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## MDEA TARKIBIDAGI TERMİK BARQAROR TUZLARNI TOZALASHDA MIMBRANALI FILTRLARDAN FOYDALANISH JARAYONINI TADQIQ ETISH



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**Annotatsiya.** Sho'rtan neft gaz boshqarmasi tasarrufidagi gazlarni nordon gazlardan absorbsion tozalash qurilmasi ASO-2 qurilmasi metildietanolamin eritmasi tarkibidagi termobarqaror tuz ionlarini olib tashlash va absorbentni sorbentlik xossalarini tiklash taqdim etilgan. Ma'lumki aminli eritmalar tarkibida termik barqaror tuzlarning ortishi, sorbentning yutish qobiliyatining yo'qotilishi, ifloslanish va korroziyaga olib keladi, shuning uchun ularni olib tashlash jarayonning yanada samarali ishlashi uchun juda muhimdir. MDEA eritmasidagi termik barqaror tuzlardan tozalashda membranali filtrlardan foydalangan holda, ularning miqdorini kamaytirishda tahlil qilingan.

**Kalit so'zlar:** aminlarni tozalash, salbiy yuzaga ega membrana, termostabil tuzlarni olib tashlash, aminlarni olib tashlash, nanofiltratsiya membranasini.

## ИССЛЕДОВАНИЕ ПРОЦЕССА ПРИМЕНЕНИЯ МЕМБРАННЫХ ФИЛЬТРОВ ПРИ ОЧИСТКЕ ТЕРМОСТАБИЛЬНЫХ СОЛЕЙ, СОДЕРЖАЩИХ МДЭА

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**Аннотация.** Представлена установка абсорбционной очистки газа АСО-2 от высокосернистых газов, находящаяся в распоряжении Шортанского нефтегазового управления для удаления термостабильных ионов солей, содержащихся в растворе метилдиэтанолamina, и восстановления сорбентных свойств сорбента. Известно, что увеличение термически стабильных солей в составе растворов аминов приводит к потере поглотительной способности сорбента, загрязнению и коррозии, поэтому их удаление очень важно для более эффективного проведения процесса. Проанализировано удаление термостабильных солей из раствора МДЭА с помощью мембранных фильтров на предмет снижения их количества.

**Ключевые слова:** очистка аминов, мембрана с отрицательной поверхностью, удаление термостабильных солей, удаление аминов, нанофильтрационная мембрана.

## STUDY OF THE PROCESS OF USING MEMBRANE FILTERS IN THE PURIFICATION OF THERMOSTABLE SALTS CONTAINING MDEA

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**Abstract.** The installation for absorption gas purification ASO-2 from high-sulfur gases, which is at the disposal of the Shortan oil and gas department, is presented to remove thermostable salt ions contained in the methyldiethanolamine solution and restore the sorbent properties of the sorbent. It is known that an increase in thermally stable salts in the composition of amine solutions leads to a loss of sorbent absorption capacity, contamination and corrosion, so their removal is very important for a more efficient process. The removal of thermostable salts from MDEA solution using membrane filters was analyzed to reduce their amount.

**Keywords:** amine purification, negative surface membrane, heat stable salt sremoval, amine rejection, nanofiltration membrane.

**Kirish.** Mamlakatimiz energiya manbai asosan manbalari qayta tiklanmaydigan yoqilg'i, shu jumladan tabiiy gaz, ko'mir va neftdir. Ushbu manbalar orasida tabiiy gaz boshqa qazib olinadigan yoqilg'ilarga nisbatan afzalliklari katta, ya'ni qazib olinadigan tabiiy gazni boshqa manbalar turlari bilan solishtirganda olinadigan mahsulotlari ekologik jihatdan toza hisoblanadi [1]. Bundan tashqari, yoqilg'idan tashqari gaz kimyo sanoatida polimer mahsulotla va boshqa kimyoviy mahsulotlari sintezidan ham qo'llaniladi [2]. Umu-man olganda, tabiiy gaz tarkibida metan (75-98%), etan, propan, butan, og'ir uglevodorodlar (1-3%), shuningdek, suv bug'i, karbonat angidrid ( $\text{CO}_2$ ), vodorod sulfidi ( $\text{H}_2\text{S}$ ), va merkaptanlar. (RSH), karbonil sulfid ( $\text{COS}$ ), uglerod disulfidi ( $\text{CS}_2$ ) va azot mavjud [3-5]. Tabiiy gaz tarkibidagi zararli komponentlardan tozalash juda muhimdir,

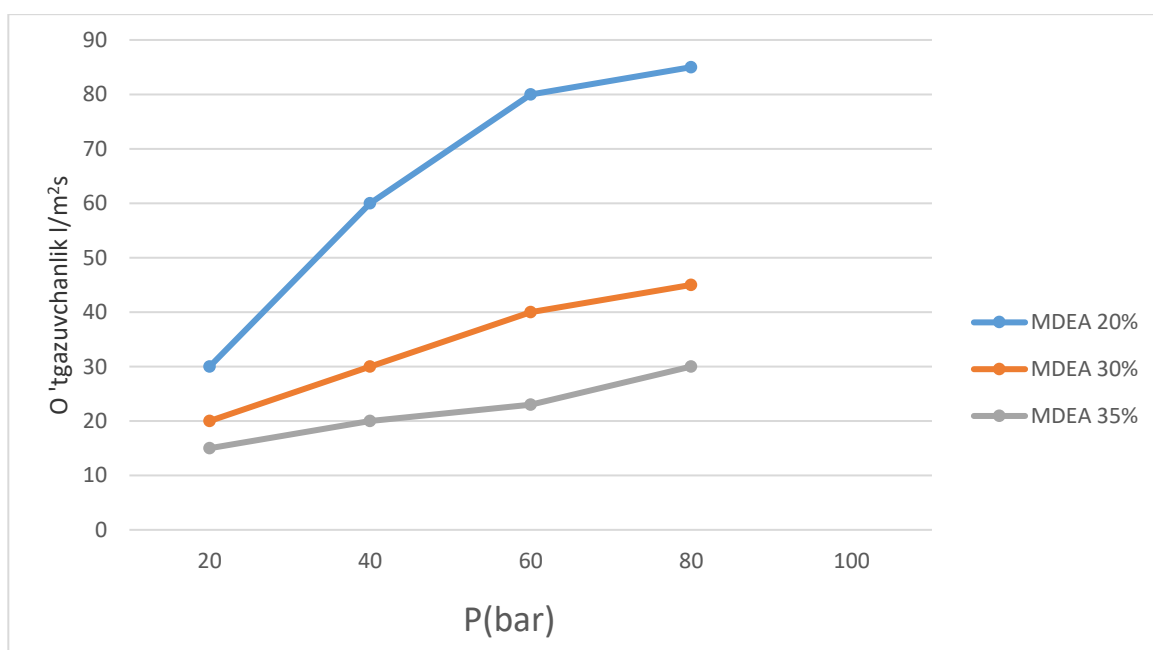
chunki ushbu nordon gazlar qurilmalarda korroziyning ortishi va yonishdan keyin atrof-muhitning ifloslanishiga sabab bo'ladi [6,7]. Tabiiy gazni nordon komponentlardan tozalash usullaridan biri aminlarning 25-35% suvli eritmasidan foydalanishdir, masalan, metildietanolamin (MDEA) [8-11].

MDEA uch asosli alkanolamin bo'lib, gazni oltingugurtdan tozalash sanoatida aralashmalarni olib tashlash uchun ishlatiladi [12]. Gazlarni  $\text{H}_2\text{S}$  va  $\text{CO}_2$  lardan tozalash jarayonida MDEA+ va SCN-,  $\text{HCOO}$ -,  $\text{H}_3\text{CCOO}$ - va  $\text{H}_3\text{CH}_2\text{CCOO}$ - kabi boshqa yon birikmalar hosil bo'ladi. Ushbu qo'shimcha mahsulotlar MDEA regeneratsiyasi to'liq amalga oshirish imkonini bermaydigan termik barqaror tuzlar parchalanmasdan qoladi [13]. Ushbu termik barqaror tuzlar miqdorining ortishi absorpsiya jarayonida ko'piklanish hodisasini or-

tishi bu esa o'z navbatida gazlar tozaligini pasayishi, korroziya tezligini ortishi, qurilmadagi filtrlarni tez-tez ifloslanishi kabi turli muammolarni keltirib chiqaradi [14, 15]. Umuman olganda, termik barqaror tuzlar gazlarni CO<sub>2</sub> va H<sub>2</sub>S dan tozalash samaradorligiga sezilarli darajada salbiy ta'sir ko'rsatadi. Shuning uchun ularni amin eritmasidan olib tashlash va doimiy sorbsiya va regeneratsiya jarayoni borishi uchun juda muhimdir. Ushbu termik barqaror tuzlar

ionlarini MDEA eritmasidan ajratib olishda termal regeneratsiya, distillash, ion almashinadigan qatronlar, elektrodializ (ED) va nanofiltratsiya (NF) kabi turli texnologiyalar qo'llaniladi [16-19].

Ingiliz olimlari Pal va boshqalar [20] o'zlarining patentlarida mavjud bo'lgan A-D anion almashinadigan qatronlar yordamida elektroliz usulida MDEA erituvchisidan TBT anionlarini ajratib olish jarayonlarni o'rgandilar. Ular bergan ma'lumotlarga ko'ra



1-rasm. 20-35% li MDEA eritmasi uchun o'tkazuvchanlik oqimiga bosimning ta'siri.

1-jadval

Ishlatilgan ionlarning zaryadi, molekulyar og'irligi, gidratsiya radiusi va gidratsiya energiyasi.

Ionlar	Molekulyar massa(g/mol)	Gidratsiya radiusi (nm)	Energiyasi (kJ/mol)	Ion kuchi
C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	59.04	0.260	328.94	0.00346
HCO <sub>2</sub> <sup>-</sup>	46.02	0.240	347.95	0.0065
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	88.02	0.298	1113.05	0.00928
SO <sub>4</sub> <sup>2-</sup>	96.06	0.306	1072.84	0.00637
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	112.13	0.323	1004.77	0.00547

ra elektroliz jarayoni anod va katod qatronlari orqali tuzlarni parchalashi ko'rsatilgan. Biroq, yuqorida keltirilgan elektroliz jarayonidan foydalanish ba'zi kamchiliklarga ega, jumladan, yuqori energiya iste'moli va ko'proq chiqindilarni ishlab chiqarish. Bundan tashqari, yuqori pH va amin erituvchilarga chidamli membranalar ishlab chiqarish bilan bog'liq yuqori xarajat elektroliz tizimlaridan foydalanishni cheklaydi.

Adabiyotlar ma'lumotlariga qaraganda, ilmiy tadqiqod ma'lumotlari MDEA suvli eritmalardan termik barqaror tuzlar ionlarni nanofiltratsiya jarayoni yordamida ajratishning oddiy va juda samarali usuli ekanligi ko'rsatilgan. Teskari osmos (TO) va ultrafiltratsiya (UF) jarayonlari o'rtasida ajratish xususiyatlariga ega bo'lgan nisbatan yangi bosimli filtrlash jarayoni bo'lgan nanofiltratsiya bir qator afzalliklarga ega, jumladan, bir valentli ionlar uchun yuqori o'tkazuvchanlik, ko'p valentli ionlar uchun past o'tkazuvchanlik, ishchi bosimning past bo'lishi, unumdorlikni yuqoriligi [21-27].

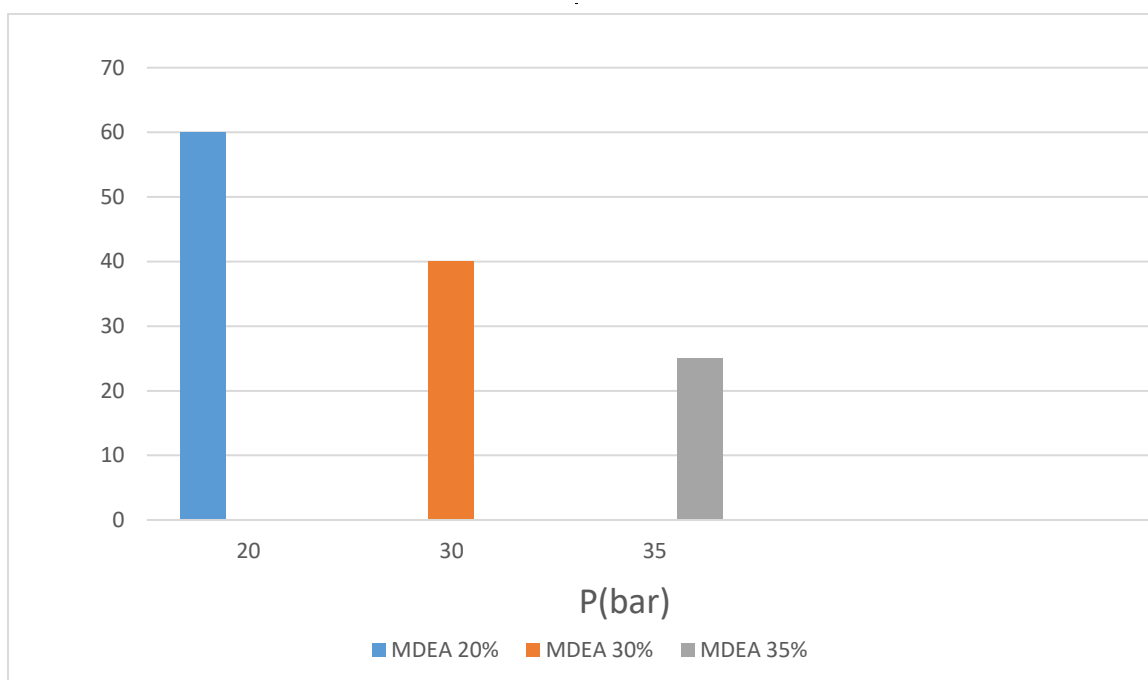
**Natijalar va muhokama.** NF membranalarida ajratish mexanizmlari odatda tashqi elektron zaryadlar va zaryadlangan ionlarni biriktirish qobilyati bilan tavsiflanadi. NF membrananing ajralish xususiyatlarini aniqlashda membrananing sirt zaryadi muhim rol o'ynaydi [28]. Shu maqsadda NF-3 membranasining o'lgangan o'rtacha sirt yuza potentsiali pH 7,4 da  $\pm 0,54\%$  xatolik bilan -42 mV edi. Shuning uchun, bu pH da membrana manfiy sirt zaryadiga ega. Bu natija Lin va boshqalar tomonidan olingan natijaga mos keladi [29]. Ular Sepro NF membranasining sirt zaryadini pH ni 2,5 dan 10,6 gacha o'zgartirish orqali zeta potentsiali bilan o'lchadilar. Membrana pH 2,5 da musbat zaryadga ega,

zeta potentsial qiymati 31 mV, izo elektrik nuqta (IEN) pH 5 da. Zeta potentsiali pH 10,6 da -72 mV bo'lib, membrananing sirt zaryadining nihoyatda manfiy ekanligini ko'rsatadi. Membrananing manfiy zaryadi membrananing yuqori o'zaro bog'langan poliamid sirt qatlami yuzasida karboksil guruhlarining deprotonatsiyasi bilan bog'liq.

#### *Osmotik sistemada membranali filtrlar tadbiqi.*

Ajratish tizimlarida foydalanish uchun nanofiltratsiya membranalar erituvchi oqimini membrana tashqi qismidan filtr ichki quvuriga o'tkazish uchun tizimning osmotik bosimidan foydalanishi kerak. Amin eritmasida erigan moddalar MDEA va TBT lardir, ammo amin konsentratsiyasi (20-35 % massa ulushda) TBT ionlarining konsentratsiyasidan sezilarli darajada oshadi; shunday qilib, bu ionlarning ajratib olish amin konsentratsiyasidan kelib chiqqan holda osmotik bosimga nisbatan filtrlash jarayoni o'rganilgan, bunda membrane filtr oqimi MDEA konsentratsiyasiga juda bog'liq. MDEA ning turli konsentratsiyalari uchun osmotik bosim hisoblab chiqilgan va quyidagi rasmdagi qo'shimcha sifatida keltirilgan, osmotik bosim amin konsentratsiyasining oshishi bilan ortadi.

MDEA eritmasining turli konsentratsiyalarida ionlar aralashmasi mavjudligida ish bosimining o'tkazuvchanlik oqimiga ta'sirini ko'rishimiz mumkinki, barcha amin konsentratsiyalarida membrane filtr orqali o'tadigan oqimi o'tkazuvchanlik, bosimning oshishi bilan MDEA ning 20% eritmasi uchun 60 bargacha va 30 va 35% MDEA eritmasi uchun 80 bargacha ko'tariladi [30,31]. Ushbu chiziqli tendentsiyani membrana penetratsiyasi uchun harakatlantiruvchi kuch qo'llaniladigan bosim gradienti ekanligini hisobga olish bilan



**2-rasm. MDEA konsentratsiyasining (a) o'tkazuvchanlik oqimi va (b) ish bosimi 70 bar, 0,693 l/soat, 350°C va pH=10 da ionlarni olib tashlashga ta'siri.**

izohlash mumkin. Shunday qilib, qo'laniladigan bosimni oshirish o'tkazuvchanlik oqimini oshiradi. Bundan tashqari, MDEA konsentratsiyasining funksiyasi sifatida bosimning ma'lum bir qiymatga oshishi bilan kuzatilgan erituvchi oqimining chiziqli tendentsiyasi konsentratsiyaning qutblanish hodisasining ahamiyatsiz ta'sirini ko'rsatadi.

Har xil MDEA konsentratsiyasida TBT ionlarini olib tashlash va o'tkazuvchanlik oqimi quyidagi rasmda ko'rsatilgan. MDEA konsentratsiyasining oshishi natijasida hosil bo'lgan o'tkazuvchanlik oqimining pasayishi va ion birikishini to'xtashi osmotik bosimning oshishi bilan bog'liq bo'lishi mumkin.

Nano filtratsiya tajriba qurilmasining sxemasi 3-rasmda ko'rsatilgan. Ushbu tizimda MDEA eritmalaridan TBTni olib tashlash uchun nanofiltratsiya membranasi ishlatilgan. NF filtr moduliga joylashtirishdan oldin membrana bir kechada

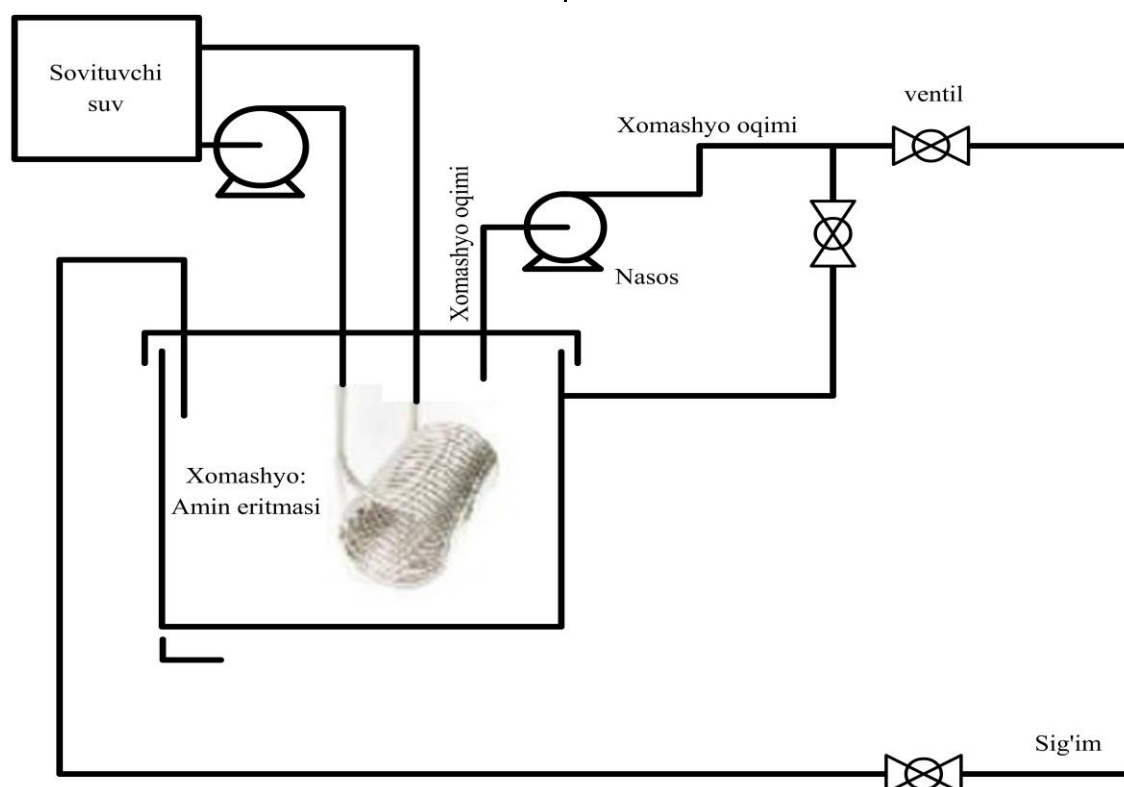
distillangan suvga botirildi. Filtrlash tizimi dastlab tizimning va membrana nuqsonlarisizligini ta'minlash uchun 20 bar da ishladi. Doimiy ozuqa konsentratsiyasi va hajmini saqlab turish uchun konsentrat va o'tkazuvchan oqimlar ozuqa idishiga qaytarildi. Permeat namunalari barqaror holatga kelgandan keyin turli bosimlarda to'plangan. Yuqori amin konsentratsiyasi osmotik bosimni oshiradi; shuning uchun NF tajribalari 40-80 bar oralig'ida yuqori ish bosimida o'tkazildi. Eritmaga quvurli sovutish lasanini qo'yish orqali saqlanadi. Oziqlantirish va ushlab turuvchi oqim tezligi yuqori bosimli nasos va kirish va chiqish vannalari tomonidan nazorat qilindi.

Ushbu tadqiqotda, past samarali membrana maydonini hisobga olgan holda, barcha sinovlar uchun o'rtacha ozuqa oqimi tezligi va tiklanish omili mos ravishda saqlanib qoldi. Har bir tajribadan so'ng membrana ifloslanishini kamaytirish va dastlabki oqim tezligini tiklash uchun



membranani 20 bar bosim ostida distillangan suv bilan bir necha marta yuvdi. Xususan, membrana har 3 kunda bir marta o'tkazuvchanlik oqimining dastlabki 42% ga kamayishi bilan yuviladi. Dastlabki eritmalarda asetat, format, sulfat, tiosulfat va oksalat ionlarining konsentratsiyasi mos ravishda 200, 300, 150, 150 va 200 mg/l ni tashkil qildi. Ion konsentratsiyasi mahalliy gazni qayta ishlash zavodida aylanma amin

nanofiltratsiya jarayoni bilan 20-35 og'irlikdagi MDEA eritmalaridan termobarqarorli tuzlarni olib tashlash o'rganildi. Ish bosimi, TBT ion konsentratsiyasi va MDEA eritmasidagi konsentratsiyasining oqimi va bosimiga bog'liqligi o'rganildi. NF membranasi pastroq MDEA konsentratsiyalarida yuqori TBT ionlarini olib tashlash samaradorligini ko'rsatdi. Osmotik bosim va konsentratsiyaning qutblanish



3-rasm. Eksperimental qurilmaning sxemasi (a) va nanofiltratsiya (NF) membrana ushlagichining tasvirlari (b).

eritmasidagi konsentratsiyasiga qarab tanlangan. Sintetik amin eritmasining ionlar aralashmasi ishtirokida pH qiymati 12 edi, lekin aylanma amin eritmasida oz miqdorda CO<sub>2</sub> va H<sub>2</sub>S borligi sababli uning pH qiymati 10 edi. Shuning uchun sintetik amin eritmasining pH qiymati 10 ga o'rnatildi. tegishli miqdorda HCl qo'shish orqali.

**Xulosa.** Xulosa qilib shuni ta'kidlashimiz mumkinki ushbu ishda membrana

hodisalari ortishi hisobiga MDEA konsentratsiyasining oshishi bilan o'tkazuvchanlik oqimi kamaydi. 70 va 80 bar bosimlarda MDEA konsentratsiyasining ortishi bilan, MDEA eritmasidan foydalananda membrana orqali amin chiqishi kamaydi. Filtratsiya jarayonida NF membrana filtrlarini qo'llash orqali MDEA eritmasini qayta tiklanishga erishildi.

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