Concentration / Recovery of H_2SO_4 using Electrodialysis

Dhaval N. Yadav[1], **Beena K. Sheth**[2]

[1]Chemical Engineering Department, Vishwakarma Government Engineering College Chandkheda, Gujarat, Ahmedabad

[2]Associate Professor, Chemical Engineering Department, Vishwakarma Government Engineering College Chandkheda, Gujarat, Ahmedabad

Abstract: ***Sulphuric acid known as universal solvent is used widely in chemical industry where acidic or anhydrous conditions are required, in its various forms either as dilute or concentrated, as a raw material or a catalyst. The effluent/spent acid generated from industries containing sulphuric acid being hazardous is a major environmental problem that needs to be recovered /separated. Many methods Conventional or Advance have been applied successfully for the recovery of sulphuric acid from waste streams. Membrane separation methods being advantageous and eco-friendly compared to conventional techniques is now being used widely. The present work here focuses on recovery/concentration of laboratory made sample of sulphuric acid using Electrodialysis for different concentration of sulphuric acid solution.***

Keywords: Sulphuric Acid, Ion exchange membrane, Electrodialysis

1. Introduction

It is well established fact that the metal finishing industries, such as electroplating, acid pickling, etc have played important roles in the consumption of various acids including HCl, H_2SO_4 and HNO_3. The waste generated from such industries poses considerable problems in waste disposal. Approximately billion gallons of such solutions are produced annually in the United States with an average composition of 15% $FeSO_4$ and 5% free H_2SO_4 and more than 25 million tons per year of relevant waste acid in China only according to a roughly estimation[1]. Various methods both conventional and advanced have been proposed for the recovery/ disposal of acids from such streams.

The conventional processes for the recovery of sulphuric acid comprises of neutralization/ precipitation, crystallization, thermal decomposition[2]. Though these processes are well established a considerable amount of acid is still discharged into the waste stream. With developing stringent environment pollution norms aiming toward zero discharge policy advanced (membrane) separation processes have come into existence. The different membrane process for the recovery of sulphuric acid include diffusion dialysis[3], electro dialysis[4] and membrane distillation[5]. All these process include membrane as their principle mode of separation but differ from each other in working principle.

2. Electrodialysis

Electrodialysis is an electro membrane process in which ions are transported through an ion exchange membrane (IEM) from one solution (catholyte/ anolyte) to another (anolyte/ catholyte) respectively under the influence of an electrical potential gradient. The electrical charge on the ions (anions, cations) allows them to be transported through the IEM. Basically there are two different types of IEM viz. Anion Exchange Membrane, AEM and Cation Exchange Membrane, CEM [6].

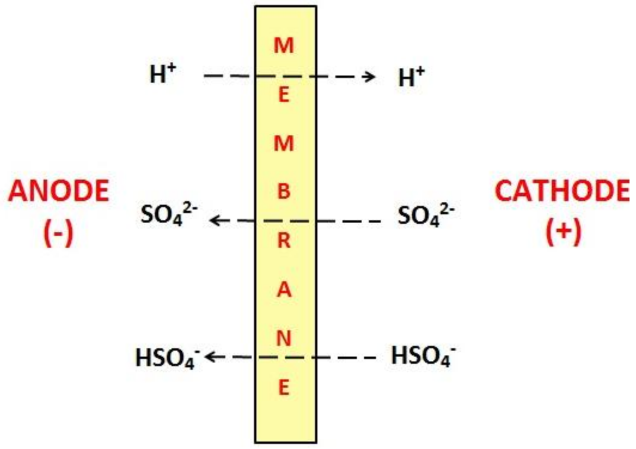

Figure 1 : Movement across AEM

The AEM contains a positively charged group fixed to a polymer matrix whereas the CEM contains a negatively charged group fixed to a polymer matrix. The basic principle governing the process is that on application of current/voltage across the two electrodes (Anode +ve and Cathode -ve) an electrical potential is generated and under the influence of this electrical potential the negatively charge anions (Cl^-, SO_4^{2-} etc)move across the AEM and the positively charge cations (Na^+, Ca^+ etc) move across the CEM [7]. The anions and cations cannot pass through the CEM and AEM respectively. A single operation of ED gives two streams viz. Concentrate and Diluate. Depending upon the purpose to be served any one of the concentrate and dilute has the desired product(s).

3. Experimental Work

3.1 Chemicals

All the chemicals used in the experiments like Sulphuric Acid, Sodium Hydroxide, Potassium Chloride were prepared from Analytical Grade chemicals which were purchased from Finar Chemical Co. Ahmedabad.

3.2 Ion Exchange Membranes

The anion exchange membrane used in the experiment is Selemion AAV supplied by Asahi Glass Company of Japan. The properties of which are mentioned in Table 1:

Table 1: Ion Exchange Membrane Properties

Type	Anion Exchange Membrane
Product name	Selemion AAV
Characteristics	Low proton leakage
Usage	Electro dialysis
Thickness	0.12 mm
Counterion	SO_4^{2-}
Resistance	16 Ω cm^2
Burst Strength	300 kPa

3.3 Electrodialyzer

The membrane electrolysis of sulphuric acid is carried out in batch mode (without circulation) using a laboratory made electrodialyzer equipped with Anion Exchange Membrane as shown in the figure 2.

Figure 2: Experimental Set Up

The laboratory electrodialyzer is fabricated from 5 mm thick transparent plate of Acrylic. It consists of two chambers of equal volume open from the top and equipped with drain/flush valve at the side bottom. The opening at the top enables easy insertion of electrodes, glass rods for stirring and easy loading/unloading of the acid into the chambers. The anion exchange membrane (effective area 49.5 cm^2 is housed between these two chambers. A constant DC current is supplied using Regulated DC Power Supply from TESTRONIX D-32.

3.4 Experimental Procedure

The membrane to be used was first washed with distilled water in order to remove of any contaminants deposited onto it and later was soaked in 1 wt% sulphuric acid solution for 48 hour. Before the starting of the experiment all the apparatus comprising of beakers, glass rods, burette, pipette and the dialyzer were washed with distilled water thoroughly. Solutions of desired concentrations (0.23M, 0.34M, and 0.45M) were prepared and their concentrations were cross checked by measuring the conductivity using a digital conductivity Meter. The prepared solutions were then poured into the dialyzer, with graphite electrodes already immersed in it. The DC power source was turn on and maintained at desired values (i.e. 500, 1000, 1500mA). The increase and decrease in acid concentration was measured every 30 minutes both by titration with 0.1N NaOH and by measuring the conductivity also. The experiments were conducted for a fixed time of 3 hours.

4. Results

The results of different experiments are shown in Table 2:

Table 2: Results

Exp. No	Current (mA)	Initial Anode Conc. (M)	Initial Cathode Conc. (M)	Current Efficiency (%)	Flux 10^{-8} (mol /cm^2sec)
1	500	0.23	0.23	39.40	0.98
	1000	0.23	0.23	45.96	2.29
	1500	0.23	0.23	31.89	2.38
2	500	0.23	0.34	43.18	1.07
	1000	0.23	0.34	47.88	2.38
	1500	0.23	0.34	40.30	3.01
3	500	0.23	0.45	46.64	1.16
	1000	0.23	0.45	50.95	2.54
	1500	0.23	0.45	43.97	3.28

4.1 Characteristics Curve

The figure 3 represents the characteristics curve for change in anode and cathode concentration with respect to time on the basis of applied current values.

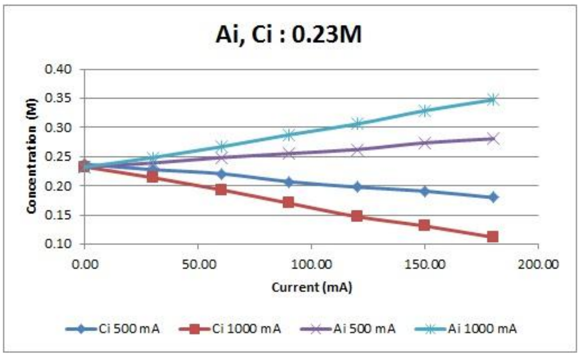

Figure 3 : Characteristics Curve for ED

The graphical results presented here are for experiments conducted at equal anode and cathode concentration of 0.23M and dialyzer operated at varying value of applied current. It is 2found that the concentration of acid in the anolyte increases from 0.23 M to 0.28 M and 0.347 M for current values of 500 and 1000 mA respectively. At the same time the catholyte concentration decreases from 0.23 M to 0.18 M and 0.11 M for the same current values respectively. This increase in concentration is due to the fact that if the current is increased, the rate of electrical transport is increased as a result of which the mobility of ions also increases, which leads to an increase in the diffusive transport.

Bottom Line: The amount of acid loss or gain is affected by the applied value of current.

4.2 Current Density and Current Efficiency

The limiting current density in Electrodialysis is an important factor which determines the electrical resistance and the current utilization. The value of limiting current density depends on the membrane under use (AEM, CEM, BPM), properties of solution to be treated, Electrodialysis unit design and various other operating parameters. Current Efficiency is an important factor which determines the overall performance of an Electrodialysis unit. The success of an Electrodialysis process depends upon the effective utilization of the applied current, which is known as current efficiency. Current efficiency value determines the portion of the total current that passes through an ED stack that is actually used to transfer ions from a feed solution. The values of current efficiency are calculated using the following equation[8]:

$$CE_{\alpha} = V_{\alpha}\frac{dC_{\alpha}}{dt};\ \alpha = An, Ca \qquad (1)$$

Where,
CE = current efficiency (%),
α = represents the corresponding stream i.e. anode, cathode
C = represents the Concentration of acid

In order to determine the effect of current density on current efficiency experiments were conducted for different initial acid concentration. The results are shown in figure 4. It can be seen from the plot that the overall current efficiency increases until a maximum value is reached, and then decreases with an increase of current density.

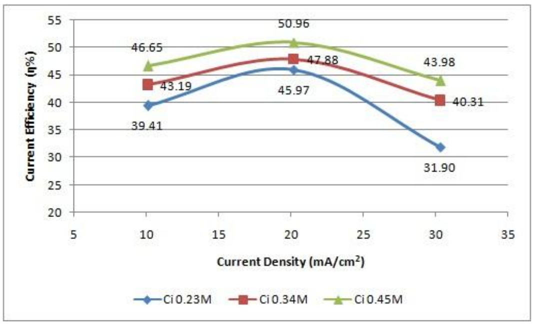

Figure 4 : Effect of Current Density.

The main reason for this increase is that if the current is less than the limiting current density, the increase of current density will not cause negative effects such as higher electrical resistance, co-ion leakage through the membrane, and water splitting on the surface of the membranes. In the experiments conducted it is found that the maximum value of efficiency is obtained at applied current of 1000 mA.

Bottom Line: For a fixed initial acid concentration, the current efficiency value increases for an increase in current density if operated below the limiting current density value.

4.3 Initial Acid Concentration

Initial acid concentration is also one of the factors influencing the recovery of acid. The graphical representation of the initial acid concentration is presented below in figure 5.

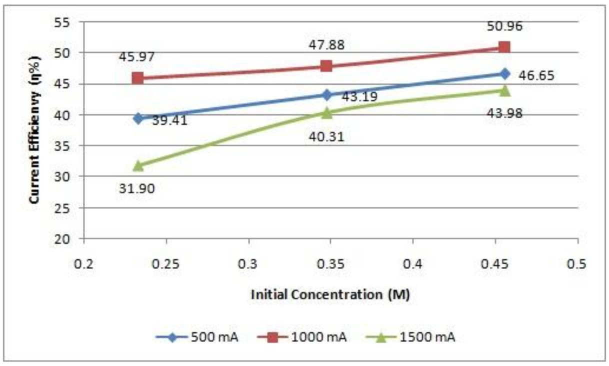

Figure 5 : Effect of Initial acid concentration.

It is evident from the plot that an increase in acid concentration leads to an increase in the overall efficiency. This is due to the fact that our system is a dilute one. Hence the number of ions present in the system is very less. On operating the system at current of 500 mA the efficiency of 0.23M, 0.34Mand 0.45M acid is found to be 39%, 43%, 46% respectively which increases to 45%, 48% and 51% respectively at 1000 mA. This increase is due to the increase in the ionic mobility of the ions which thereby increases the efficiency. But for the same system when operated at 1500 mA a completely reverse phenomenon is observed i.e. the efficiency is reduced to values below the 500 mA. This is because at a constant current density, the current efficiency is low when the H_2SO_4 concentration is also low, because of a larger amount of water leakage through the membrane.

Bottom Line: On increasing the initial acid concentration, the current efficiency increases up to a certain value and thereafter decreases. It is confirmed that current efficiency is strongly influence by acid concentrations.

4.4 Flux of H_2SO_4

The flux of acid is greatly influenced by the initial concentration of the acid and the current applied. It is found that for a fixed anode concentration, increasing the cathode concentration leads to an increased value of flux. The increase in cathode concentration increases the concentration difference across the dialyzer which in turn favours the rate of diffusion. Secondly as stated earlier increasing the current leads to an increase in mobility of ions which causes an increase in flux too.

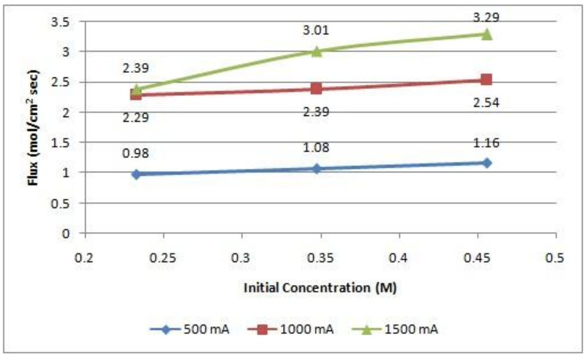

Figure 6 : Effect of initial acid concentration on flux.

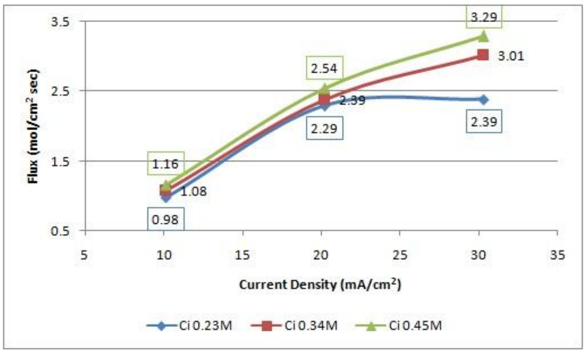

Figure 7 : Effect of current density on flux

5. Conclusion

It is found that sulphuric acid can be efficiently concentrated and recovered from the process stream using electrodialyis. Initial acid concentration, applied current, time, exposed membrane area (yet to be verified), temperature (yet to be verified) and the mode of operation (yet to be verified) are some of the factors which affect the process. Of all the various factors, current plays a vital role in the success of the process. Both the flux and current efficiency are greatly dependent on initial acid concentration and applied current values. The above parameter needs to be optimized for proper and effective operation of an Electrodialysis process. There exists a scope for further work in the recovery of acids from streams contaminated with other impurities (both anionic and cationic) in nature.

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