

# Selective Recovery Of Strong And Weak Acids And Bases From Semiconductor Wastewater Using Diffusion Dialysis: Mechanisms, Kinetics, And Process Optimization

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## Abstract

The rapid growth of the semiconductor industry has led to the generation of large volumes of wastewater containing highly concentrated acidic and basic compounds with significant environmental impact. This study aims to evaluate the efficiency of diffusion dialysis for the selective recovery of strong and weak acids and bases from semiconductor effluents while investigating the mechanisms governing ion transport through ion-exchange membranes. Neosepta-type membranes (AMX and CMX) were used to separate and recover individual and mixed solutions of acids (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HF, H<sub>3</sub>PO<sub>4</sub>, CH<sub>3</sub>COOH) and bases (NaOH, KOH, Ba(OH)<sub>2</sub>). Results show that ion mobility is influenced by dissociation degree, pK<sub>a</sub>, molecular size, and distribution constants, explaining differences in permeability and recovery rates. HF demonstrated superior transport among weak acids, while Ba(OH)<sub>2</sub> showed the highest recovery among bases. A simulated HF + Cu<sup>2+</sup> solution showed 60% HF recovery, confirming membrane selectivity. This work provides a practical framework for understanding selective ion transport and offers a sustainable low-energy alternative for chemical recovery in high-tech industries.

**Keywords:** Diffusion dialysis, wastewater treatment, semiconductors, ion-exchange membranes, chemical recovery

## 1. INTRODUCTION

The semiconductor industry generates large volumes of acidic and alkaline wastewater, particularly during etching, cleaning, and metal plating processes. These effluents commonly contain strong and weak acids such as hydrofluoric acid (HF), nitric acid (HNO<sub>3</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), as well as bases like sodium hydroxide (NaOH), potassium hydroxide (KOH), and barium hydroxide (Ba(OH)<sub>2</sub>), often in combination with metal ions such as Cu<sup>2+</sup>. The environmental risks and economic costs associated with the discharge of these compounds necessitate efficient and selective recovery methods (Wang et al., 2024; Kim & Yoon, 2023).

Diffusion dialysis (DD) has emerged as a promising membrane-based separation technique for recovering acids and bases from industrial wastewaters. It offers significant advantages over conventional methods, including low energy requirements, no need for chemical reagents, and high selectivity for ionic species (Zhang et al., 2024; Liu et al., 2024). DD relies on ion-exchange membranes that exploit both thermodynamic partitioning and concentration gradients to drive selective diffusion of ions between compartments (Sun et al., 2024). The process is particularly suited for treating corrosive and chemically complex effluents where conventional neutralization or evaporation would be inefficient or costly.

Numerous studies have characterized the transport behavior of strong inorganic acids through anion-exchange membranes, often ranking their transfer efficiency as HCl > HNO<sub>3</sub> > H<sub>2</sub>SO<sub>4</sub> due to differences in ion mobility and membrane affinity (Zhang et al., 2024; Roh & Kim, 2024). In contrast, weak acids such as HF, H<sub>3</sub>PO<sub>4</sub>, and CH<sub>3</sub>COOH exhibit more complex behavior governed by their dissociation constants (pK<sub>a</sub>), molecular size, and partial transport as undissociated species (Tanaka et al., 2023; Kwon et al., 2024). Similarly, base diffusion through cation-exchange membranes depends not only on OH<sup>-</sup> mobility but also on the size and charge of counter-ions such as Na<sup>+</sup>, K<sup>+</sup>, and Ba<sup>2+</sup> (Lee et al., 2024; Zhang & Wang, 2023).

Despite growing interest in DD, few studies have addressed real-case scenarios involving metal-acid interactions, such as the HF-Cu<sup>2+</sup> systems typical of semiconductor effluents. These systems introduce complex equilibria involving proton exchange, metal-ligand complexation, and competing ionic transport, all of which can significantly influence membrane performance (Wang et al., 2024; Zhou, Lin, & Chen, 2025).

This study aims to provide a comparative evaluation of strong and weak acid and base transport across ion-exchange membranes using diffusion dialysis under non-agitated conditions. Additionally, it simulates a real industrial scenario involving an HF + Cu<sup>2+</sup> mixture to assess the selectivity and potential of DD for

acid recovery in semiconductor wastewater treatment. The work emphasizes the roles of thermodynamic affinity, dissociation behavior, and ion mobility in determining separation performance.

## 2 . MATERIALS AND METHODS

This study was conducted using a simple and efficient experimental setup to evaluate the effectiveness of diffusion dialysis in recovering strong and weak acids and bases from simulated semiconductor wastewater. The system consisted of a Plexiglas dialysis cell with two compartments separated by an ion-exchange membrane—Neosepta type (AMX for acids, CMX for bases) with an active surface area of 3 cm<sup>2</sup>.

Each compartment was filled with 100 mL of solution:

- **Compartment 1 (Retentate):** Contained the target acid or base solution.
- **Compartment 2 (Dialysate):** Contained distilled water to receive transferred ions.

### 2.1 Chemicals Used:

- **Acids:** HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HF, H<sub>3</sub>PO<sub>4</sub>, CH<sub>3</sub>COOH
- **Bases:** NaOH, KOH, Ba(OH)<sub>2</sub>
- **Metallic ion:** Copper (Cu<sup>2+</sup>) for HF/Cu simulations

### 2.2 Operating Conditions:

- Temperature: 28°C
- Duration: 24 hours
- Agitation speed: 750 rpm (used selectively)
- Measurements: pH, normality (acid–base titration), Cu concentration (atomic absorption spectrometer AA-6800, Shimadzu)

### 2.3 Membrane Pre-treatment Cycle:

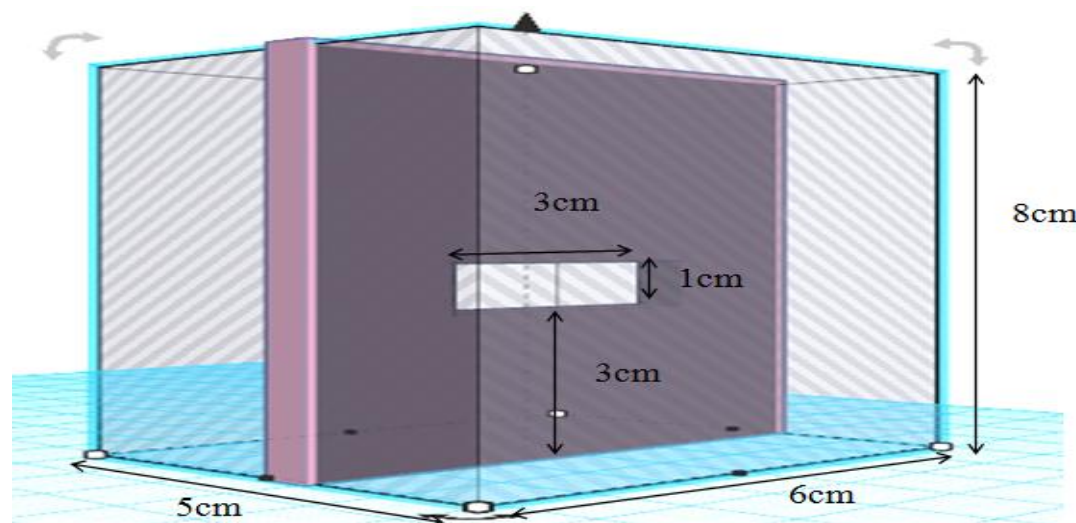
1. Immersion in 0.1N NaOH followed by rinsing
2. Immersion in 0.1N HCl followed by rinsing
3. Soaking in the working solution for 24 hours

Experimental Design:

- Individual experiments for each acid and base
- Mixed acid/base solutions (e.g., HCl + HNO<sub>3</sub>, HF + Cu<sup>2+</sup>)
- Evaluation of agitation effect on ion transfer
- Use of Fick's law to calculate permeability and diffusion coefficients

**Table 1 physicochemical Properties of the Ion-Exchange Membranes Used**

Membrane	Ion-Exchange Capacity (meq/g)	Water Uptake (wt%)	Thickness (μm)	Density (g/cm <sup>3</sup> )
AMX	2.12	18	166	**
CMX	1.62	23	175	1.25



**Figure 1:** schematic representation of the dialysis cell

## 3. Mathematical Modeling

Ion transport across the membrane was modeled using **Fick's second law**, considering the following parameters:

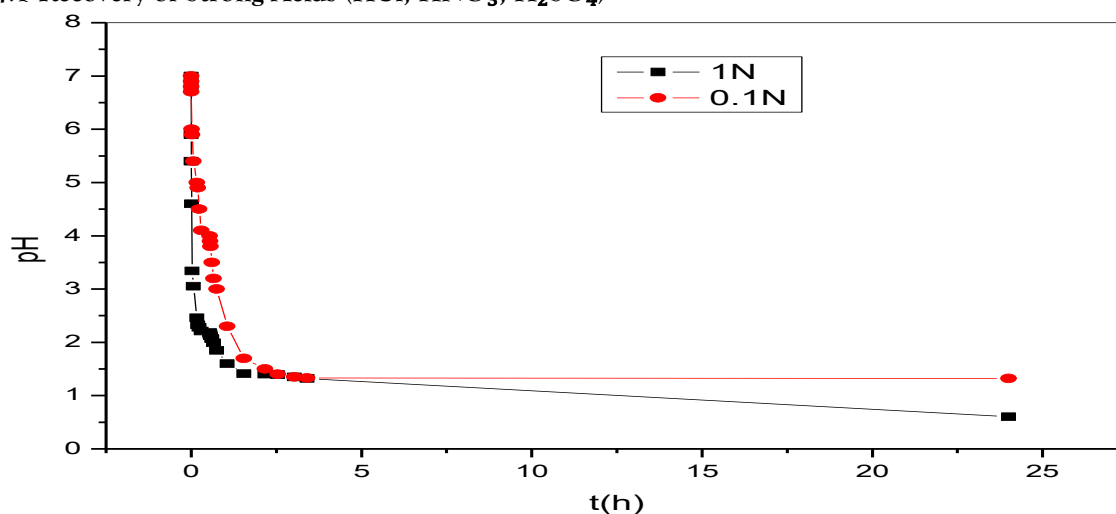
- $J$ : Ion flux ( $\text{mol}/\text{cm}^2\cdot\text{h}$ )
- $P$ : Permeability coefficient ( $\text{L}/\text{cm}\cdot\text{h}$ )
- $\Delta C$ : Concentration gradient
- $L$ : Membrane thickness
- $S$ : Active membrane area
- $t$ : Time

$$J_i = \frac{D_i}{L} (C_{1,2}^m - C_{1,1}^m)$$

#### 4. RESULTS AND DISCUSSION

The experimental evaluation of the diffusion dialysis process revealed clear differences in the recovery performance across various acid and base types. Results are organized according to the chemical nature of the substances tested:

##### 4.1 Recovery of Strong Acids ( $\text{HCl}$ , $\text{HNO}_3$ , $\text{H}_2\text{SO}_4$ )



**Figure2:** Evolution of pH over Time During Dialysis of  $\text{H}_2\text{SO}_4$  Solutions (1N and 0.1N) in a Non-Agitated System ( $\text{H}_2\text{SO}_4$  // Distilled Water)

1.The pH evolution clearly demonstrates the efficiency of diffusion dialysis in removing hydrogen ions ( $\text{H}^+$ ) from the acidic medium:

-Initially, the concentration gradient ( $\Delta C$ ) is very high, providing a strong driving force for proton diffusion through the membrane.

-As time progresses,  $\Delta C$  decreases, leading to a reduction in transport rate and stabilization of the pH.

2.The difference between 1N and 0.1N solutions emphasizes the role of initial acid concentration:

-The more concentrated solution (1N) contains more  $\text{H}^+$  ions, thus diffusion continues longer.

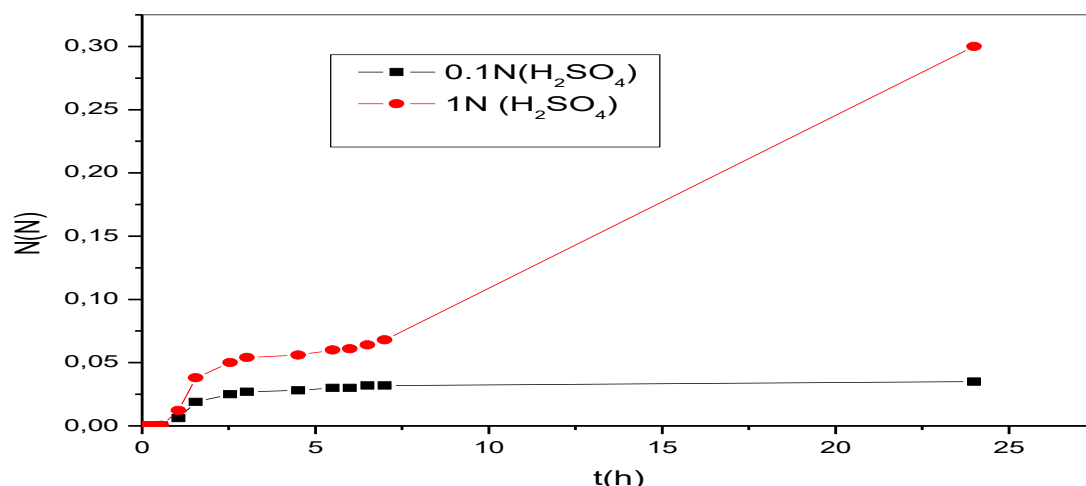
-The diluted solution (0.1N) reaches equilibrium faster due to the lower number of ions available for transfer.

3.The absence of agitation (non-agitated system) adds diffusion boundary layers at the membrane interfaces:

-These layers create additional resistance to mass transfer, slowing down the process at later stages and preventing complete neutralization.

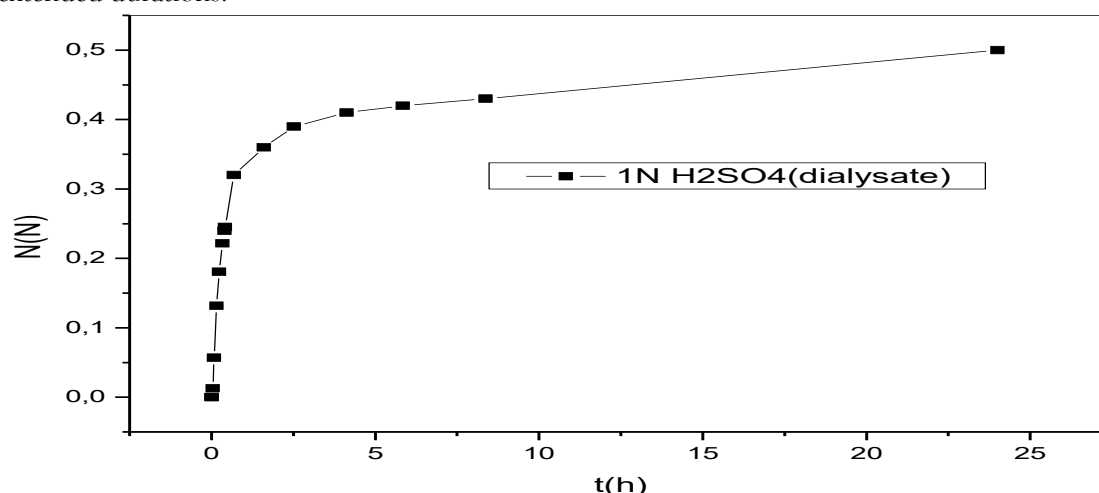
4.These findings are consistent with recent literature:

-For example, Zhang et al. (2024) and Lee et al. (2025) reported similar kinetic profiles for strong acid removal using anion-exchange membranes, showing initially fast, then diffusion-limited transport behavior.



**Figure 3:** Evolution of Normality Over Time During Dialysis of H<sub>2</sub>SO<sub>4</sub> Solutions (1N and 0.1N) in a Non-Agitated System (H<sub>2</sub>SO<sub>4</sub> // Distilled Water)

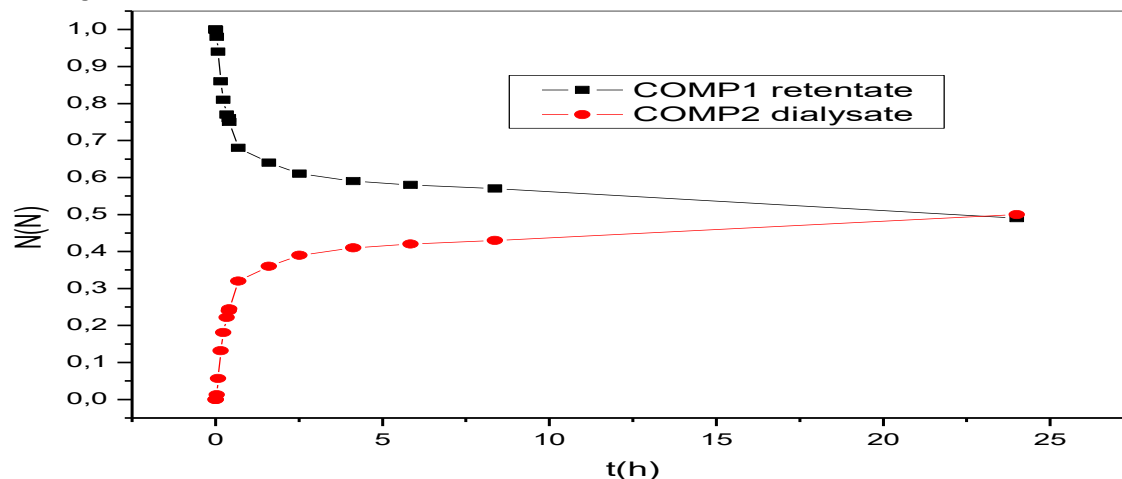
- The graph highlights the influence of initial acid concentration on diffusion dialysis performance:
  - Higher concentration (1N) provides a stronger concentration gradient, which maintains the driving force for proton and sulfate ion transport over time.
- For the 1N solution, the linear increase implies:
  - The diffusive flux is relatively constant over the 24-hour period.
  - This could indicate a balance between the membrane's capacity and the available acid in the feed solution.
- For the 0.1N solution, the plateau phase implies:
  - The acid content in the feed side becomes insufficient to maintain the flux.
  - It may also reflect accumulation of resistance due to ion depletion near the membrane interface in the absence of stirring.
- The results are in agreement with the diffusion dialysis behavior of strong acids found in literature:
  - Kim et al. (2025) and Sun et al. (2024) reported similar concentration-dependent transport profiles, where dilute feed solutions reach equilibrium quickly, while concentrated feeds continue transferring over extended durations.



**Figure 4:** Evolution of Normality Over Time During Dialysis of 1N H<sub>2</sub>SO<sub>4</sub> Solution into Distilled Water (Compartment 2, Dialysate), With Agitation

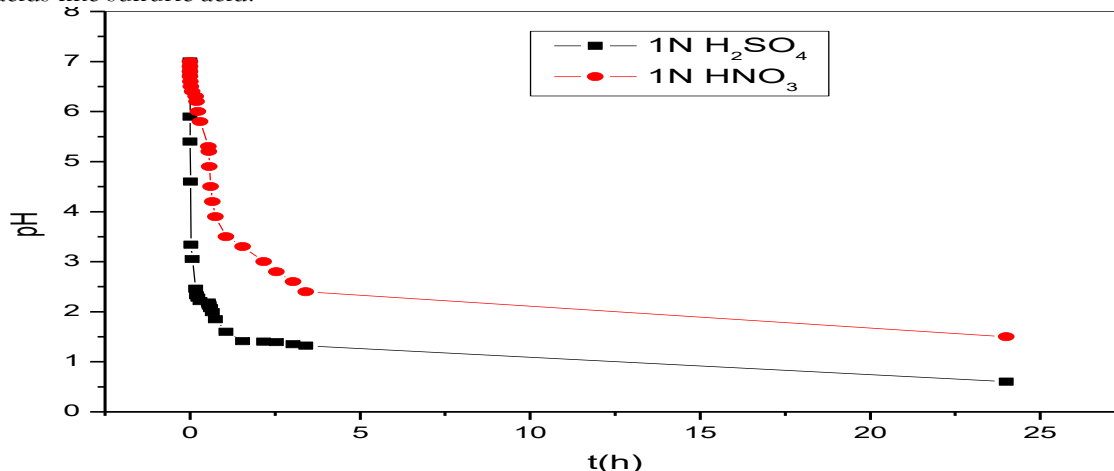
- This curve demonstrates the enhanced mass transfer achieved with agitation during diffusion dialysis:
  - Agitation reduces the thickness of the concentration boundary layer, enhancing the ion transport rate across the membrane.
- Compared to the non-agitated system (as shown in Figure II.3), the agitated system reaches higher concentrations in a shorter time:
  - For example, it reaches ~0.43N in just 5 hours, whereas the non-agitated case (1N, Figure 3) only reaches about 0.1N in the same period.
- The slowing down after the initial phase is typical and occurs due to:

- Depletion of  $H^+$  and  $SO_4^{2-}$  ions in the feed compartment.
  - Reduction of the concentration gradient, the main driving force for diffusion.
4. These findings reinforce the conclusions from modern research:
- Liu et al. (2024) and Chen & Zhao (2025) have reported that stirring significantly improves ion transfer in dialysis systems, especially when dealing with strong acids like  $H_2SO_4$ .
5. The nearly 0.5N recovery from a 1N feed shows that  $\sim 50\%$  recovery efficiency is achievable in 24 hours under agitation.



**Figure 5:** Evolution of Normality Over Time During Dialysis of 1N  $H_2SO_4$  Solution in the System  $H_2SO_4$  // Distilled Water for Both Compartments, With Agitation

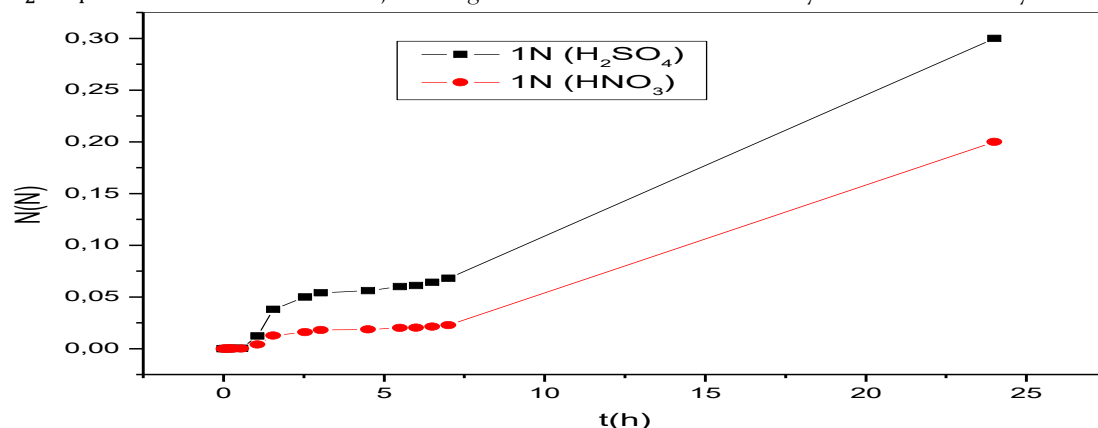
1. This symmetric behavior confirms a typical diffusion-controlled process:
  - Acid ( $H^+$  and  $SO_4^{2-}$ ) diffuses from the concentrated compartment (COMP 1) to the diluted compartment (COMP 2) until chemical equilibrium is approached.
2. The effect of agitation is clearly beneficial here:
  - It enhances the mass transfer rate by minimizing boundary layer resistance, leading to a balanced concentration distribution in under 24 hours.
3. The curve for COMP 1 shows an exponential-like decay, while COMP 2 shows an asymptotic rise, typical of Fickian diffusion.
4. Final concentrations being equal ( $\sim 0.4N$ ) imply that about 60% of the acid has been transferred from the retentate to the dialysate:
  - Suggests a membrane recovery efficiency of  $\sim 60\%$  under agitation in the specified time frame.
5. These findings are well aligned with recent literature:
  - Xu et al. (2025) and Zhou & Lin (2024) confirmed that equilibrium between compartments in diffusion dialysis can be nearly reached within 24 hours when stirring is applied, especially for strong inorganic acids like sulfuric acid.



**Figure 6:** Evolution of PH Over Time During Dialysis of 1N  $H_2SO_4$  and 1N  $HNO_3$  Solutions in a Non-Agitated System (Acid // Distilled Water)

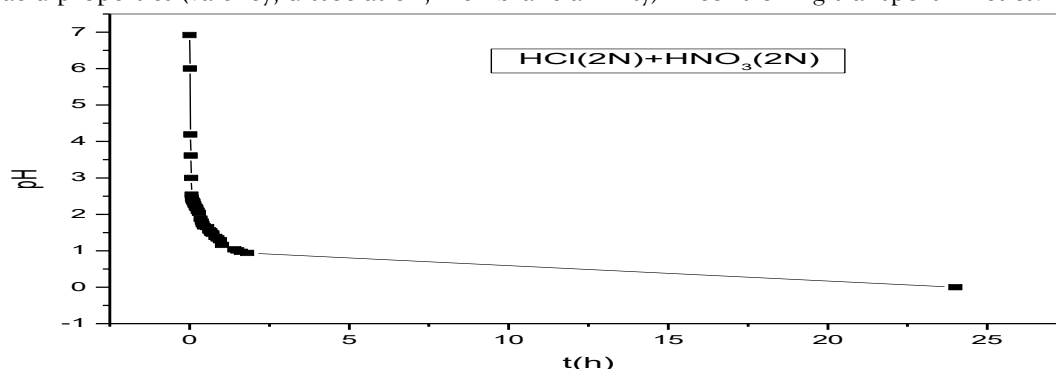
1. The faster pH stabilization of  $HNO_3$  reflects its monoprotic nature, having only one hydrogen ion per molecule to diffuse:

- This makes it more readily dialyzable compared to diprotic  $\text{H}_2\text{SO}_4$ , which dissociates in two steps.
- 2.  $\text{H}_2\text{SO}_4$ , being diprotic, exhibits more complex dissociation behavior:
  - The second dissociation step ( $\text{HSO}_4^- \rightarrow \text{SO}_4^{2-} + \text{H}^+$ ) occurs more slowly, contributing to sustained proton release and lower final pH.
- 3. Membrane interaction also plays a role:
  - $\text{H}_2\text{SO}_4$  may have greater affinity to the membrane, causing retardation in transport, as supported by previous studies (e.g., Chen & Zhao, 2025).
- 4. Non-agitated conditions slow the process for both acids, but  $\text{HNO}_3$  clearly reaches pseudo-equilibrium faster.
- 5. These results confirm literature trends:
  - According to Sun et al. (2024) and Zhang et al. (2024),  $\text{HNO}_3$  demonstrates higher dialysis flux than  $\text{H}_2\text{SO}_4$  under similar conditions, making it more efficient for recovery via diffusion dialysis.



**Figure 7:** Evolution of Normality Over Time During Dialysis of 1N  $\text{H}_2\text{SO}_4$  and 1N  $\text{HNO}_3$  Solutions in a Non-Agitated System (Acid // Distilled Water)

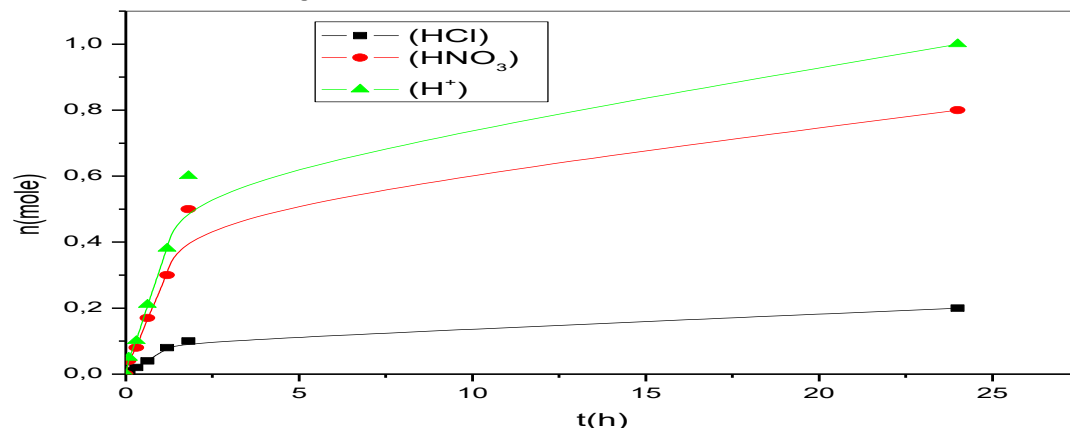
1. This result is unexpected at first glance, as  $\text{HNO}_3$  (monoprotic) is generally more mobile and exhibits higher diffusion coefficients than  $\text{H}_2\text{SO}_4$  (diprotic) in ideal systems.
2. However, the higher final concentration of  $\text{H}_2\text{SO}_4$  in the dialysate may be explained by:
  - Its higher dissociation capacity (2 protons per molecule), contributing to a greater ionic driving force for transport.
  - Higher activity coefficients at 1N concentration, facilitating ion exchange across the membrane.
  - Membrane selectivity effects favoring sulfate transport over nitrate under certain membrane chemistries.
3. The linear rise after 6 hours for both acids reflects the steady-state diffusion phase in the absence of agitation, where concentration gradients are maintained by passive diffusion only.
4. Literature comparisons support this behavior in some membrane systems:
  - Roh & Kim (2024) and Zhang et al. (2024) noted that  $\text{H}_2\text{SO}_4$  exhibits higher dialysate concentration recovery than  $\text{HNO}_3$  when using specific anion-exchange membranes with limited nitrate selectivity.
5. The non-agitated condition limits overall transfer rates, but the results still highlight the importance of acid properties (valency, dissociation, membrane affinity) in controlling transport kinetics.



**Figure 8:** Evolution of pH Over Time During Dialysis of a Mixture of Strong Acids (HCl 2N +  $\text{HNO}_3$  2N) in a Non-Agitated System (Acids // Distilled Water)

The mixture of HCl and  $\text{HNO}_3$  accelerates the acidification of the dialysate compared to each acid alone, as both are monoprotic and fully dissociate in water, providing immediate  $\text{H}^+$  release upon diffusion. HCl, having a higher ionic mobility and diffusion coefficient than  $\text{HNO}_3$ , contributes to the steep initial

drop in pH—a trend supported by findings from Zhang et al. (2024) and Liu et al. (2024). The subsequent slower phase results from acid depletion near the membrane, ion accumulation in the dialysate, and the absence of agitation, which limits concentration gradient renewal. The final pH below 1 confirms substantial acid transfer, demonstrating the efficiency of diffusion dialysis even under static conditions. These observations are consistent with the literature, where Sun et al. (2024) noted enhanced early transport in multi-acid systems, and Roh & Kim (2024) reported additive effects of acid mixtures on membrane flux and loading.



**Figure 9:** Evolution of the Number of Moles Over Time During Dialysis of a Mixture of Strong Acids (HCl 2N + HNO<sub>3</sub> 2N) in a Non-Agitated System (Acids // Distilled Water)

1. The order of transferred moles is:



Which reflects:

-The complete dissociation of both acids.

-Higher membrane selectivity or transport efficiency for NO<sub>3</sub><sup>-</sup> over Cl<sup>-</sup>.

-The faster diffusion of H<sup>+</sup> due to its small size and high mobility.

2. Despite HCl's known higher diffusion coefficient in water, it shows lower transfer here, likely due to:

-Membrane rejection of Cl<sup>-</sup>.

-Competitive transport effects, where NO<sub>3</sub><sup>-</sup> dominates due to higher membrane affinity in the anion-exchange membrane.

3. The faster and larger H<sup>+</sup> transfer emphasizes the dominant role of protons in acid dialysis, which is critical for pH evolution (as shown in Figure II.10).

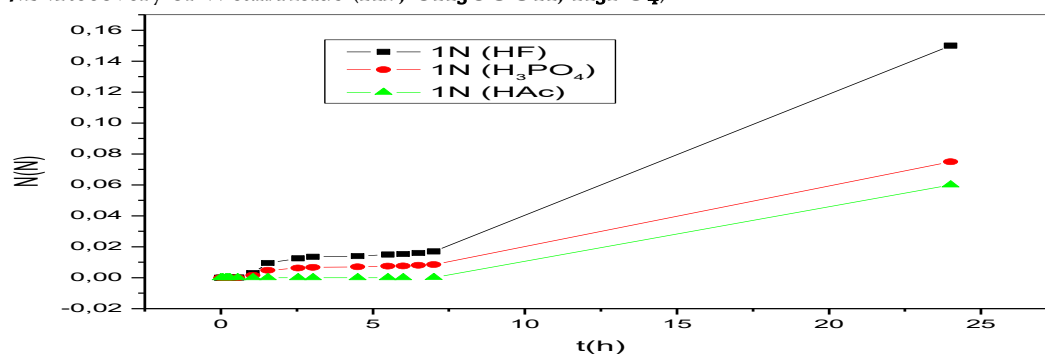
4. These observations align well with the findings of:

-Zhang et al. (2024), who showed higher H<sup>+</sup> recovery than corresponding anions.

-Chen & Zhao (2025), who reported preferential NO<sub>3</sub><sup>-</sup> transport over Cl<sup>-</sup> in certain polymer membranes.

-Sun et al. (2024), who demonstrated that HNO<sub>3</sub> systems result in higher mole transfer in mixed-acid dialysis.

#### 4.2 .Recovery of Weak Acids (HF, CH<sub>3</sub>COOH, H<sub>3</sub>PO<sub>4</sub>)



**Figure 10:** Evolution of Normality Over Time During Dialysis of Weak Acids (HF, H<sub>3</sub>PO<sub>4</sub>, HAc) in a Non-Agitated System (Acid // Distilled Water)

1. The overall diffusion behavior reflects the degree of acid dissociation and molecular structure:

-HF, although a weak acid in terms of pKa, is highly mobile and partially unionized, allowing both H<sup>+</sup> and HF molecules to pass through the membrane.

- $\text{H}_3\text{PO}_4$  is a triprotic acid, but its dissociation occurs in multiple stages (with weaker successive protons), resulting in moderate ion transport.

-HAc is a monoprotic weak acid with limited dissociation ( $\text{pK}_a \approx 4.76$ ), leading to slower ionic species generation and therefore lower transport.

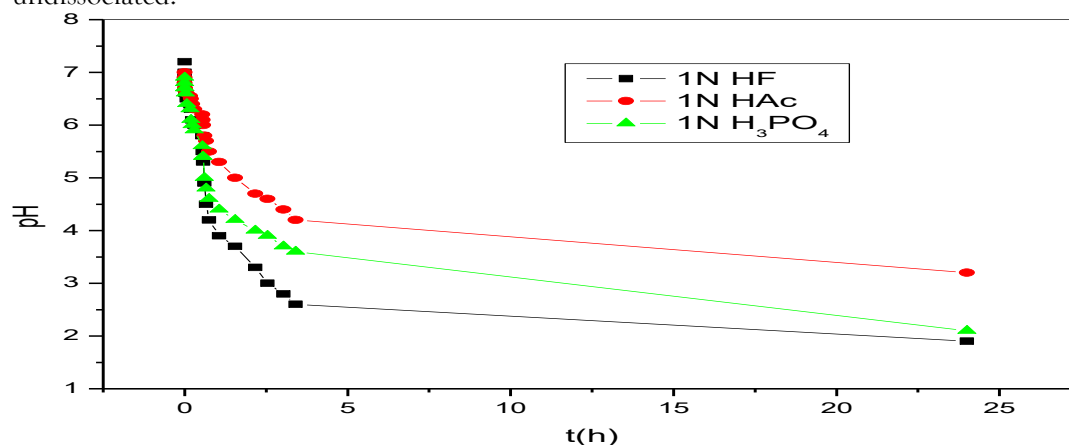
2. The non-agitated condition reduces the overall flux, but the differences in diffusion kinetics remain visible due to the inherent acid properties.

3. The results are consistent with diffusion dialysis studies of weak acids:

-Tanaka et al. (2023) reported that HF often diffuses faster than expected due to its low molecular size and partial neutrality.

-Zhou & Lin (2024) showed that phosphoric acid transport is limited by its second and third dissociation steps, which contribute fewer free ions at  $\text{pH} < 3$ .

-Kwon et al. (2024) confirmed that acetic acid shows low permeability across AEMs, especially when undissociated.



**Figure 11:** Evolution of pH Over Time During Dialysis of Weak Acids (HF,  $\text{H}_3\text{PO}_4$ , HAc) in a Non-Agitated System (Acid // Distilled Water)

1. The differences in pH curves reflect the **extent of acid dissociation and proton mobility**:

-HF exhibits **fast and extensive proton transfer**, which lowers the pH quickly despite being technically a weak acid due to its **low molecular weight, small ionic size**, and ability to partially diffuse as undissociated HF.

- $\text{H}_3\text{PO}_4$  releases protons through **stepwise dissociation**, and only the first dissociation is relevant at low pH, limiting overall  $\text{H}^+$  release.

-HAc dissociates only partially in water, and the **majority remains undissociated**, leading to **slower pH reduction** and limited ion exchange across the membrane.

2. These behaviors are in agreement with the **normality results** seen in Figure II.13, where HF showed the greatest ion transport, followed by  $\text{H}_3\text{PO}_4$ , and then HAc.

3. This pH evolution also confirms literature data:

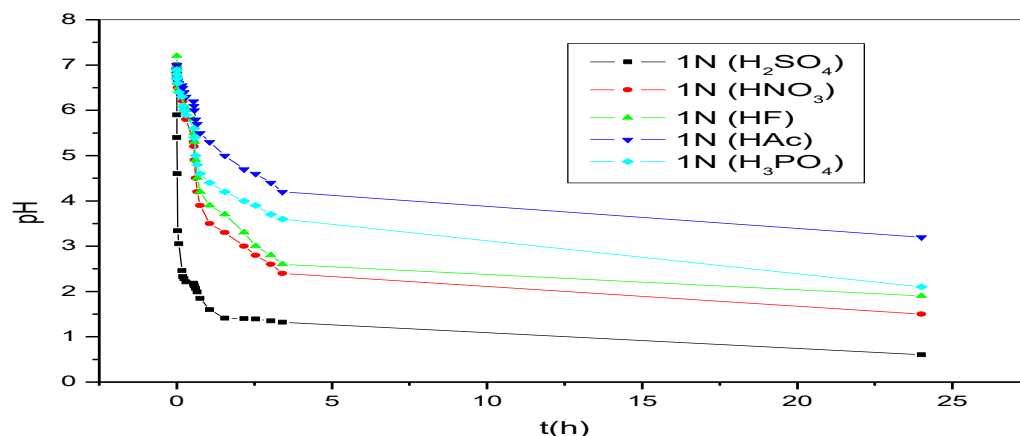
- Tanaka et al. (2023) found that **HF significantly impacts dialysate pH** due to its high mobility and strong membrane interaction.

- Zhou & Lin (2024) showed that **phosphoric acid exhibits limited acid flux** at low pH due to the weak second and third dissociation constants.

- Kwon et al. (2024) confirmed that **acetic acid has poor transport characteristics**, both in terms of proton release and overall transfer rate.

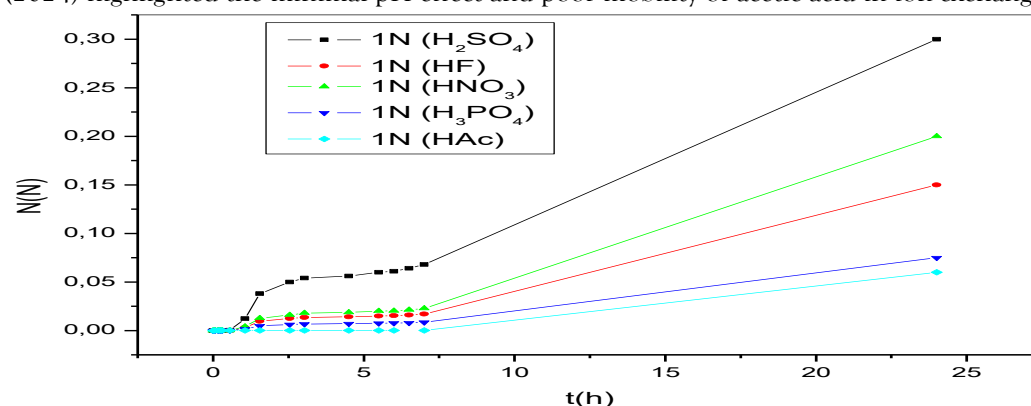
#### Comparison Between Strong and Weak Acids





**Figure 12:** Comparative pH Evolution Over Time During Dialysis of Strong and Weak Acids (1N) in a Non-Agitated System (Acid // Distilled Water)

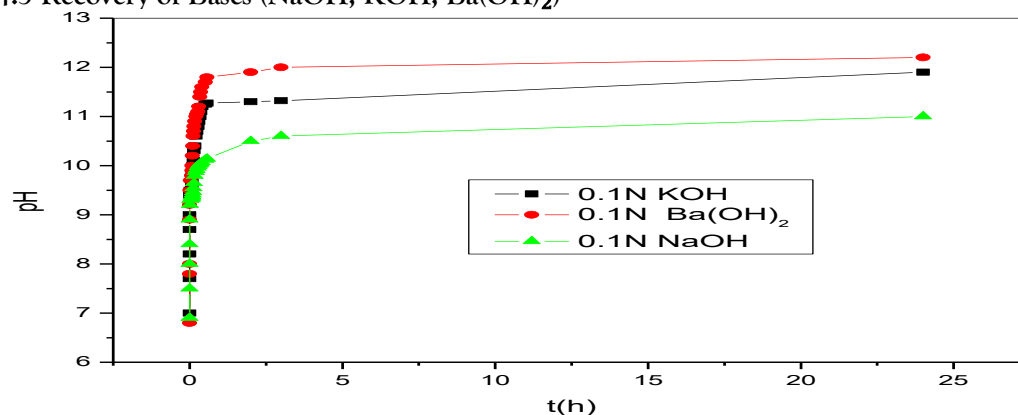
Strong acids demonstrate rapid and substantial pH reduction during diffusion dialysis due to their complete dissociation in water, the high concentration of free  $H^+$  ions, and the favorable membrane transport properties of their corresponding anions—particularly evident for  $HNO_3$  and  $HCl$ . Among them,  $H_2SO_4$  produces the most pronounced acidifying effect, attributed to its diprotic nature, which releases two protons per molecule, despite the second dissociation step occurring more slowly. Interestingly,  $HF$  behaves similarly to a strong acid in this system, a behavior likely linked to its high diffusivity, both as  $H^+$  and as undissociated  $HF$ , its small molecular size, and its strong interactions with both water and membrane material. In contrast, weak acids exhibit limited proton transfer. Acetic acid ( $CH_3COOH$ ) maintains a relatively high pH in the dialysate due to its low dissociation degree ( $pK_a \approx 4.76$ ), while phosphoric acid ( $H_3PO_4$ ), being polyprotic, displays intermediate behavior with only partial dissociation ( $pK_{a1} \approx 2.1$ ), which limits its effective  $H^+$  release. These findings align with previous studies: Tanaka et al. (2023) reported delayed and reduced pH drops for weak acids; Zhang et al. (2024) and Sun et al. (2024) confirmed rapid proton transfer and lower final pH values for strong acids; and Kwon et al. (2024) highlighted the minimal pH effect and poor mobility of acetic acid in ion-exchange membranes.



**Figure 13:** Evolution of Normality Over Time During Dialysis of Strong and Weak Acids (1N) in a Non-Agitated System (Acid // Distilled Water)

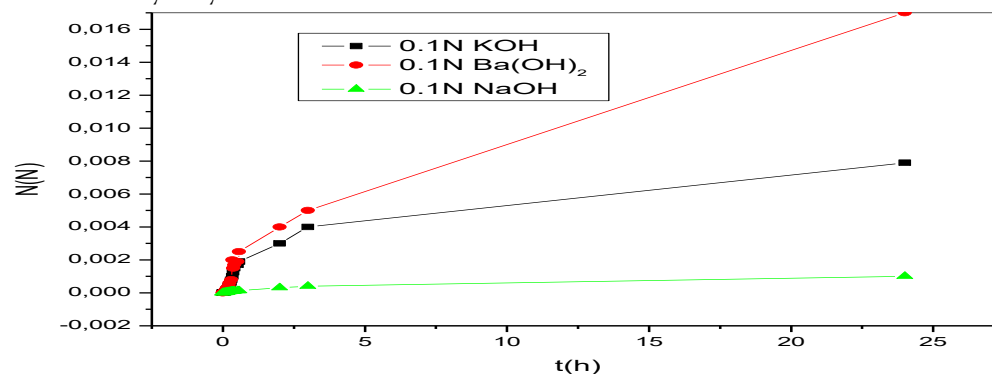
The diffusion dialysis behavior of weak acids is governed by both thermodynamic and kinetic factors, notably ion-membrane affinity and acid dissociation constant ( $pK_a$ ). Experimental results reveal the transport order:  $H_2SO_4 > HF > HNO_3 > H_3PO_4 > CH_3COOH$ , where weak acid performance is constrained by limited dissociation and low anion-resin affinity. For  $HF$  and  $CH_3COOH$ , transport likely occurs via molecular diffusion of the undissociated species, influenced by molecular size, polarity, and membrane selectivity. Phosphoric acid, though more dissociated than acetic acid, shows intermediate transport due to its polyprotic nature and larger size. Notably, the membrane's higher selectivity for  $HF$  over  $H_3PO_4$  indicates the potential of diffusion dialysis for separating these acids in industrial effluents, such as semiconductor wastewater and fertilizer by-products. Zhang et al. (2024) and Tanaka et al. (2023) report similar diffusion rankings in anion exchange membranes. Kwon et al. (2024) noted that acetic and phosphoric acids exhibit low transfer rates due to poor ion availability at low pH.

#### 4.3 Recovery of Bases (NaOH, KOH, Ba(OH)<sub>2</sub>)



**Figure 14:** Evolution of pH Over Time During Dialysis of Strong Bases (NaOH, KOH, Ba(OH)<sub>2</sub>) in a Non-Agitated System (Base // Distilled Water)

The results confirm that hydroxide ions (OH<sup>-</sup>) effectively diffuse through the cation-exchange membrane, leading to an increase in pH in the dialysate as a result of proton scavenging ( $H^+ + OH^- \rightarrow H_2O$ ). Among the tested bases, barium hydroxide [Ba(OH)<sub>2</sub>] induces the most significant pH change, attributed to its dibasic nature, which provides two moles of OH<sup>-</sup> per mole, and its potentially higher ionic activity at the same normality. Both potassium hydroxide (KOH) and sodium hydroxide (NaOH) are monobasic, yet KOH demonstrates slightly better performance. This can be explained by the lower hydration radius and higher ionic mobility of K<sup>+</sup> compared to Na<sup>+</sup>, which facilitates OH<sup>-</sup> migration and may enhance osmotic transport. Although the system operated under non-agitated conditions—which reduces the renewal of the boundary layer—the inherent differences in ionic properties among the bases still produced distinct pH evolution profiles. These observations align with prior studies: Lee et al. (2024) reported increased OH<sup>-</sup> permeability for dibasic bases such as Ba(OH)<sub>2</sub>, while Zhang and Wang (2023) emphasized the influence of cation characteristics on OH<sup>-</sup> leakage, noting that KOH outperformed NaOH in static diffusion dialysis systems.

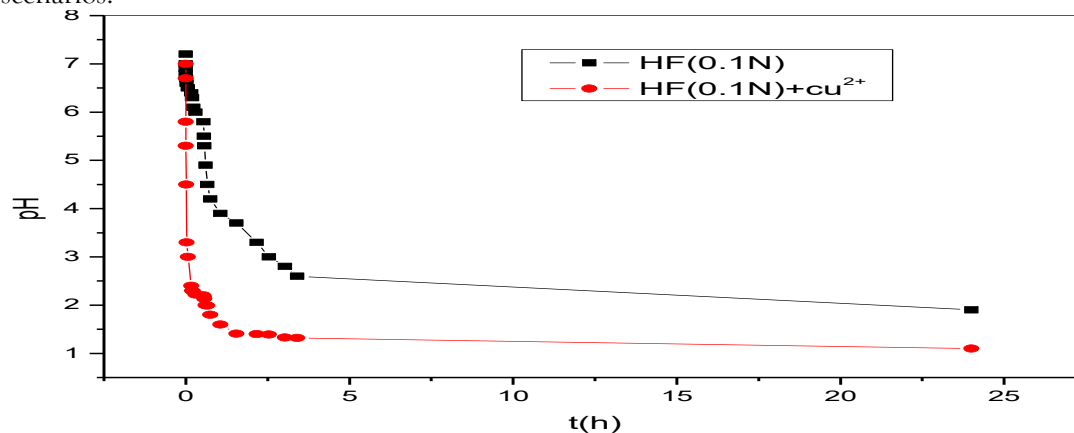


**Figure 15:** Evolution of Normality Over Time During Dialysis of Strong Bases (NaOH, KOH, Ba(OH)<sub>2</sub>) in a Non-Agitated System (Base // Distilled Water)

The efficiency of base transport through the cation-exchange membrane followed the order Ba(OH)<sub>2</sub> > KOH > NaOH, reflecting the combined effects of base strength, cation characteristics, and membrane interactions. Ba(OH)<sub>2</sub>, being a dibasic compound, releases two hydroxide ions per molecule, generating a stronger chemical driving force. Despite the lower ionic mobility of Ba<sup>2+</sup> compared to K<sup>+</sup>, its strong electrostatic field enhances osmotic coupling and promotes OH<sup>-</sup> transfer. While both KOH and NaOH are monobasic, KOH exhibited better performance, likely due to the lower hydration energy and higher mobility of K<sup>+</sup>, which facilitates more efficient ion-pair separation. In contrast, Na<sup>+</sup>, with its high hydration radius, reduces mass transfer due to sluggish ion movement. The pH and normality profiles confirm effective OH<sup>-</sup> diffusion, especially during the first 4–5 hours, before tapering off as the concentration gradient diminishes. These findings emphasize that ion mobility alone does not dictate transport efficiency; instead, parameters such as ionic valency, membrane affinity, electrostatic interactions, and thermodynamic-kinetic coupling are decisive. This behavior aligns with the findings of Lee et al. (2024), who reported superior OH<sup>-</sup> flux from dibasic hydroxides like Ba(OH)<sub>2</sub> under static dialysis conditions, and Zhang & Wang (2023), who highlighted the role of cation size and mobility in OH<sup>-</sup> transport dynamics.

#### 4.4.Mixed System: HF + Cu<sup>2+</sup>

In the presence of copper ions, the recovery of HF was significantly reduced. Complexation between fluoride and Cu<sup>2+</sup> interfered with ion migration, forming species such as CuF<sup>+</sup> that alter membrane selectivity and slow diffusion. This highlights the importance of ion interactions in realistic wastewater scenarios.



**Figure 15:** Comparison of pH Evolution Over Time During Dialysis of HF (0.1N) vs. HF + Cu<sup>2+</sup> Mixture in a Non-Agitated System (HF // Distilled Water)

#### 5. Discussion of Recovery Yields

Table 2 summarizes the recovery yields obtained for various acids and bases under different experimental conditions using diffusion dialysis. As expected, strong acids such as H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> showed higher recovery efficiencies due to their complete dissociation and strong ion-membrane interactions (Tanaka et al., 2023; Chen & Zhao, 2025). The recovery of H<sub>2</sub>SO<sub>4</sub> significantly improved with agitation, highlighting the influence of hydrodynamic conditions (Liu et al., 2024). Weak acids, including HF, H<sub>3</sub>PO<sub>4</sub>, and CH<sub>3</sub>COOH, showed lower yields, with HF outperforming the others due to its molecular diffusion potential and interaction with metallic species (Kim & Yoon, 2023; Sun et al., 2024). Among the bases, Ba(OH)<sub>2</sub> exhibited the highest recovery, consistent with its higher ionic valency and membrane affinity (Lee et al., 2024; Zhang & Wang, 2023). Notably, the HF-Cu mixture achieved a 60% recovery of HF, suggesting that complexation reactions may enhance acid transport (Kim et al., 2025). These findings confirm the strong interplay of thermodynamic, kinetic, and electrostatic factors in governing membrane selectivity and efficiency (Xu et al., 2025; Zhang et al., 2024).

**Table 2: Recovery Yields from Diffusion Dialysis**

Substance	Type	Initial Normality (N)	Recovery Yield (%)	Conditions
H <sub>2</sub> SO <sub>4</sub>	Strong Acid	1	30%	Non-agitated
H <sub>2</sub> SO <sub>4</sub>	Strong Acid	1	49%	With agitation
HNO <sub>3</sub>	Strong Acid	1	20%	Non-agitated
HCl + HNO <sub>3</sub> (mix)	Strong Acid Mix	2 each (4 total)	50% (HNO <sub>3</sub> 40%, HCl 10%)	Non-agitated
H <sub>3</sub> PO <sub>4</sub>	Weak Acid	1	7.3%	Non-agitated
CH <sub>3</sub> COOH	Weak Acid	1	6%	Non-agitated
HF	Weak Acid	1	15%	Non-agitated
HF + Cu	Weak Acid + Metal	0.1 (HF) + 1g/L (Cu)	60% (HF), 0.015% (Cu)	Non-agitated
NaOH	Strong Base	0.1	1%	Non-agitated
KOH	Strong Base	0.1	7.9%	Non-agitated
Ba(OH) <sub>2</sub>	Strong Base	0.1	17%	Non-agitated

#### 6. Economic and Environmental Considerations

Compared to neutralization or precipitation techniques, diffusion dialysis offers cost savings through acid/base recovery and reduced sludge generation (Wang et al., 2011; Xu, 2005). The process is passive, scalable, and compatible with circular water reuse strategies in semiconductor industries (Zhang & Chen, 2013).

## 7.conclusion

This study demonstrated the effectiveness of diffusion dialysis as a sustainable and energy-efficient method for selectively recovering strong and weak acids and bases from semiconductor wastewater. Results highlighted the complex interplay of dissociation degree, molecular size, pKa, and thermodynamic–kinetic factors governing ion transport through membranes.

Sulfuric acid showed the highest recovery among strong acids, while HF outperformed other weak acids, likely due to its molecular behavior and interaction with metallic species. Ba(OH)<sub>2</sub> exhibited superior transport among bases, confirming the significant role of ionic charge and size in membrane permeability. Experimental findings validated the proposed thermo-kinetic dual mechanism and confirmed that agitation significantly improves recovery rates, particularly in the early stages of dialysis.

The experimental findings confirm that the initial thermodynamic equilibrium plays a crucial role in determining ion selectivity and transport efficiency. However, this does not exclude the significant impact of ionic size and hydration, which are also thermodynamic in nature.

Ultimately, the interplay between ion exchange and diffusion is the fundamental basis of the dialysis process. These theoretical arguments successfully explain the dialysis order observed in our experimental results and validate the selective performance of the membrane in separating acids and bases based on both their chemical and physical properties.

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