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Selective Separation of $\text{Ni}^{2+}/\text{Co}^{2+}$ and H^+ from MWCNT Purification Waste Acid by an Acid-Resistant Nanofiltration Membrane and Reuse Evaluation

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Abstract

The sulfuric acid purification process of multi-walled carbon nanotubes (MWCNTs) generates waste acid streams with high acidity and high metal concentrations, simultaneously containing valuable metals such as Ni^{2+} and Co^{2+} along with large amounts of free sulfuric acid. Direct discharge of these streams results in both resource waste and environmental pollution. In this study, a commercial acid-resistant nanofiltration membrane was employed for batch concentration and separation of two types of waste acid streams, one containing cobalt and the other containing nickel. The effects of operating pressure and concentration factor on metal ion rejection, acid permeation rate, and membrane flux were investigated. The results showed that the membrane achieved Co^{2+} rejection of 81.01% – 92.35%, Ni^{2+} rejection consistently above 90%, and acid permeation rates ranging from 73% to 96%. After 20 – 25-fold concentration, Co^{2+} was enriched 15.6-fold to 4.5 g/L and Ni^{2+} was enriched 18.6-fold to 16.7 g/L, yielding a concentrate suitable as a high-concentration feed for downstream metal recovery processes. The recovered sulfuric acid was directly reused for MWCNT reflux purification, reducing residual catalyst content from 6.45 wt% to 0.41 wt% for Co-MWCNTs and from 7.16 wt% to 0.50 wt% for Ni-MWCNTs, which is comparable to the results obtained with fresh sulfuric acid (0.40 wt% and 0.45 wt%, respectively), thereby achieving a closed-loop sulfuric acid cycle. This process replaces conventional neutralization-precipitation methods with membrane separation without introducing additional neutralizing reagents, providing a feasible route for resource-oriented treatment of MWCNT purification waste acid.

Keywords: acid-resistant nanofiltration membrane; MWCNTs; metal ion recovery; sulfuric acid recovery; ion selective transport

1. Introduction

Multi-walled carbon nanotubes (MWCNTs) are widely used in lithium-ion batteries, composite materials, and other fields [1-6]. Industrially, MWCNTs are produced at scale by chemical vapor deposition using Ni, Co, and Fe as catalysts [7]. The as-produced material typically contains 5%-15% residual metal catalyst particles, which require purification to achieve high purity [8, 9]. Sulfuric acid reflux purification is one of the mainstream processes, but this process generates large volumes of highly acidic, high-salinity wastewater [10-12]. Co^{2+} and Ni^{2+} possess carcinogenic and aquatic toxicity, and the discharge of free sulfuric acid lowers the pH of receiving water bodies [13-15]. Direct discharge therefore causes environmental pollution while wasting both sulfuric acid and non-ferrous metal resources. Furthermore, Ni^{2+} and Co^{2+} are core metal components of NCM ternary cathode materials for lithium-ion batteries, and recovering these metals from waste acid streams therefore offers significant resource recycling value [16, 17].

Conventional neutralization-precipitation methods are simple to operate but require high alkali consumption, generate large volumes of heavy-metal-laden hazardous sludge, and completely neutralize the sulfuric acid, resulting in waste [18-21]. Diffusion dialysis drives acid recovery by concentration gradients but suffers from low treatment efficiency and high metal ion leakage [22-25]. Conventional nanofiltration membranes exhibit excellent rejection of multivalent metal ions under neutral conditions but have limited service life in strongly acidic environments [26]. Acid-resistant nanofiltration membranes can withstand up to 20% H_2SO_4 , and their separation performance relies on the synergistic action of size sieving and Donnan electrostatic exclusion. Under high-acidity conditions, the high concentration of H^+ compresses the electric double layer on the membrane surface, and rejection behavior gradually shifts toward size sieving as the dominant mechanism [27]. In recent years, cross-linking modification and sulfonation modification strategies have significantly improved the acid resistance of

nanofiltration membranes , providing a technical foundation for membrane-based treatment of strongly acidic waste streams [28].

In recent years, acid-resistant nanofiltration membranes have been preliminarily applied to acid recovery and metal enrichment from various industrial acidic waste streams, including copper smelting acidic effluents , titanium dioxide waste acid, steel pickling waste acid, and electroplating rinse wastewater [29]. López et al. [30] used a sulfonamide-based nanofiltration membrane to treat copper smelting acidic effluent (pH 0.5-1.5, Fe 11 - 14 g/L), achieving rejection rates exceeding 90% for Fe, Zn, and Cu. Bai et al. [31] employed a positively charged acid-resistant nanofiltration membrane for electroplating rinse wastewater, achieving rejection rates exceeding 98% for Cu^{2+} and Ni^{2+} . However, systematic nanofiltration studies on MWCNT purification waste acid have not been reported. This type of waste stream differs from previously studied objects in two significant respects: first, the concentrations of multivalent catalyst residues (Ni^{2+} , Co^{2+} , Mg^{2+} , Al^{3+}) are relatively low (250 - 1000 mg/L), while the free sulfuric acid concentration is high (0.6 - 2 mol/L); second, the cobalt-containing and nickel-containing sub-streams differ significantly in acidity (pH 0.2 vs. pH -0.35) and impurity composition, requiring separate process validation. Whether a single commercial acid-resistant nanofiltration membrane can simultaneously achieve metal rejection and free acid permeation under low-concentration multivalent ion conditions, and whether the permeate acid can be directly reused in the MWCNT purification process, remains unclear.

In this study, two typical waste acid streams generated from the carbon nanotube purification process—a cobalt-containing waste acid and a nickel-containing waste acid—were selected as the research objects. A commercial acid-resistant nanofiltration membrane was employed for systematic process investigation. This study aims to verify the separation performance of the acid-resistant nanofiltration membrane under strongly acidic conditions, systematically analyze the effects of operating pressure and concentration factor on metal ion

rejection, inorganic acid permeation rate, and membrane flux, and evaluate the enrichment factor of valuable metals through batch concentration experiments, while examining the residual metal concentration in the recovered acid and assessing its feasibility for direct reuse in MWCNT purification.

2. Experimental

2.1. Materials

The acid-resistant nanofiltration membrane used in this study was a commercial polyamide thin-film composite nanofiltration membrane (A-3014, Xiamen, China) with an effective membrane area of approximately 6.2 m², a molecular weight cutoff of 400 Da, and compatibility with 20% H₂SO₄. The cobalt-containing and nickel-containing waste acids were generated during the purification of different MWCNTs using H₂SO₄ (98% industrial sulfuric acid, diluted to working concentration; Ganzhou, China). MWCNTs synthesized with a Co-based catalyst system are designated as Co-MWCNTs (KDC, Ganzhou, China); the product was refluxed with 1 mol/L sulfuric acid at 80 °C for 2 h. MWCNTs synthesized with a Ni-based catalyst system are designated as Ni-MWCNTs (NA04, Ganzhou, China); the product was refluxed with 2 mol/L sulfuric acid at 90 °C for 2 h. These reflux treatments dissolve the metal catalyst particles into soluble ionic species in the liquid phase, producing the cobalt-containing and nickel-containing waste acids that served as the feed solutions for the experiments. Because washing water partially enters the waste acid during the industrial reflux process, the actual sulfuric acid concentration of the collected waste acid varies within a range, which is reported as follows: Co-MWCNT waste acid: Co²⁺ 250 – 350 mg/L, Mg²⁺ 150 – 250 mg/L, Al³⁺ 200 – 250 mg/L, H₂SO₄ 0.6 – 1 mol/L, pH 0.2 – 0.3; Ni-MWCNT waste acid: Ni²⁺ 800 – 1000 mg/L, Mg²⁺ 10 – 50 mg/L, H₂SO₄ 1.7 – 2.0 mol/L, pH –0.35 to –0.40. All parameter measurements were performed using the same

process feed solution, with three replicate experiments conducted for each condition. Data are reported as the mean of three parallel experiments, with error bars representing the standard deviation ($n = 3$) to ensure result reproducibility.

2.2. Experimental Procedure

The nanofiltration apparatus mainly consists of a feed tank, a filter, a booster pump, a nanofiltration membrane module, a circulating cooling system, a pressure-regulating valve, a flow meter, and a data acquisition system. The process flow and concentration principle are illustrated in Figure 1. For each experiment, 2 tons of waste acid was pumped from the feed tank through the filter to preliminarily remove MWCNTs, carbon black, and other impurities. The filtrate was then pumped by the booster pump to the nanofiltration membrane module. Under pressure driving force, water molecules and inorganic acid permeated through the nanofiltration separation layer to obtain the filtrate. The filtrate continuously flowing out of the permeate outlet at any given moment was designated as the instant filtrate, which entered a filtrate tank and was mixed to obtain the mixed filtrate. Multivalent metal ions such as Ni^{2+} and Co^{2+} were rejected by the nanofiltration membrane to form the concentrate. The concentrate was cooled by the cooling device and recirculated through the filtration system. Different volumetric concentration factors X were investigated (based on the observation that metal enrichment was insufficient below $X = 10$, while permeate flux decayed significantly above $X = 20 - 25$). Samples were collected at $X = 1, 2, 5, 10, 15, 20$, and 25 . The concentration factor is defined as the ratio of the initial feed volume to the current concentrate volume. Permeate volume, feed pressure, and permeate flow rate were recorded at each volumetric concentration step, and feed, concentrate, and filtrate samples were simultaneously collected for subsequent chemical composition analysis. The resulting Co-MWCNT filtrate was then used to reflux and purify Co-MWCNTs at $80\text{ }^{\circ}\text{C}$ for 2 h, and the Ni-MWCNT filtrate was used to reflux and purify Ni-MWCNTs at $90\text{ }^{\circ}\text{C}$ for 2 h. Fresh sulfuric acid was also used under identical reflux conditions as a

control group.

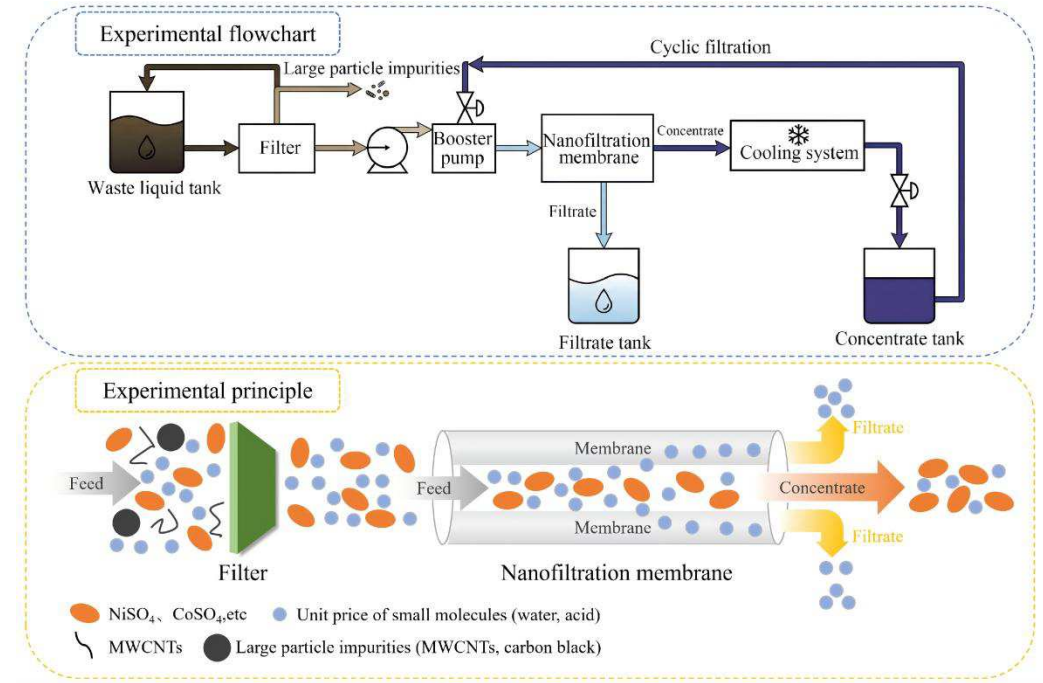


Figure 1 Schematic diagram of the concentration experimental apparatus and principle.

2.3. Analytical Methods and Performance Evaluation

Inductively coupled plasma optical emission spectrometry (ICP-OES; ICPS-7510, Shimadzu) was used to determine the elemental composition of MWCNTs before and after purification. The molar concentration of sulfuric acid in solution was determined by acid – base titration using standard NaOH solution (xcy-1N, Guangdong, China). High-resolution transmission electron microscopy (HRTEM; JEM 2100f) was used to analyze the MWCNT walls and metal catalyst particles before and after purification. Thermogravimetric-differential thermal analysis (TG-DTA; Shimadzu TG8120, Kyoto, Japan) at a heating rate of 5 °C /min was performed to evaluate the metal content and thermal stability of the carbon nanotubes. The pH of the solutions was measured using a pH meter (PHS-3C, Shanghai, China).

Membrane flux (J , $L \cdot m^{-2} \cdot h^{-1}$) was measured under constant-pressure

conditions and calculated using Equation (1):

$$J = \frac{V}{At} \quad (1)$$

where V denotes the permeate volume (L), A represents the effective membrane area (m^2), and t is the filtration duration (h).

The rejection rate (R) of metal ions was calculated using Equation (2):

$$R = \frac{(C_c - C_f)}{C_c} \times 100\% \quad (2)$$

where C_c denotes the metal ion concentration in the concentrate at the time of sampling (mg/L), and C_f denotes the metal ion concentration in the corresponding instant filtrate (mg/L). This parameter reflects the membrane's ability to separate a given solute; a higher rejection rate corresponds to superior retention performance.

The acid permeation rate (T) was calculated using Equation (3):

$$T = \frac{C_{(f,m)}}{C_{(c,m)}} \times 100\% \quad (3)$$

where $C_{(c,m)}$ denotes the acid molar concentration in the concentrate at the time of sampling (mol/L), and $C_{(f,m)}$ denotes the acid molar concentration in the corresponding instant filtrate (mol/L). This parameter reflects the membrane's permeability to free acid and serves as a key metric for assessing acid recovery efficiency.

3. Results and discussion

3.1. Recovery of Co-MWCNT Waste Acid

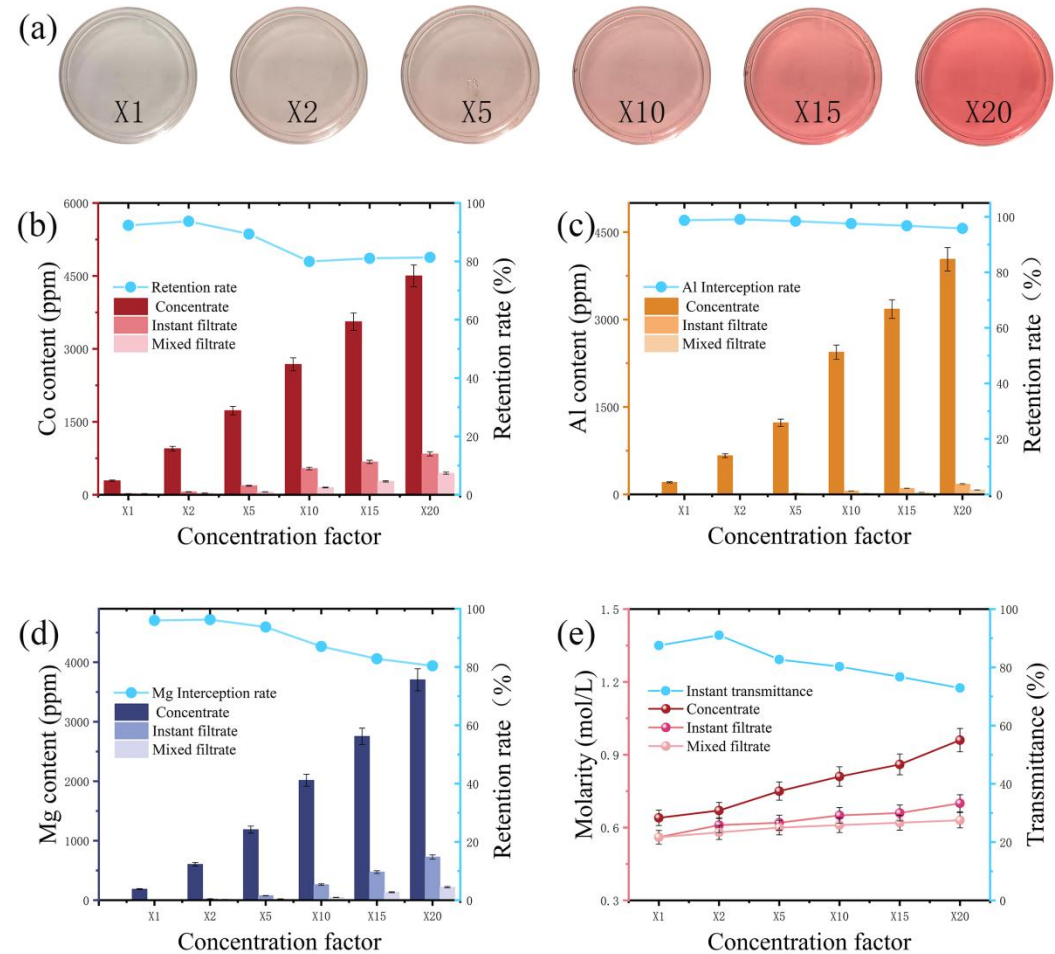


Figure 2 (a) Appearance changes of Co-MWCNT waste acid concentrate during 1 - 20-fold concentration; (b), (c), and (d) show the Co^{2+} , Al^{3+} , and Mg^{2+} concentrations and rejection rates with increasing concentration factor, as analyzed by ICP-OES; (e) shows the sulfuric acid molar concentration and permeation rate with increasing concentration factor, determined by acid - base titration with standard NaOH solution.

As shown in Figure 2(a), during progressive concentration to 20-fold, the metal ions in the concentrate were gradually enriched and the color deepened from light red. As shown in Figure 2(b) - (d), the Co^{2+} concentration increased from an initial 287.7 mg/L to 4500.7 mg/L, representing an actual concentration factor of

15.6, with rejection gradually decreasing from 92.35% to 81.01%. The Al^{3+} concentration increased from 206.2 mg/L to 4033.8 mg/L (actual concentration factor 19.56), with rejection decreasing from 98.73% to 95.81%. The Mg^{2+} concentration increased from 198.3 mg/L to 3704.8 mg/L (actual concentration factor 18.68), with rejection decreasing from 95.98% to 80.41%. The cumulative mixed filtrate contained Co^{2+} , Al^{3+} , and Mg^{2+} at concentrations of 66.604, 4.669, and 13.824 mg/L, respectively, which are well below the feed concentrations, consistent with the high metal rejection of the membrane.

With increasing concentration factor, the rejection rates of Co^{2+} , Mg^{2+} , and Al^{3+} all exhibited decreasing trends. This phenomenon may be attributed to three factors: first, the accumulation of rejected ions on the membrane surface forms a concentration polarization layer, increasing the driving force for ion diffusion into the membrane and potentially reducing effective rejection [32-34]; second, the continuously increasing ionic strength of the feed compresses the electric double layer on the membrane surface, potentially weakening the Donnan exclusion effect and enhancing charge screening [35]; third, under high-concentration conditions, the tendency for SO_4^{2-} to form ion pairs with metal cations increases, potentially altering the effective hydrated radius and charge state of the target ions and allowing some low-charge ion pairs to more readily pass through the membrane pores [36, 37]. Under the conditions of this study, trivalent Al^{3+} , owing to its higher charge valence and larger hydration energy, exhibited the smallest decline in rejection (98.73% $\rightarrow$ 95.81%), while divalent Co^{2+} (92.35% $\rightarrow$ 81.01%) and Mg^{2+} (95.98% $\rightarrow$ 80.41%) showed relatively more pronounced decreases.

As shown in Figure 2(e), with increasing concentration factor, the free acid concentration in the concentrate gradually increased from 0.64 mol/L to 0.96 mol/L. The instant filtrate concentration and mixed filtrate acid concentration increased from 0.58 mol/L to 0.70 mol/L and from 0.58 mol/L to 0.63 mol/L, respectively, and the acid permeation rate gradually decreased from 93.71% to 72.92%. However, because the concentration process operates on a volumetric basis, as a large amount

of water permeates through the membrane, the cumulative filtrate volume far exceeds the remaining concentrate volume. Consequently, most of the free acid is carried into the filtrate, and the overall sulfuric acid recovery rate consistently remains above 90%. These results indicate that, although the local acid permeation rate decreased due to concentration polarization, the acid recovery performance of the acid-resistant nanofiltration membrane was excellent from the overall mass balance perspective.

Membrane flux is an important parameter for evaluating membrane separation efficiency and is jointly affected by operating pressure and feed flow rate. Table 1 lists the membrane flux data for the Co-MWCNT waste acid nanofiltration experiments under different operating conditions. The membrane flux increased significantly with increasing operating pressure and feed flow rate. When the operating pressure was increased from 10 bar to 25 bar, the membrane flux increased from 8.17 LMH to 26.53 LMH.

Table 1 Effect of operating conditions on membrane flux for Co-MWCNT waste acid.

Pressure(bar)	Volume(L)	Time(s)	Flow rate (L/h)	Flux(LMH)
10	3.04	60	50.65	8.17
15	4.46	60	74.40	12.00
20	6.77	60	112.90	18.21
25	9.87	60	164.49	26.53

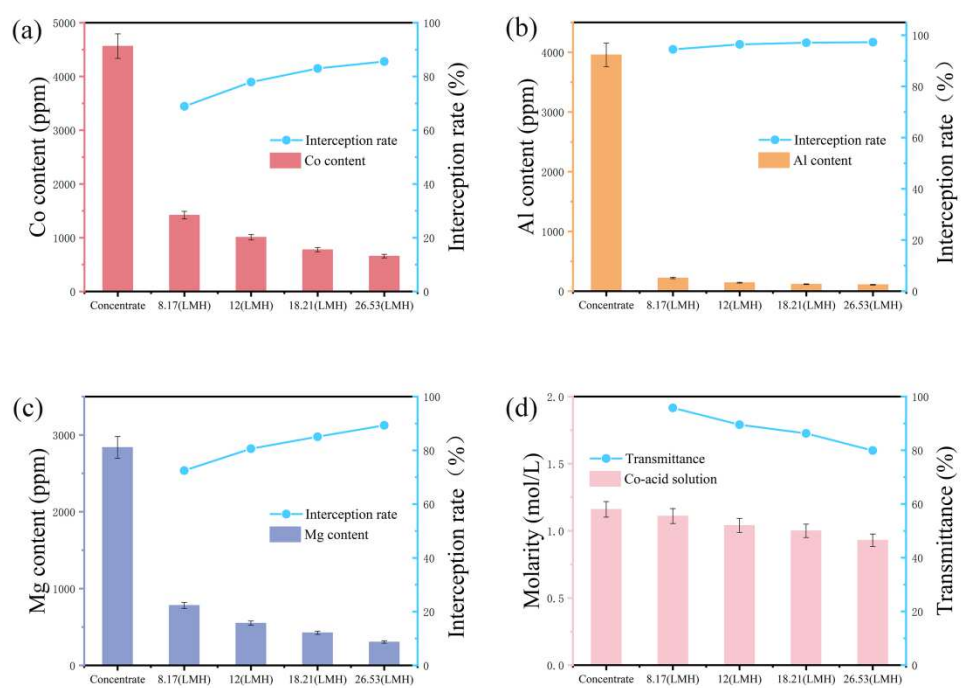


Figure 3 (a), (b), and (c) show the metal ion concentrations and rejection rates as functions of membrane flux for Co^{2+} , Al^{3+} , and Mg^{2+} , respectively, as analyzed by ICP-OES; (d) shows the relationship between membrane flux and acid concentration as well as acid permeation rate.

Approximately 20-fold Co-MWCNT concentrate was used to test the effect of membrane flux on separation performance. As shown in Figure 3(a) - (c), the Co^{2+} , Al^{3+} , and Mg^{2+} concentrations in the concentrate were 4563.29, 3956.33, and 2838.26 mg/L, respectively. As the membrane flux increased from 8.17 LMH to 26.53 LMH, the Co^{2+} rejection increased from 68.89% to 85.58%, the Al^{3+} rejection increased from 94.54% to 97.28%, and the Mg^{2+} rejection increased from 72.49%

to 89.30%. The higher the membrane flux, the better the rejection of Co^{2+} , Al^{3+} , and Mg^{2+} . This may be because the feed flow rate also increased simultaneously with rising pressure, and the increased cross-flow velocity weakened the concentration polarization layer, thereby improving rejection. As shown in Figure 3(d), the sulfuric acid molar concentration in the concentrate was 1.16 mol/L. As the membrane flux increased from 8.17 LMH to 26.53 LMH, the permeate acid molar concentration decreased from 1.11 mol/L to 0.93 mol/L, and the acid permeation rate decreased from 95.78% to 79.92%. This indicates that increasing membrane flux improved the membrane's retention of H^+ to some extent, while the inorganic acid permeation rate remained at a relatively high level.

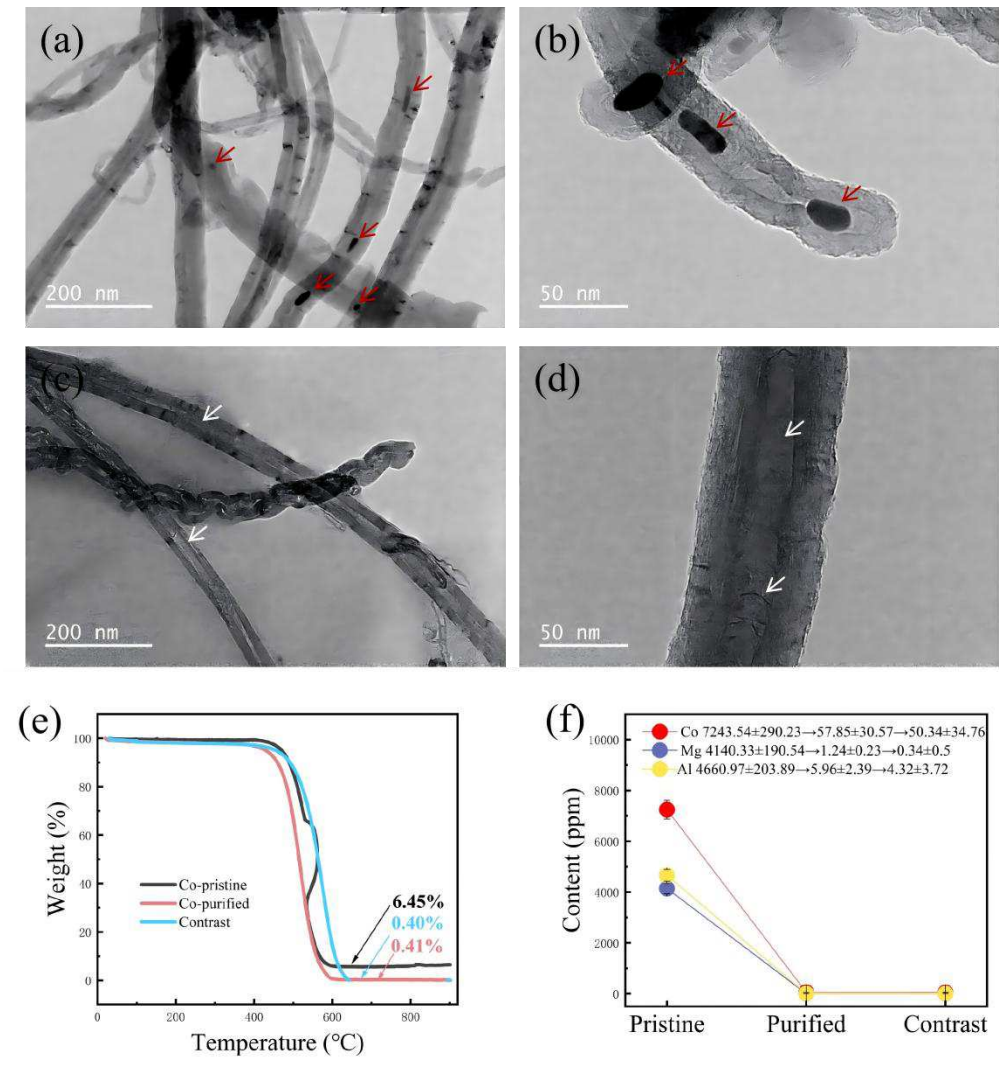


Figure 4 (a) and (b) show TEM images of Co-MWCNTs before purification; (c) and (d) after filtrate

purification; (e) shows TG curves before and after purification; (f) shows the Co, Mg, and Al content changes before and after purification, analyzed by ICP-OES.

Figure 4 compares unpurified Co-MWCNTs with Co-MWCNTs purified by the filtrate. In the unpurified samples (a) and (b), as indicated by the red arrows, numerous black metal catalyst particles were densely distributed within the MWCNT cavities and on the outer tube walls. After purification with the Co-MWCNT filtrate (c) and (d), as indicated by the white arrows, the tube walls appeared clean and smooth, and black particle impurities were essentially removed. High-magnification TEM images clearly revealed the regular multi-walled graphite layered structure of the purified MWCNTs, with no wall expansion, rupture, or changes in layer number observed, indicating that the purification process only removed metal catalyst residues without damaging the carbon nanotube body structure. The TG curve (e) shows that within the 400 – 650 °C range, the weight loss of the unpurified sample was 6.45%, which decreased to 0.41% after filtrate purification and to 0.40% after fresh sulfuric acid purification. The ICP-OES results (f) show that after filtrate purification, the Co content decreased from 7243.54 ppm to 57.85 ppm, Mg from 4140.33 ppm to 1.24 ppm, and Al from 4660.97 ppm to 6.96 ppm. The corresponding results with fresh sulfuric acid purification were 50.34 ppm, 0.34 ppm, and 4.32 ppm, respectively. These results indicate that the Co-MWCNT filtrate can effectively remove catalyst residues and has direct reuse value.

3.2. Recovery of Ni-MWCNT Waste Acid

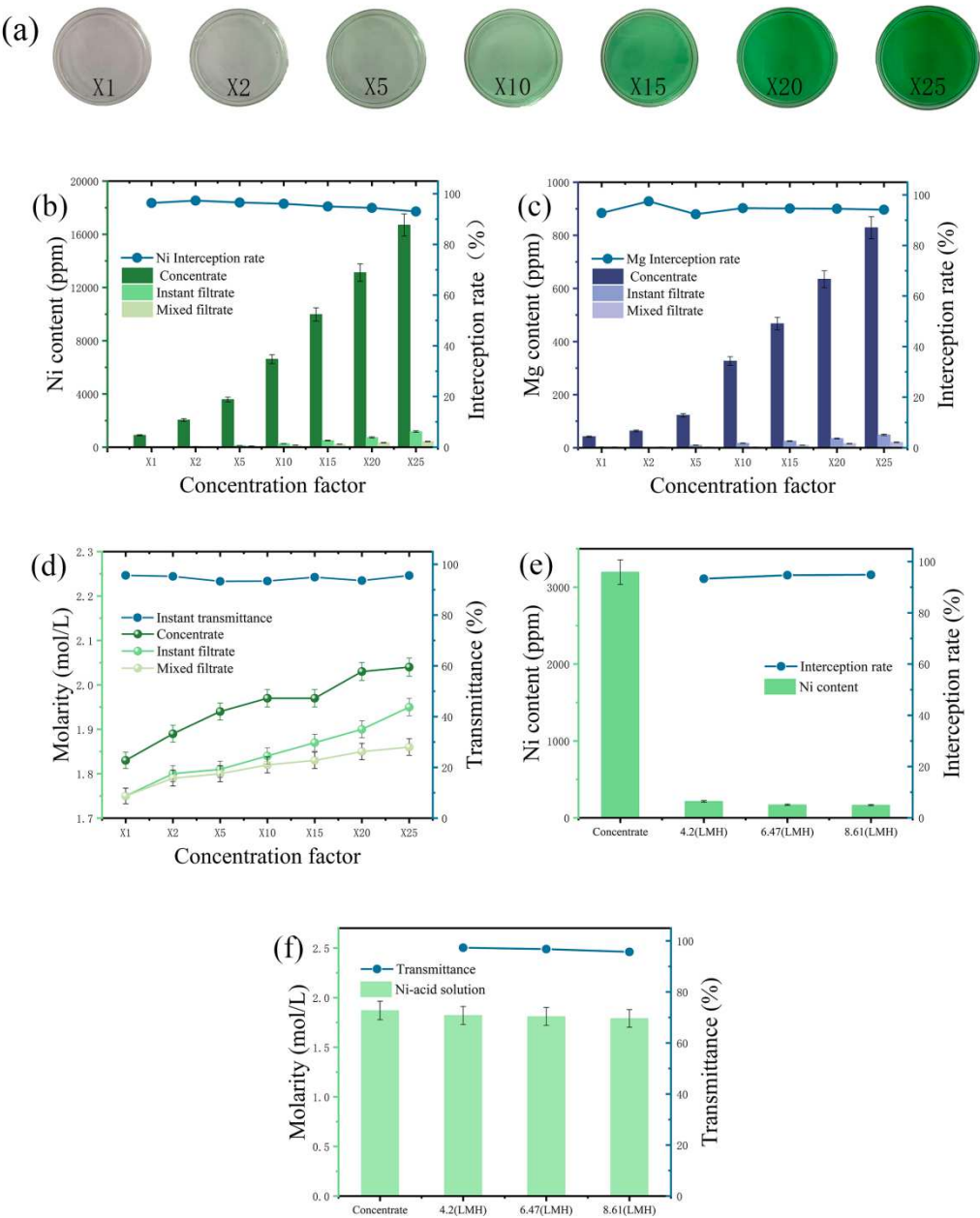


Figure 5 (a) Appearance changes of Ni-MWCNT concentrate during 1 - 25-fold concentration; (b) and (c) show the Ni^{2+} and Mg^{2+} concentrations and rejection rates with increasing concentration factor, as analyzed by ICP-OES; (d) shows the sulfuric acid molar concentration and permeation rate with increasing concentration factor; (e) shows the Ni^{2+} concentration and rejection rate as a function of membrane flux; (f) shows the relationship between membrane flux and acid concentration as well as acid permeation rate.

Table 2 Effect of operating conditions on membrane flux for Ni-MWCNT waste acid.

Pressure(bar)	Volume(L)	Time(s)	Flow rate (L/h)	Flux(LMH)
15	0.43	60	26.053	4.20
20	0.67	60	40.131	6.47
25	0.89	60	53.400	8.61

During progressive concentration to 25-fold, as shown in Figure 5(a), the metal ions in the Ni-MWCNT concentrate were gradually enriched, and the color deepened from light green to dark green. Figure 5(b) and (c) show the relationships between concentration factor and Ni^{2+} and Mg^{2+} concentrations as well as rejection rates in the Ni-MWCNT concentrate. The Ni^{2+} concentration increased from an initial 897.1 mg/L to 16697.1 mg/L at 25-fold concentration (actual enrichment 18.6-fold), and the Mg^{2+} concentration increased from 41.8 mg/L to 828.5 mg/L (actual enrichment 19.8-fold). The rejection rates of both ions remained above 90%. The cumulative mixed filtrate contained Ni^{2+} and Mg^{2+} at concentrations of 238.244 and 9.525 mg/L, respectively, confirming effective metal rejection while allowing acid permeation.

Figure 5(d) shows the variation of sulfuric acid molar concentration with concentration factor. The free acid concentration in the concentrate gradually increased from 1.83 mol/L to 2.04 mol/L. The instant filtrate concentration and mixed filtrate concentration increased from 1.75 mol/L to 1.95 mol/L and from 1.75 mol/L to 1.86 mol/L, respectively. The acid permeation rate consistently remained in the high range of 93% – 96%, indicating that the nanofiltration membrane achieved stable and efficient acid recovery performance in the Ni-MWCNT waste acid system.

As shown in Table 2, under constant feed flow rate conditions, the membrane flux increased significantly with increasing operating pressure. At 10 bar, the flux was zero. When the pressure was increased from 15 bar to 25 bar, the flux increased from 4.20 LMH to 8.61 LMH.

Five-fold Ni-MWCNT concentrate was used to test the effect of membrane

flux on separation performance. As shown in Figure 5(e), the Ni^{2+} concentration in the concentrate was 3195.908 mg/L. As the membrane flux increased from 4.20 LMH to 8.61 LMH, the Ni^{2+} concentration in the permeate decreased from 214.42 mg/L to 164.93 mg/L, and the Ni^{2+} rejection increased from 93.29% to 94.84%. As shown in Figure 5(f), the molar concentration in the concentrate was 1.87 mol/L. As the membrane flux increased from 4.20 LMH to 8.61 LMH, the molar concentration in the permeate decreased from 1.82 mol/L to 1.79 mol/L, and the permeation rate decreased from 97.33% to 95.72%. These results fully demonstrate the excellent rejection and permeation performance of the nanofiltration membrane for metal ions and acid solutions.

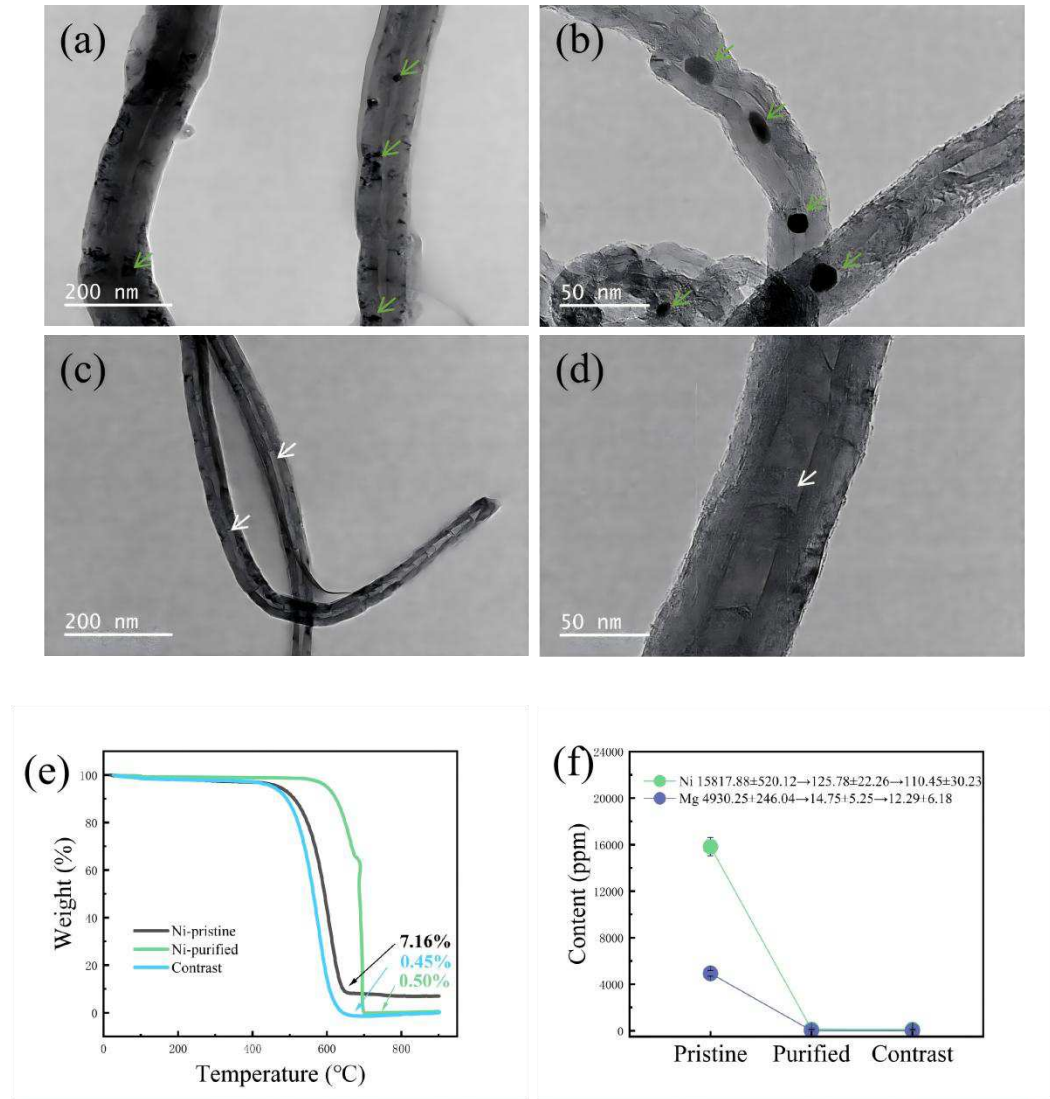


Figure 6 (a) and (b) show TEM images of Ni-MWCNTs before purification; (c) and (d) after filtrate

purification; (e) shows TG curves before and after purification; (f) shows the Ni and Mg content changes before and after purification, analyzed by ICP-OES.

Figure 6 compares unpurified Ni-MWCNTs with Ni-MWCNTs purified by the filtrate. In (a) and (b), as indicated by the green arrows, black metal catalyst particles were clearly densely distributed within the MWCNT cavities and tube walls. In the filtrate-purified samples (c) and (d), as indicated by the white arrows, the tube walls became clean. High-magnification TEM images clearly revealed the regular multi-walled graphite layered structure of the purified MWCNTs, with no wall expansion, rupture, or changes in layer number observed, indicating that the purification process only removed metal catalyst residues without damaging the carbon nanotube body structure. For the TG analysis (e) in the 550 – 700 °C range, the unpurified MWCNTs contained 7.16% residual material, which decreased to 0.50% after Ni-MWCNT filtrate purification and to 0.45% after fresh sulfuric acid purification. The ICP-OES results (f) show that after Ni-MWCNT filtrate purification, the Ni content decreased from 15817.88 ppm to 125.78 ppm, and the Mg content decreased from 4930.25 ppm to 14.75 ppm. The corresponding results with fresh sulfuric acid purification were 110.45 ppm and 12.29 ppm, respectively. These results demonstrate that the Ni-MWCNT filtrate can effectively remove catalyst residues from Ni-MWCNTs, significantly improving MWCNT purity and confirming the good reuse value of the Ni-MWCNT filtrate.

A comprehensive comparison of the cobalt-containing and nickel-containing systems reveals that operating acidity is the key factor determining membrane separation behavior. The cobalt-containing system has lower acidity (0.6 – 1.0 mol/L) and higher membrane flux (8.17 – 26.53 LMH), and can operate effectively at 10 bar. However, with increasing concentration factor, the rejection of divalent ions decreased significantly (Co^{2+} : 92.35% → 81.01%, Mg^{2+} : 95.98% → 80.41%), while trivalent Al^{3+} only decreased from 98.73% to 95.81%. This indicates that under lower ionic strength conditions, Donnan exclusion still

contributes to divalent ion rejection, but as concentration proceeds, electrostatic exclusion gradually weakens and rejection shifts toward size sieving as the dominant mechanism. In the nickel-containing system, the acidity is higher (1.7 – 2.0 mol/L), and from the initial stage the electric double layer is already fully compressed by the high concentration of H^+ . Metal rejection throughout the process is therefore dominated by size sieving, with Ni^{2+} and Mg^{2+} rejection consistently above 90%. However, the membrane flux is relatively low (4.20 – 8.61 LMH), with no net flux at 10 bar and operation requiring 15 bar or above. The above comparison demonstrates that the acid-resistant nanofiltration membrane can achieve both metal rejection and acid permeation over a wide acidity range. The low-acidity system is suitable for high-throughput operation, although attention should be paid to rejection decay at later concentration stages; the high-acidity system offers stable rejection but with limited treatment flux.

4. Conclusion

In this study, a commercial acid-resistant nanofiltration membrane was used for concentration separation and reuse validation of two types of waste acid streams generated from MWCNT purification, one containing cobalt and the other containing nickel. The cobalt-containing system has lower acidity (0.6 – 1.0 mol/L H_2SO_4) and higher membrane flux (8.17 – 26.53 LMH) with a large treatment capacity, but the rejection of Co^{2+} and Mg^{2+} attenuates significantly with increasing concentration factor (decreasing to 81.01% and 80.41%, respectively), indicating that Donnan exclusion still contributes to rejection under moderate acidity but gradually weakens as ionic strength increases. The nickel-containing system has higher acidity (1.7 – 2.0 mol/L H_2SO_4), with Ni^{2+} and Mg^{2+} rejection consistently above 90% and acid permeation rates maintained at 93% – 96%. Ni^{2+} was enriched 18.6-fold to 16.7 g/L, but the membrane flux is lower (4.20 – 8.61 LMH), requiring higher operating pressure to initiate, reflecting that under high acidity conditions,

the electric double layer is fully compressed and rejection behavior is dominated by size sieving. After 20 - 25-fold concentration, Co^{2+} and Ni^{2+} were enriched to 4.5 g/L and 16.7 g/L, respectively, yielding concentrates suitable as high-concentration feeds for downstream metal recovery processes. After the recovered permeate acid was reused for MWCNT purification, the residual catalyst content in Co-MWCNTs and Ni-MWCNTs decreased to 0.41 wt% and 0.50 wt%, respectively, which is comparable to the results obtained with fresh sulfuric acid purification (0.40 wt% and 0.45 wt%), verifying the feasibility of a closed-loop acid cycle.

Compared with conventional neutralization-precipitation methods, this process replaces chemical neutralization with membrane separation without introducing additional neutralizing reagents, thereby avoiding the generation of heavy-metal-laden hazardous sludge and the consumption of alkali reagents while reducing waste acid discharge. It should be noted that this study did not systematically investigate long-term membrane stability and membrane fouling behavior, and the deep recovery of metals from the concentrate as well as the economic feasibility of process scale-up require further investigation.

Author contributions

Longyao Hu: Writing - draft, validation, methodology, investigation, formal analysis, data organization, conceptualization; **Shengwen Zhong:** Resources, validation, funding acquisition, paper supervision; **Ziting Guo:** Writing - draft, language editing and review validation; **Hanjin Wang:** Language editing and review validation; **Yuqian Gao:** Writing - draft, language editing and review validation; **Lianjun Luo:** Operations support, data management; **Liangqi Zhao:** Operations support, data management; **Tingting Yan:** Language editing and review validation.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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