the anolyte (wherein the salt is added). So, there is always a decrease in catholyte volume in the end because of water electrolysis and EOD, whereas there is an increase in the anolyte volume

TABLE 3: Minimum voltage required for different feed concentrations.

Feed cathode concentration (normality)	Electrode distance (cm)	Minimum voltage (V)
4	14	1.7
2	14	2.3
4	7.2	1.5
2	7.2	1.6

due to EOD. Figure 6 shows EOD for 4 N experiments; EOD increases as conversion increases due to increase in the quantity of chlorine anions passing through membrane. The volume of water electrolysed is determined by subtracting the volume gain in anolyte from volume decrease in catholyte.

Similar to that of chlorine, hydrogen material balance is established to calculate hydrogen recovery. The amount of hydrogen to be captured is the quantity of hydrogen decreased in catholyte and hydrogen formed through water electrolysis (see (9)). Amount of hydrogen captured is simply the value calculated from real gas law where the volume is volume of hydrogen captured using downward displacement of water technique:

3.3. Feed Catholyte Concentration. The effect of initial concentration is mainly studied at 16 V, 4 hrs of electrolysis, and ED of 0.14 m for 2 N (7.08 wt%), 4 N (13.73 wt%), and 6 N (20 wt%) with at least three different experimental runs performed to check reproducibility; conversion values can be seen in Figure 7. Effect of parameters in the following sections is presented for 2 N and 4 N experiments only because experiments were also carried out with higher concentrations of HCl (such as 8 N (25.96 wt%)), but it was observed that the temperature increased to nearly boiling point of HCl, the anolyte started to boil, and these liquid droplets began to move out along with chlorine. This could be even due to the very small batch size considered. However, detailed experimentation was not continued with such higher concentrations, since most industrial waste HCl is nearly 17–20% or lesser. On the other side, even at lower normality, rise in temperature was noticed but was just not sufficient to boil the anolyte. Moreover, current study is confined to dealing with industrial waste HCl; hence further detailed experimentations on 6 N and 8 N were not done.

3.4. Electrode Potential Difference. In an electrolysis process, voltage applied plays a crucial role because power is the major operating cost of the process. An attempt to study the effect of voltage on 2 N and 4 N has been carried out. Figure 8 shows the effect of voltage on CE and total charge for a 2 N feed catholyte concentration solution subjected to 4 hrs of electrolysis at an ED of 0.072 m. CE increases as voltage increases, but the slope of increment decreases after 16 V; the slope is increasing clearly after 12 V and then reduces when it reaches 16 V. So it can be inferred that 14 V and 16 V

FIGURE 6: Electroosmotic drag (mL) versus conversion (—).

FIGURE 7: Conversion percent (—) versus feed cathode concentration (normality).

are most suitable to work with to get optimum conversion. Experiments conducted for voltages above 20 V led to an increase in temperature of the entire reaction chamber. From the above discussions it was decided to work with 16 V. Figure 9 shows the effect of voltage for the experiments conducted with 4 N feed concentration for the same ED. The same can be inferred from Figure 9; that is, 14 V and 16 V are optimum choices. In both feed concentrations the nature of graphs remains the same. To minimize cell voltage which is the main factor influencing the specific energy requirement,

FIGURE 8: Conversion percent (—) and total charge (ampere hour) versus voltage (volts) for 2 N feed concentration.

many parameters are being considered for further studies; some experiments are performed to determine the minimum required cell voltage; these results can be seen in Table 3. Minimum voltage is required for different feed concentrations. The minimum required voltage is considered as voltage at 0.001 amp. As ED decreases, the resistance offered to ionic movement decreases and this explains the decrease in minimum required voltage.

3.5. Time of Operation. The reported literature had indicated that most electrolysis experiments of HCl have been conducted for long hours of operation to study the effect of parameters. Since this work has been initiated with an objective of recovering chlorine and hydrogen simultaneously such that the entire operation could be made self-sufficient in terms of energy consumption, it was thought apt to study the effect of time of operation. Further, time of operation becomes a very crucial parameter when the batch system would have to be scaled to continuous system. The time of operation is examined by taking intermediate samples for every hour. Figure 10 shows that curve becomes flat after 3 hours (89% CE till 3 hours) for 4 N experiment and after 2 hours for 2 N (90.79% CE in 2 hours).

3.6. Electrode Distance (ED). ED plays a significant role on variation in CE because the lesser the value of ED, the more the surface area of electrode that is available, thus increasing the number of ions generated every time instance, thereby increasing the ionic movements across the membrane. And also by decreasing the ED, the resistance is reduced because of the decrease in distance to be travelled by ions. Experiments

FIGURE 9: Conversion percent (—) and total charge (ampere hours) versus voltage (volts) for 4 N feed concentration.

were performed mainly maintaining two different ED, 0.14 m and 0.072 m. Figures 11 and 12 show CE at different ED for two feed concentrations; it can be seen that both graphs have similar nature. We can see that as ED increases, the CE as well as total charge decreases. Further reduction in ED was not performed since almost 97-98% electrolysis was already obtained. To study the parameters which contributed more to increased conversion for reduction in ED, some experiments were performed by bending the electrodes. For instance, the electrodes initially were placed at 0.072 m and they were bent till the tips are at distance of 0.14 m; by this we increased the surface area of electrodes without changing the electrode distance. The conversion for 4 N feed concentration at 16 V for increased surface area is 46.36% which is almost the same as the conversion at 0.072 m, indicating that after all the main dominating parameter is ED rather than increased concentration of ions (increased area of electrode). The same cannot be generalized without looking into more similar results for different voltages and surface area of electrodes.

3.7. Current Density. Current density herein is defined as the amount of current passing through unit surface area of membrane shown as follows:

$$\text{Current Density} = \frac{\text{Current being generated}}{\text{Membrane Surface area}}. \quad (10)$$

The membrane surface area has been constant to 7.068 cm², but the active surface area while performing the experiments has been only 70% (owing to the capacity of catholyte and anolyte chambers) with a surface area of 4.946 cm². Table 4 shows maximum current values when operating at different

TABLE 4: Current density values for different feed concentrations and UHDE ODC process.

Process	Feed cathode concentration (normality)	Maximum charge generated (amperes)	Active membrane surface area (cm ²)	Current density (kAm ⁻²)
AEM	2	1.13	4.9602	2.283936
AEM	4	1.26	4.9602	2.546689
AEM	2	1.13	7.068	1.598755
AEM	4	1.26	7.068	1.782683
UHDE ODC [2]	4.6		25000	5

FIGURE 10: Catholyte concentration (normality) versus time of operation (hours) for 4 N and 2 N feed concentrations.

normality for 16 V and corresponding current density values in kAm⁻². The values at 4 N for different active membrane surface areas are 2.54 kAm⁻² (assuming 70%) and 1.78 kAm⁻² (assuming 100%) when comparing these with those reported in the literature, whose value is 5 kAm⁻² [2] at 2.5 m² membrane surface area for 14 wt% (4.6 N) feed concentration; we can say that this method of AEM has high feasibility to become a better alternative in the future.

3.8. Current Efficiency. Electricity expense constitutes the largest fraction of economics of electrolysis processes. High hydrogen production expenses is one of the main deficiencies of commercial and industrial electrolyzers, so the current efficiency (sometimes referred to as Faradaic efficiency) [24] is determined by dividing the amount of current used to convert hydrogen chloride to chlorine by total charge supplied to the cell:

$$\varepsilon_{\text{current efficiency}} = \frac{z * n * F}{Q}, \quad (11)$$

FIGURE 11: Conversion percent (—) and total charge (ampere hour) versus ED (mm) for 2 N feed concentration.

where z is the number of electrons exchanged per mole of the electrolyte (here, $z = 1$), n is the number of moles electrolysed (here dilute HCl), F is Faraday's constant ($F = 96,485 \text{ C/mole}$), and Q is the total charge passed through the membrane in coulombs. Figure 13 shows average current efficiency values for 4 N and 2 N feed concentrations at different voltages for ED of 0.072 m. The average current efficiency values are in range of 60%; the remaining could be majorly due to oxygen formation. The current efficiency gives an understanding on optimizing the performance of whole unit with minimum electrical input and maximum efficiency.

3.9. Energy and Economic Efficiency. The specific energy requirement for the present study is not considered for comparison with commercial processes because the experimentation is presently in batch mode and the efficiency would obviously be much less; however it is felt needed to discuss the economic efficiency. The calculated economicity and energy efficiency for 16 V and 4 N were 77.83% and 35.66%; the costs assumed are for hydrogen 129 Rs/Kg, chlorine

FIGURE 12: Conversion percent (—) and total charge (ampere hour) versus ED (mm) for 4 N feed concentration.

FIGURE 13: Current efficiency percent (—) versus voltage (volts) for ED of 0.072 m.

52 Rs/Kg, and electricity 4 Rs/unit. These costs vary from place to place and very much depend on local market demand and supply. Economicity is simple ratio of revenue to cost; although only variable costs are considered, these values are enough to depict the economic feasibility as variable costs are more important in the long run than fixed costs. Energy efficiency is calculated by considering HHV (141.8 MJ/Kg) of hydrogen and dividing it by electrical energy input to the system (average current for 4 hrs, 0.837 amperes). Economic efficiency of 77.8% for a batch process seems commendable which will be definitely increased in continuous phase.

4. Conclusion

Simultaneous recovery of chlorine and hydrogen from industrially waste hydrochloric acid has been carried out using electrolysis in an electrolytic cell as a batch process. Intensifying this process to a continuous one will also be industrially significant, and especially owing to minimal carbon footprint, the process can provide and maximize benefit it can offer to meet future energy demand. As norms for environment are expected to be more firm in the future, this process would prove to be an economical solution for companies and with the advent of renewable energy the cost of electricity would come down significantly in the long run. The high economic efficiency of 90% for a simple batch process adds to commercial feasibility of this paper; the process would be more economical if scaled to continuous operation and this will be of great value addition to company in terms of energy savings and also mitigating the risk of environment impact.

The highlights of the entire paper are summarized as follows:

- (i) The results of this paper confirm that simultaneous recovery of hydrogen and chlorine is feasible with electrolysis process using an Anionic Exchange Membrane as separator. The hydrogen and chlorine recovery up to 90% is achieved.
- (ii) Fixing the anolyte concentration at 0.55 N is proved to be effective by minimizing oxygen formation and at the same time use of platinum electrodes showed long time durability.
- (iii) Total charge generated and conversion for a fixed feed catholyte concentration are directly proportional to voltage applied, but the values increase less significantly after 16 V.
- (iv) The electrode distance has a direct effect on the resistance of the process when electrode distances are reduced from 0.14 m to 0.072 m; the conversion values increased to 98%. Such high single pass conversions are not reported in the literature.
- (v) One of the main limitations is water transport through membrane which continuously builds up the volume of anolyte; however this is not covered in the scope of this paper.
- (vi) The catholyte concentration decreases based on the extent of electrolysis, but as for anolyte it was observed that with an increase in the conversion, as the ion movement increased, osmotic drag increase along with a reduction in anode concentration was noted.

- (vii) Current efficiency values shown are calculated only on basis of decrease in catholyte chlorine concentration; the values obtained are in range of 60%.
- (viii) The current density value of 2.54 kA/m^2 is comparable to processes reported in the literature even at very low membrane surface area and low feed concentration of 13.79 wt% makes this process a feasible alternative in the future.
- (ix) The recovery of chlorine and hydrogen from waste dilute HCl using electrolysis is highly recommended because not only it is possible to recover both hydrogen and chlorine but also it is a sustainable process which decreases waste quantity by producing a clean fuel and highly demanding base chemical with minimum process steps.
- (x) It is resource conserving and has low environmental impact when compared to catalytic oxidation process.
- (xi) The high cost of platinum can be offset by coating platinum on surface of a cheaper base metal like titanium.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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