Electrodialysis in the separation of Sulfuric acid from the mixture of Sulfuric and Hydrochloric acid

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ABSTRACT

Sulfuric acid has a wide array of applications in chemical industry. Most of the chemical industries produces acidic effluent, from which the acids must be recovered. Recovery of valuable acids leads to economic operation and safer disposal of waste. For recovery, many technologies can be used by which acids can be regained as such or can be converted into other value-added products. Membrane processes are being researched academically and practiced industrially. Ion-exchange membranes are used for many commercially relevant processes such as in electrodialysis and diffusion dialysis.

Keyword : - *electrodialysis, ion exchange membrane, diffusion dialysis*

1. INTRODUCTION

Sulfuric acid (H_2SO_4) solution has been widely used in chemical and metal industries for various surface treatments as electrolysis, electroplating, and acid pickling because of its relative inexpensiveness compared with other acids. The waste sulfuric acid solution can be treated by conventional methods (such as cooling, evaporation, distillation, thermal decomposition, solvent extraction) and advance separation techniques (such as electrodialysis, diffusion dialysis, membrane distillation). From various separation methods electrodialysis is more efficient techniques for acid recovery/separation because of low energy consumption and more efficiency. Electrodialysis is also better than diffusion dialysis as Ed uses electric potential difference and the concentration difference, both as a driving force.

By using diffusion dialysis, the concentration of acid is not possible because it only uses chemical potential difference as a driving force, while that is not the case in electrodialysis.

Ion exchange membrane is the key component of electrodialysis cell. The performance of ED is largely depends upon the properties of ion exchange membranes. For acid recovery mainly anion exchange membranes are used. Anion exchange membranes only allow anion to pass through it. Therefore, the negative ions of the acidic solution can pass through the membrane and get concentrated on the other side. The selectivity of any membrane decides the degree of separation in electrodialysis.

Many industries like electroplating industry, metal processing industries, semiconductor industry generate acidic effluents which contain H_2SO_4 and HCl. This mixtures of acid have an adverse effect on environment and living bodies. Acidic effluent should be neutralized or treated before discharge. These type of effluent can be treated with this system and sulfuric acid can be separated. Recovered sulfuric acid can be used in number of ways.

For separation of HCl and H_2SO_4, electrodialysis is the most suitable method in terms of environmental and economic aspect. Therefore, the aim of present study is to separate/recover sulfuric acid from the mixture of sulfuric and hydrochloric acid using electrodialysis.

2. Literature Survey

M Tomaszewska, A. Mientka et al [4] separated HCl from the mixture of HCl and H_2SO_4 by using membrane distillation. They observed that the increase in sulfuric acid flux would decrease the permeate flux which contained HCl. The increase in HCl concentration in feed would increase the permeate flux.

S. Koter et al [5] separated the mixture of H_2SO_4 and acetic acid using two different membranes, CMX and ACM. He proved that the efficiency of retention of acetic acid is high (>0.9) when the process is run below the limiting current density. The current efficiency for the sulfuric acid removal was 0.7 with initial H_2SO_4 concentration of 1 or 2M. R. Audinosa, A. Nassr-Allah et al [2] separated the dilute mixtures of sulfuric acid and nitric acid. Sulfuric acid in the concentrate increased with time and reached to the maximum value at around 90 minutes and normalized concentration of nitric acid decreases immediately from the beginning of the experiment. M. Suresh Kumar,Nikhil Y. Ghare et al [3] got the recovery of HCl of around 85%and the removal of iron was 90%. they used the wastewater and sludge samples collected from the steel processing industry. X. Tongwen, Y.Weihua et al [6] recovered sulfuric acid from waste liquor and studied the effect of some important factors such as ion exchange capacity, content of benzyl-halogen and the relative compositions of the liquor. It was found that the acid recovery rate was increased by benzyl substitution, while the selectivity of membrane was improved by substitution of aryl. By adjusting proper balance between substitutions and adjusting the feed composition, Higher selectivity and acid recovery can be achieved.

3. EXPERIMENTAL WORK

3.1 Chemicals

All the chemicals used for the experiments are prepared from AR grade chemicals purchased from Finar Chemicals Co. The synthetic solutions were prepared from distilled water.

3.2 Ion Exchange Membranes

Two anion exchange membranes are used which are Selemion AAV and AMV. Both the membranes have been provided by Asahi Glass Company, Japan.

Properties of AAV: It is used for electrodialysis. The thickness of the membrane is 0.12 mm. Resistance to SO_4^{2-} is 16 Ωcm^2 and burst strength is 300 KPa.

Properties of AMV: It is used for electrodialysis. The thickness of membrane is 0.11 mm and the counter ions is Cl^- Resistance to counter ions is 2.5 Ωcm^2. Burst strength is 200 KPa.

3.3 Electrodialyzer:

The membrane electrolysis of sulfuric acid is carried out in batch mode (without circulation) using a laboratory made electrodialyzer equipped with Anion Exchange Membrane as shown in the Figure 1. The laboratory electrodialyzer is fabricated from5mmthick 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.

Figure 1: Experimental Setup

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. The membrane was soaked in 1 wt% acid solution for 48 hours of which it is to be used. (1 wt% H_2SO_4 for H_2SO_4 concentration and 1 wt% HCl for HCl concentration). 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 were prepared from analytical grade reagents. The concentrations of the prepared solutions 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 fix current value of 1000 mA. The increase and decrease in acid concentration was measured every 15 minutes both by titration with 0.1N NaOH and by measuring the conductivity also. The probe of the conductivity meter was washed with distilled water after every measurement. The obtained values were thus noted down and further calculation were done. Same procedure was followed for another acid concentration and membrane. In the same way diffusion dialysis were carried out in batch mode for both the membranes. The concentration was checked by titration with standard solution of 0.1M NaOH and it was cross checked by conductivity meter.

For the mixture of two acids (4 wt% H2SO4 and 1 wt% HCl) pure sulfuric acid (4 wt%, 250 mL) was taken at cathode side and at anode side mixture of two acids (125 ml each) was taken. The experiment was run for 2 hours with above procedure. The sulfate and chloride analysis are done by Envisafe environmental consultancy.

4. RESULTS

The electrodialysis were carried out for three different concentrations of H_2SO_4 for 180 minutes. The current was kept constant at 1000 mA. The results for ED of H_2SO_4 are mentioned below.

Membrane	Sr No.	Initial Anode	Initial Cathode	Final Anode	Final Cathode	Flux (Cathode)

		C_{Ai} (moles)	C_i (moles)	C_{Af} (moles)	C_f (moles)	10^8 (molcm^{-2}sec^{-1})
AMV	1	0.023	0.023	0.0364	0.0104	2.356
	2	0.023	0.0349	0.0350	0.0212	2.581
	3	0.023	0.0411	0.0359	0.0301	2.768
AAV	1	0.023	0.023	0.0333	0.011	2.282
	2	0.023	0.0349	0.0322	0.022	2.375
	3	0.023	0.0411	0.0306	0.032	2.525

Table 1: Results of electrodialysis for sulfuric acid

4.3 Flux of H₂SO₄

Flux of H₂SO₄ is calculated for each initial cathode concentration from the following equation.

$$Flux = \frac{C_i - C_f}{A * t}$$ .... (1)

Where,

C_i = Initial cathode concentration

C_f = Final cathode concentration
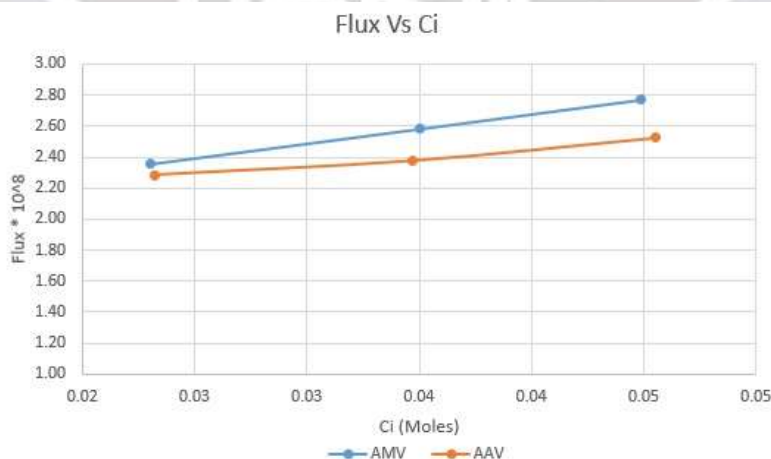
A = Membranes area
t = time

Figure 2: Flux of sulfuric acid vs initial concentration

From fig. 2 we can say that the flux of SO_4^{2-} was increased with increase in C_i for both membranes. Flux for AMV is higher than AAV for particular initial acid concentration. The flux is higher for high initial concentration because

ions present in electrolyte solution are higher and can carry higher current. Therefore, movement of ions through membrane increased and ultimately flux of ions are increased. For, higher recovery/ concentration of sulfuric acid, the initial concentration of the acid should be high.

4.4 Mixture of two acids

Electrodialysis for the mixture of two acids was carried out for 2 hours for both membranes. The flux of sulfate and chloride ions were calculated with eq. (1) and the result is tabulated below:

Process	Membrane	Cathode				Flux of SO_4^{2-} *10^8	Flux of Cl^- *10^8
		SO_4^{2-}		Cl^-			
		Initial Moles	Final Moles	Initial Moles	Final Moles	Mol cm^{-2}s^{-1}	Mol cm^{-2}s^{-1}
ED	AAV	0.052	0.0454	0.124	0.1177	1.767	1.964
	AMV	0.052	0.0439	0.124	0.115	2.272	2.525
DD	AAV	0.052	0.0502	0.124	0.122	0.252	0.280
	AMV	0.052	0.0495	0.124	0.12	0.350	0.420

Table 2: Results for the mixture of two acids

From fig. 3 and 4 it can be seen that flux of SO_4^{2-} and Cl^- are higher in AMV compared to AAV membrane for electrodialysis. For diffusion dialysis the same trend is observed. Here, the flux of sulfate ions is less than the chloride ions for both the membranes and both the processes. This can be justified by the fact that the chloride ions are smaller in size compared to sulfate ions. Therefore, chloride ions can easily permeate through the pores of the membranes.
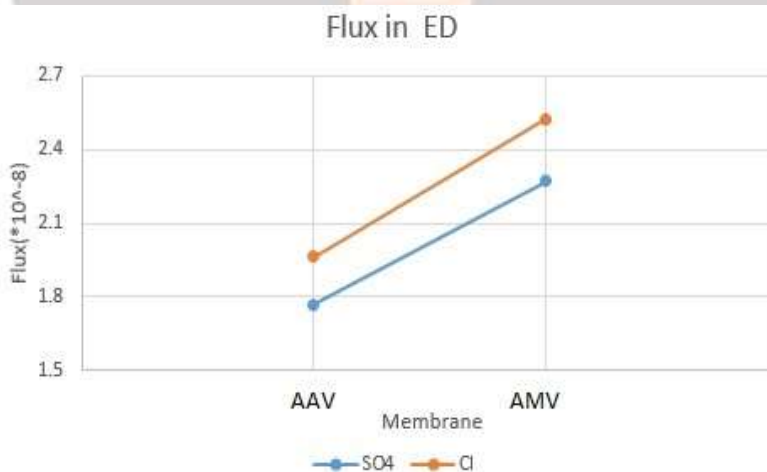

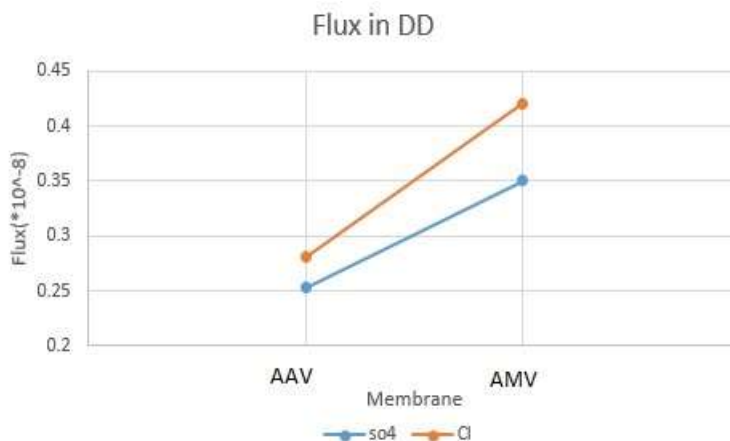**Figure 3: Flux of SO_4^{2-} and Cl^- ions for two membranes for electrodialysis**

Figure 4:Flux of SO$_4^{2-}$ and Cl⁻ions for two membranes for diffusion dialysis

5. CONCLUSION

Sulfuric acid can be recovered by electrodialysis. From the experiments of Electrodialysis of H$_2$SO$_4$ it can be concluded that AMV is better than AAV for the concentration of sulfuric acid. For a particular membrane flux increases with initial acid concentration. For recovery of sulfuric acid from the mixture of two acids AAV gives better separation compared to AMV. ED has a higher recovery of sulfuric acid compared to diffusion dialysis because ED has an additional electrical force to accelerate the movement of ions in solution.

For the mixture of two acids (H$_2$SO$_4$ and HCl) separation is possible to some extent. AAV should be used for the separation of sulfuric acid because it has a favorable property for the sulfate transfer.

Electrodialysis has a potential for the efficient recovery of particular acids from the waste acidic stream. It has a benefits over conventional methods in terms of environmental merits and energy requirement.

6. REFERENCES

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