**TERMIZ DAVLAT UNIVERSITETI HUZURIDAGI
ILMIY DARAJALAR BERUVCHI DSc.03/31.01.2023.K/T.78.01
RAQAMLI ILMIY KENGASH**

**SHAROF RASHIDOV NOMIDAGI SAMARQAND DAVLAT
UNIVERSITETI**

**BEGIMQULOVA SHAHNOZA AKBARJON QIZI**

**Li-Mn SHPINELLARI ASOSIDA NANOTUZILISHLI SORBSION
MATERIALLARNING ZOL-GEL SINTEZI VA FIZIK-KIMYOVIY
XOSSALARI**

**02.00.01 – Noorganik kimyo**
**02.00.04 – Fizik kimyo**

**KIMYO FANLARI BO'YICHA FALSAFA DOKTORI (PhD) DISSERTATSIYASI
AVTOREFERATI**

**Termiz – 2025**

**Kimyo fanlari boʻyicha falsafa doktori (PhD)
dissertatsiyasi avtoreferati mundarijasi**

**Contents of dissertation abstract of doctor of philosophy (PhD)
on chemical sciences**

**Оглавление автореферата диссертации доктора философии (PhD)
по химическим наукам**

# TERMIZ DAVLAT UNIVERSITETI HUZURIDAGI ILMIY DARAJALAR BERUVCHI DSc.03/31.01.2023.K/T.78.01 RAQAMLI ILMIY KENGASH

## SHAROF RASHIDOV NOMIDAGI SAMARQAND DAVLAT UNIVERSITETI

## BEGIMQULOVA SHAHNOZA AKBARJON QIZI

## Li-Mn SHPINELLARI ASOSIDA NANOTUZILISHLI SORBSION MATERIALLARNING ZOL-GEL SINTEZI VA FIZIK-KIMYOVIY XOSSALARI

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### KIMYO FANLARI BO'YICHA FALSAFA DOKTORI (PhD) DISSERTATSIYASI AVTOREFERATI

**Termiz – 2025**

**Kimyo fanlari bo'yicha falsafa doktori (PhD) dissertatsiyasi mavzusi O'zbekiston Respublikasi Oliy ta'lim, fan va innovatsiyalar vazirligi huzuridagi Oliy attestatsiya komissiyasida B2024.2.PhD/K7700raqam bilan ro'yxatga olingan.**

Dissertatsiya Sharof Rashidov nomidagi Samarqand davlat universitetida bajarilgan.

Dissertatsiya avtoreferati uch tilda (o'zbek, ingliz, rus (rezyume)) Ilmiy kengash veb-sahifasida (www.tersu.uz) va "ZiyoNet" axborot ta'lim portalida (www.ziyonet.uz) joylashtirilgan.

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# KIRISH (falsafa doktori (PhD) dissertatsiyasi annotatsiyasi)

**Dissertatsiya mavzusining dolzarbligi va zarurati.** Bugungi kunda dunyoda yuqori energiya sig'imiga ega qurilmalar, litiy-ion batareyalarning keng ko'lamda qo'llanilishi natijasida global miqyosda litiyning sanoatga bo'lgan talabi keskin oshdi. Bu esa yer qobig'ida 16,7 million tonna atrofida taxmin qilinayotgan litiy resurslarining cheklanganligi va ularning kamayishi, muqobil manbalardan litiyni ajratib olishga bo'lgan ehtiyojni yanada kuchaytirmoqda. An'anaviy konlardan litiy qazib olish jarayonining ekologik va iqtisodiy jihatdan murakkabligi sababli, hozirgi ilmiy izlanishlar sho'rlangan ko'l suvlari va dengiz suvidan litiyni samarali ajratib olish usullarini ishlab chiqishga qaratilgan. Ayniqsa, Li-Mn asosidagi sorbsion materiallardan foydalanish bunday jarayonlar orasida eng istiqbolli texnologik yechimlardan biri sifatida qaralmoqda. Bu turdagi materiallar yuqori selektivlik va adsorbsion qobiliyatga ega bo'lib, $Li^+$ ionini $Na^+$, $K^+$, $Mg^{2+}$ va $Ca^{2+}$ kabi ionlarga nisbatan tanlab sorbsiya qilish xususiyatiga ega. Shu boisdan, ular nafaqat tabiiy sho'r suvlardan, balki litiy-ion batareyalarini qayta ishlash jarayonida hosil bo'ladigan suvli eritmalardan litiyni qayta yig'ib olishda ilm-fan va sanoat uchun yuqori darajada ilmiy ahamiyat kasb etadi.

Jahonda litiyning cheklangan tabiiy zaxiralari fonida, uni sho'rlangan tabiiy va texnologik suvli muhitlardan selektiv ajratib olishga qaratilgan zamonaviy ilmiy izlanishlar keng ko'lamda olib borilmoqda. Bu borada, yuqori disperslikka ega, strukturaviy jihatdan barqaror va ion-selektiv xususiyatlarga ega nanotuzilishli sorbsion materiallar olish, zol-gel usuli orqali metall ionlari bilan modifikatsiyalangan Li-Mn shpinellari asosida sorbsion faolligi yuqori bo'lgan nanomateriallar sintezi, ularning fizik-kimyoviy, struktura-holat xossalarining chuqur tahlili, shuningdek, ushbu materiallarning ion almashinish kinetikasini tadqiq qilish, tanlovchanligini oshirish, regeneratsiya samaradorligi nuqtayi nazaridan litiyni ikkilamchi va tabiiy manbalardan ajratib olishda qo'llash, yuqori adsorbsion xossalarga ega bo'lgan sorbsion materiallar ishlab chiqish muhim amaliy ahamiyat kasb etadi.

Respublikamizda olib borilgan tadqiqotlar maxsus fizik-kimyoviy xossalarga ega nanotuzilishli sorbsion materiallarni olish imkoniyatini ko'rsatadi. Metall oksidi asosidagi adsorbentlarning ko'p fazali nanoo'lchamli tizimlarida "tuzilish-adsorbsion, xossalar-barqaror" kabi bog'liqliklarni o'rganish kimyoviy texnologiya va nanotexnologiyaning eng muhim vazifasi bo'lib, ularni amaliyotda qo'llashning yangi istiqbollarini ochmoqda. O'zbekiston Respublikasi Prezidentining 2022 yil 28 yanvardagi PF-60-son "2022-2026 yillarga mo'ljallangan Yangi O'zbekistonning taraqqiyot strategiyasi to'g'risida"gi Farmonida[1] "mavjud imkoniyatlarni to'liq ishga solgan holda mahalliy sanoat tarmoqlari eksport salohiyatini yanada rivojlantirish"ga yo'naltirilgan muhim vazifalar belgilab berilgan. Iqtisodiyotimizning asosiy tarmoqlaridan biri bo'lgan kimyo sanoatini rivojlantirishda litiy ionlari uchun Li-Mn asosidagi nanotuzilishli sorbsion materiallarni zamonaviy ussul sorbtsionlar yordamida sintez qilish va ularning

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[1] O'zbekiston Respublikasi Prezidentining 2022 yil 28 yanvardagi PF-60-son "2022-2026 yillarga mo'ljallangan Yangi O'zbekistonning taraqqiyot strategiyasi to'g'risida"gi Farmoni.

adsorbsion jarayonlarda samarali qo'llanilishi, muqobil energiya hamda ishlab chiqarish bilan bog'liq turli muammolarni hal qilishda yangi turdagi adsorbentlarni olishga qaratilgan ilmiy-amaliy tadqiqotlar katta ahamiyatga ega.

O'zbekiston Respublikasi Prezidentining 2022 yil 28 yanvardagi "2022-2026 yillarga mo'ljallangan Yangi O'zbekistonning taraqqiyot strategiyasi to'g'risida"gi PF-60-son Farmonida, 2018 yil 25 oktyabrdagi "O'zbekiston Respublikasida kimyo sanoatini jadal rivojlantirish chora-tadbirlari to'g'risida"gi PQ-3983-son, 2019 yil 3 apreldagi "Kimyo sanoatini yanada isloh qilish va uning investitsiyaviy jozibadorligini oshirish chora-tadbirlar to'g'risida"gi PQ-4265-son, 2021 yil 13 fevraldagi "Kimyo sanoati korxonalarini yanada isloh qilish va moliyaviy sog'lomlashtirish, yuqori qo'shilgan qiymatli kimyoviy mahsulotlar ishlab chiqarishni rivojlantirish chora-tadbirlari to'g'risida"gi PQ-4992-son Qarori hamda mazkur faoliyatga tegishli boshqa me'yoriy-huquqiy hujjatlarda belgilangan vazifalarni amalga oshirishda ushbu dissertatsiya tadqiqoti natijalari muayyan darajada xizmat qiladi.

**Tadqiqotning Respublika fan va texnologiyalari rivojlanishining ustuvor yo'nalishlariga mosligi.** Mazkur tadqiqot Respublika fan va texnologiyalar rivojlanishining VII. "Kimyo texnologiyalari va nanotexnologiya" ustuvor yo'nalishlariga muvofiq bajarilgan.

**Muammoning o'rganilganlik darajasi.** Turli xil metall ionlari bilan modifikatsiyalangan Li-Mn shpinellari asosida nanotuzilishli sorbsion materiallar sintezini amalga oshirish bo'yicha jahonning yetakchi olimlari tomonidan ilmiy tadqiqot ishlari olib borilgan. Jumladan, Liyan Tian, Wei Ma va Mei Hanlar tomonidan magniy ionlari qo'shilgan shpinel tuzilishli litiy marganes oksidlaridan litiy va magniyni ajratib olish yo'li bilan nanotuzilishli litiy-ion elaklar tayyorlangan. Ushbu tadqiqot Li$^+$ ning adsorbsiya-desorbsiya jarayonlarini yanada yaxshiroq tushinishga qaratilgan dastlabki tadqiqotlar uchun asos bo'lgan. Shuningdek, Li-Mn shpinellari asosidagi ilmiy tadqiqot ishlarida Ming-si Shen, Hai-bo Yuan va Ya-Xin Su kabi xorij olimlari tomonidan kalsiy qo'shilgan litiy marganes oksidlari Li$_{0,98}$Ca$_{0,02}$Mn$_2$O$_4$ gidrotermik usulda sintez qilinib, ularning morfologiyasi va fizik-kimyoviy xossalari o'rganilgan. A.I.Ivanes va uning jamoasi tomonidan Al$^{3+}$ ioni bilan modifikatsiyalangan Li$_{1,33}$Mn$_{1,67}$O$_4$ shpinel tuzilishli oksidlar sintez qilingan va natijada, past haroratli azotli adsorbsion-desorbsiya usulidan foydalanib, shpinelning ionlar bilan modifikatsiyalanishi aniqlandi.

Respublikamizda sorbsion materiallar va adsorbentlarni sintez qilish sohasida olib borilayotgan ilmiy tadqiqot ishlari ham jadal tarzda rivojlanib bormoqda. Xususan, mamlakatimiz olimlari M.G'.Muxamadiev, X.T.To'rayev, D.A.Gafurova, D.J.Bekchanov., X.T.Trobov, O.N.Ro'zimuradov, Sh.I.Mamatkulov va boshqalar tomonidan ham sorbsion materiallar sintezi, ularning fizik – kimyoviy va adsorbsion xossalari, shuningdek, ularni amaliyotda qo'llanilish sohalari atroflicha o'rganilgan.

Zol-gel usuli orqali sintez qilingan shpinel tuzilishli Li-Mn asosidagi nanotuzilishli materiallarning fizik-kimyoviy xossalari haqidagi ma'lumotlar ilmiy adabiyotlarda keltirilgan bo'lib, ammo bu nanotuzilishli oksidlarning Li$^+$ ion uchun

adsorbsion xossalari va ularga ta'sir etuvchi omillar, Li-Mn shpinel strukturasining yetarli darajada barqaror emasligi muammosini hal qilish, $Mn^{3+}$ ionlarini mos ravishda $Mg^{2+}$ va $Al^{3+}$ kationlari bilan qisman almashtirish orqali nanotuzilishli adsorbentlar sintez qilish jarayonlari to'la o'rganilmagan. Shu sababli, mazkur dissertatsiya ishi yuqoridagi jarayonlarni tizimli tarzda tadqiq etish, shuningdek, $Mg^{2+}$ va $Al^{3+}$ ionlari bilan modifikatsiyalangan Li-Mn asosidagi nanotuzilishga ega shpinellar olish va ularning fizik-kimyoviy xossalarini tadqiq qilishga qaratilgan.

**Dissertatsiya tadqiqotining dissertatsiya bajarilgan oliy ta'lim muassasasining ilmiy tadqiqot ishlari rejalari bilan bog'liqligi.** Ushbu dissertatsiya tadqiqoti Sharof Rashidov nomidagi Samarqand davlat universiteti Noorganik kimyo va materialshunoslik kafedrasi ilmiy yo'nalishiga hamda Turin Politexnika universiteti ilmiy-tadqiqotlar rejasiga muvofiq №MRB-2021-531 "Modifikatsiyalangan Li-Mn shpinellari asosida litiy ionlarining yuqori selektiv adsorbentlari: zol-gel sintezi, adsorbsion xossalari va barqarorligi" (2021-2023) mavzusidagi "O'zbekiston-Belarus" xalqaro ilmiy loyihasi doirasida bajarilgan.

**Tadqiqotning maqsadi:** zol-gel usuli orqali $Mg^{2+}$ va $Al^{3+}$ ionlari bilan modifikatsiyalangan Li-Mn shpinellari asosida nanotuzilishli sorbsion materiallarni sintez qilish, ularning fizik-kimyoviy va $Li^{+}$ ion uchun adsorbsion xossalarini aniqlashdan iborat.

**Tadqiqotning vazifalari:** Turli kimyoviy usullar bilan qayta ishlov berish haroratini o'zgartirib Li-Mn shpinellarini hosil qilish, hamda ularga $Mg^{2+}$ va $Al^{3+}$ ionlarini modifikatsiya qilish orqali $Li^{+}$ ion uchun Li-Me-Mn asosidagi nanotuzilishli sorbsion materiallar sintezini amalga oshirish;

sintez qilingan Li-Mn va Li-Me-Mn shpinellarining tuzilishi va fizik-kimyoviy xossalarini zamonaviy tadqiqot usullari yordamida o'rganish va tahlil qilish;

sintez qilingan Li-Mn va Li-Me-Mn shpinellarining teksturaviy xossalarini o'rganish;

sintez qilingan shpinel tuzilishli Li-Mn va Li-Me-Mn asosidagi nanotuzilishli sorbsion materiallarning $Li^{+}$ ion uchun adsorbsiya-desorbsiya jarayonlarida adsorbent faolligini aniqlash;

Li-Mn va Li-Me-Mn shpinellari asosida olingan adsorbentlarning $Li^{+}$ ioniga adsorbsiya izotermalarini tadqiq qilish va termodinamik parametrlarini aniqlash;

olingan Li-Mn va Li-Me-Mn shpinellaridan $Li^{+}$ ion uchun adsorbent sifatida foydalanish hamda sorbsion material sifatida tadqiq etish.

**Tadqiqotning obyekti** sifatida litiy, marganes, magniy va alyuminiy tuzlari hamda ularning ayrim oksidlari, limon kislota, xlorid kislota, sho'r suvlar olingan.

**Tadqiqotning predmetini** $Mg^{2+}$ va $Al^{3+}$ ionlari bilan modifikatsiyalangan Li-Mn shpinellari asosida sintez qilingan nanotuzilishli sorbsion materiallar tarkibi, tuzilishi, fizik-kimyoviy hamda sorbsion xossalarini aniqlash tashkil etgan.

**Tadqiqotning usullari.** Tadqiqot jarayonida olingan sorbsion materiallar tarkibi va tuzilishini aniqlashda skanerlovchi elektron mikroskopiyasi (SEM) elektron yutilish spektroskopiyasi (UV-vis), kukun rentgen difraksiyasi (XRD), IQ spektroskopiyasi, Raman spektroskopiyasi, rentgen flyuoresent spektroskopiyasi (XRF), termik analiz (TG va DTA), BET va BJH usuli kabi zamonaviy fizik

kimyoviy usullardan, shuningdek, adsorbsiya jarayonlarini tadqiq qilishda izotermalarni Lengmyur, Frendlix va Redlix-Peterson modellari bilan tahlil qilish, hamda adsorbsiya kinetikasini tasvirlash, psevdo-birinchi va psevdo-ikkinchi tartibli kinetik modellaridan foydalanilgan.

**Tadqiqotning ilmiy yangiligi** quyidagilardan iborat:

ilk bor zol-gel usulida $Mg^{2+}$ va $Al^{3+}$ ionlari bilan modifikatsiyalangan Li-Mn shpinellari asosida nanotuzilishli yuqori sorbsiya sig'imiga ega bo'lgan sorbsion materiallar sintez qilingan;

sintez qilingan $LiMn_2O_4$, $LiMg_xMn_{(2-x)}O_4$ va $LiAl_xMn_{(2-x)}O_4$ shpinellari asosidagi sorbsion materiallarning fizik-kimyoviy xossalari va $LiMg_{0.3}Mn_{1.7}O_4$ shpinel namunasi $Li^+$ ionlariga nisbatan sorbsiya sig'imi eng yuqori ekanligi aniqlangan;

$LiMn_2O_4$ va $LiMg_{0.3}Mn_{1.7}O_4$ adsorbent namunalariga $Li^+$ ioni uchun adsorbsiya izotermalari tadqiq qilingan, izotermalarning borishi olingan natijalar uchun Lengmyur modeliga mos kelishi aniqlangan;

$LiMn_2O_4$ va $LiMg_{0.3}Mn_{1.7}O_4$ adsorbent namunalarida $Li^+$ ionining adsorbsiya kinetikasi psevdo-ikkinchi tartibli kinetik modelga mos kelishi isbotlangan.

**Tadqiqotning amaliy natijalari** quyidagilardan iborat:

$Mg^{2+}$ va $Al^{3+}$ ionlari bilan modifikatsiyalangan shpinel tuzilishli Li-Mn asosidagi nanotuzilishli adsorbentlarni sintez qilishning maqbul sharoitlari aniqlangan;

$LiMg_xMn_{(2-x)}O_4$ va $LiAl_xMn_{(2-x)}O_4$ shpinellar asosida adsorbentlar hosil bo'lishida H-shaklga o'tish darajasi 43-79% oralig'ida bo'lib, Mg uchun x=0.3 bo'lgan namunada eng yuqori konversiya darajasi aniqlangan;

$LiMg_{0.3}Mn_{1.7}O_4$ shpinel asosidagi adsorbent uchun maksimal sorbsiya sig'imi 45 °C dagi $Li^+$ ion eritmasida 10,98 mmol/g ga teng ekanligi aniqlangan;

olingan Li-Mn shpinellari asosidagi nanotuzilishli adsorbentlar gidrometallurgiya korxonalari oqava suvlari tarkibidagi $Li^+$ ionlarini ajratib olishda yuqori samaradorlikka ega ekanligi ko'rsatib berilgan.

**Tadqiqot natijalarining ishonchliligi.** Ilmiy tadqiqot ishida olingan natijalar skanerlovchi elektron mikroskop (SEM), infraqizil spektroskopiya (IQ), elektron yutilish spektroskopiya (UV-vis), Raman spektroskopiya, termogravimetrik tahlil (TGA), rentgen fazaviy tahlil (XRD), rentgen flyuoresent spektrometriya (XRF), BET va BJH analizi kabi zamonaviy fizik-kimyoviy usullar qo'llanilgan. Ion muvozanati va adsorbsiya jarayonlarining kinetikasi psevdo-birinchi hamda psevdo-ikkinchi tartibli kinetik modellar asosida tavsiflangan. Adsorbsiya izotermalari Lengmyur, Frendlix, va Redlix-Petrson modellariga muvofiq hisoblab chiqilgan. Adsorbsiya termodinamikasi esa zamonaviy nazariyalar hamda tegishli tenglamalardan foydalangan holda, eksperimental natijalar asosida tahlil qilinib, matematik-statistik usullar yordamida qayta ishlanib, asosli xulosalar chiqarilgan.

**Tadqiqot natijalarining ilmiy va amaliy ahamiyati.**

Tadqiqot natijalarining ilmiy ahamiyati zol-gel usuli orqali shpinel tuzilishli Li-Mn asosida nanotuzilishli sorbsion materiallar olish asoslarini ishlab chiqish, shpinellarning shakllanish mexanizmlarini keltirish va $Mg^{2+}$ va $Al^{3+}$ bilan modifikatsiyalangan Li-Mn asosida nanotuzilishli sistemalar, shuningdek, ular asosidagi $Li^+$ ion uchun adsorbentlarni tadqiq etilganligi bilan izohlanadi.

Tadqiqot natijalarining amaliy ahamiyati $Mg^{2+}$ va $Al^{3+}$ bilan modifikatsiyalangan Li-Mn shpinellari asosida yaxshilangan teksturali xususiyatlarga ega bo'lgan nanotuzilishli sorbsion materiallarni sintez qilish hamda Respublikamizda mavjud litiy tuzlariga boy suv havzalaridan $Li^+$ ionini yig'ib olishda ushbu nanotuzilishli sorbsion materiallarning adsorbsion faolligini aniqlashdan iborat.

**Tadqiqot natijalarining joriy qilinishi.** $Li^+$ ioni sorbsiyasi $Mg^{2+}$ va $Al^{3+}$ bilan modifikatsiyalangan Li-Mn shpinellari asosida nanotuzilishli sorbsion materiallar olish texnologiyasini ishlab chiqish bo'yicha olingan ilmiy natijalar asosida:

sintez qilingan $LiMn_2O_4$, $Li_{1.33}Mn_{1.67}O_4$, $LiMg_xMn_{(2-x)}O_4$ va $LiAl_xMn_{(2-x)}O_4$ tuzilishga shpinellar asosidagi adsorbentlar "Navoiy kon-metallurgiya kombinati" aksiyadorlik jamiyatida oqava suvlar tarkibidan $Li^+$ ionini ajratib olish uchun amaliyotga joriy etilgan ("Navoiy kon-metallurgiya kombinati" AJ ning 2024-yil 6-noyabrdagi № 23/01-01-07/687-son ma'lumotnomasi). Natijada, gidrometalurgiya korxonalarining oqava suvlari tarkibidan $Li^+$ ionlarini 98% gacha adsorbsiya qilib ajratib olish imkonini bergan.

$LiMg_{0.3}Mn_{1.7}O_4$ va $LiAl_{0.3}Mn_{1.7}O_4$ tarkibga ega adsorbentlar "MOXSAR" MCHJ qo'shma korxonasi oqava suvlari tarkibidan $Li^+$ ionlarini sorbsion ajratib olish uchun qo'llanilgan ("MOXSAR" MCHJ QK ning 2025-yil 17-apreldagi №17/04-2 sonli ma'lumotnomasi). Natijada, oqava suvlar tarkibidagi $Li^+$ ionlarini sorbsion ajratishda sorbsiya sig'imi yuqori bo'lgan mahalliy xomashyolar asosida sintez qilingan $LiAl_{0.3}Mn_{1.7}O_4$ (60-62 mg/g) va $LiMg_{0.3}Mn_{1.7}O_4$ (70-74 mg/g) tarkibli shpinellarni import o'rnini bosuvchi sorbentlar sifatida qo'llash imkonini bergan.

**Tadqiqot natijalarining aprobatsiyasi.** Ushbu tadqiqot natijalari 15 ta, jumladan 9 ta xalqaro va 6 ta Respublika ilmiy-amaliy anjumanlarida ma'ruza qilingan va muhokamadan o'tkazilgan.

**Tadqiqot natijalarining e'lon qilinganligi.** Dissertatsiya mavzusi bo'yicha jami 20 ta ilmiy ishlar chop etilgan, shulardan O'zbekiston Resspublikasi Oliy attestatsiya komissiyasining falsafa doktori (PhD) dissertatsiyalari asosiy ilmiy natijalarini chop etish tavsiya etilgan ilmiy nashrlarida 5 ta maqola, shu jumladan 3 ta maqola respublika va 2 ta maqola xorijiy jurnallarda va xalqaro ilmiy anjumanlarda 9 ta, respublika ilmiy amaliy konferensiyalarida 6 ta tezislar nashr etilgan.

**Dissertatsiyaning tuzilishi va hajmi.** dissertatsiya tarkibiga kirish, to'rtta bob, xulosalar, foydalanilgan adabiyotlar ro'yxati va ilovalardan iborat. Dissertatsiyaning hajmi 119 bet.

## DISSERTATSIYANING ASOSIY MAZMUNI

**Kirish** qismida olib borilgan tadqiqotlarning dolzarbligi va ahamiyati asoslab berilgan, maqsad va vazifalari belgilangan, o'rganilayotgan obyekt va predmeti yoritilgan, tadqiqotning Respublika miqyosida fan va texnologiyalarning ustuvor yo'nalishlariga muvofiqligi ko'rsatib o'tilgan, tadqiqot natijalarining ilmiy

yangiligi, ilmiy va amaliy ahamiyati bayon etilgan, erishilgan natijalarning ishonchliligi, ilmiy va amaliy ahamiyati, ularning amaliyotga qo'llanilish imkoniyatlari ochib berilgan hamda dissertatsiya mavzusi doirasida chop etilgan ilmiy ishlar va dissertatsiya tarkibi bo'yicha ma'lumotlar ko'rsatilgan.

Dissertatsiyaning **"Li-Mn shpinellari asosidagi nanotuzilishli sorbsion materiallar shakllanishining ilmiy asoslari va istiqbolli yondashuvlari"** deb nomlangan **birinchi bobida** shpinel tuzilishga ega Li-Mn asosidagi nanotuzilishli sorbsion materiallar va ularni olishning asosiy usullari, qo'llanilish istiqbollari, $Li^+$ ion uchun metall ionlari bilan modifikatsiyalangan sorbsion materiallar olishning hozirgi holati hamda rivojlanish tendensiyalari bo'yicha adabiyot ma'lumotlarini batafsil tahlil qilish asosida tadqiqot ishining maqsadi va vazifalari asoslab berilgan.

Dissertatsiyaning **"Li-Mn shpinellari asosida nanotuzilishli sorbsion materiallarning zol-gel sintezi"** deb nomlangan **ikkinchi bobida** tadqiqot doirasida qo'llanilgan fizik-kimyoviy usullar va izotermalar uchun foydalanilgan modellarning tavsifi, materiallarning sintez usullarini tanlashga yondashuvi, zol-gel usulida shpinel tuzilishli Li-Mn asosidagi nanotuzilishli sorbsion materiallar olish hamda ularga $Mg^{2+}$, $Al^{3+}$ ionlarni turli xil nisbatlarda modifikatsiya qilish yo'llarini ishlab chiqish, metall ionlarining konsentratsiyasi va haroratni o'zgartirib material olish, olingan materiallarning tuzilishini va $Li^+$ ion uchun sorbsion xossalarini o'rganish bo'yicha ma'lumotlar keltirilgan.

Shpinel tuzilishga ega $LiMn_2O_4$ asosidagi sorbsion materiallar qattiq faza, gidrotermal va zol-gel usullaridan foydalangan holda sintez qilindi. Li-Mn asosidagi shpinellarga $Mg^{2+}$ va $Al^{3+}$ ionlarining modifikatsiyasi zol-gel usulida amalga oshirildi. Sintez qilingan materiallarning xossalari fizik-kimyoviy tadqiqot usullari yordamida tadqiq qilingan. 1-rasmda zol-gel usulida $LiMn_2O_4$ shpinelini sintez qilish sxemasi taklif qilindi.
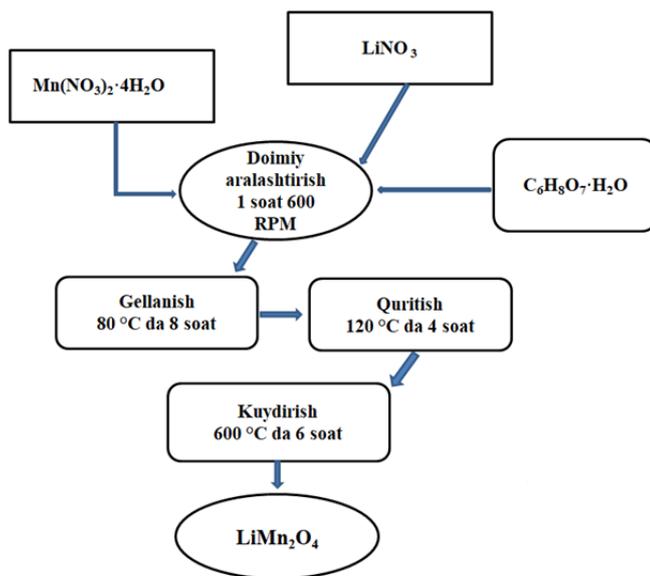


**1-rasm. $LiMn_2O_4$ shpinelining zol-gel usulida sintez sxemasi**

1-rasmda keltirilgan sxema bo'yicha $LiMn_2O_4$ shpineli hosil bo'lishida qayta ishlov berish harorati 400 °C, 600 °C va 800 °C larda olib borilgan.

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LiMg$_x$Mn$_{(2-x)}$O$_4$ (0 ≤ x <0,7) shpinel namunalarini sintez qilish uchun litiy nitrat (LiNO$_3$), marganes (II) nitrat tetragidrati (Mn(NO$_3$)$_2$·4H$_2$O) va magniy nitrat geksagidrati (Mg(NO$_3$)$_2$·6H$_2$O), limon kislotasi (C$_6$H$_8$O$_7$·H$_2$O)   ning suvli eritmalari ma'lum massa nisbatda aralashtirildi (1-jadval).

**1-jadval**

**LiMg$_x$Mn$_{(2-x)}$O$_4$ shpinel namunalari hosil bo'lishida dastlabki prekursorlarning massalari (g)**

| Namuna | LiNO$_3$ | Mn(NO$_3$)$_2$·4H$_2$O | Mg(NO$_3$)$_2$·6H$_2$O | C$_6$H$_8$O$_7$·H$_2$O |
|---|---|---|---|---|
| LiMg$_{0.1}$Mn$_{1.9}$O$_4$ | 0,552 | 3,8152 | 0,2048 | 5,04 |
| LiMg$_{0.3}$Mn$_{1.7}$O$_4$ | 0,552 | 3,4136 | 0,6144 | 5,04 |
| LiMg$_{0.5}$Mn$_{1.5}$O$_4$ | 0,552 | 3,0120 | 1,0240 | 5,04 |
| LiMg$_{0.7}$Mn$_{1.3}$O$_4$ | 0,552 | 2,6104 | 1,4336 | 5,04 |

Ushbu jadval ma'lumotlariga ko'ra LiMg$_x$Mn$_{(2-x)}$O$_4$ shpinellarning hosil bo'lishida (C$_6$H$_8$O$_7$·H$_2$O): (Li$^+$+Mg$^{2+}$+Mn$^{2+}$ tuzlari) mol nisbati 1: 1 qilib tanlanganligini ko'rish mumkin.

**"Li-Mn shpinellari asosidagi nanotuzilishli sorbsion materiallarning olinishi va fizik-kimyoviy xossalari"** deb nomlangan **uchinchi bobida** sintez qilingan Li-Mn shpinellari asosidagi nanotuzilishli sorbsion materiallarning shakllanishi, tuzilishi, fizik-kimyoviy va teksturaviy xossalarini o'rganish natijalari keltirilgan.

Zol-gel usulida LiMn$_2$O$_4$ shpinelining hosil bo'lishida dastlab prekursorlar eritmada gidrolizga uchrab tegishli metall va gidroksil ionlarini hosil qiladi.
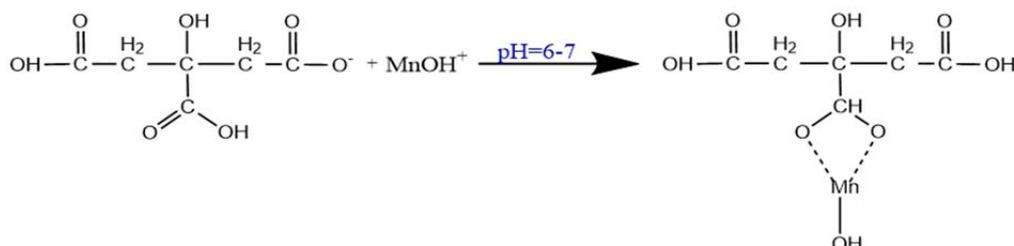


**1-reaksiya. MnOH$^+$ va limon kislotasi ishtirokida xelat komplekslar hosil bo'lish reaksiyasi**

Masalan, Mn$^{2+}$ ionlari gidrolizlanib, MnOH$^+$ hosil bo'ldi, ular pH=6-7 da limon kislotasi bilan xelat komplekslar hosil qiladi (1-reaksiya). 80 °C da gellanish jarayoni amalga oshadi va gel tomonidan adsorbsiyalangan Li$^+$ ionlari Mn(II) kompleksi bilan qo'shilib, yuqori haroratda gel parchalanadi. Natijada shpinel tuzilishli LiMn$_2$O$_4$ nanozarrachalari hosil bo'ladi
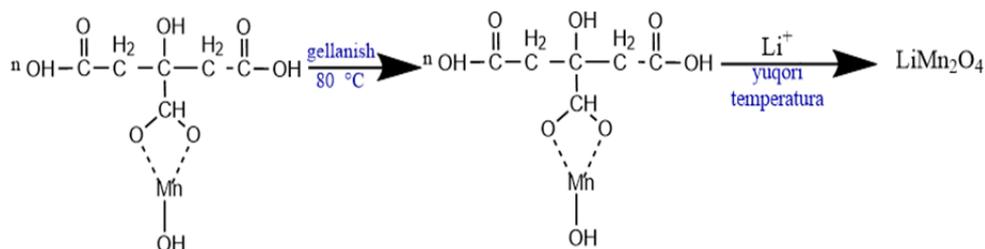


**2-reaksiya. Shpinel tuzilishli LiMn$_2$O$_4$ nanozarrachalarining hosil bo'lish reaksiyasi**

Zol-gel usulida sintez qilingan $LiMn_2O_4$, $LiMg_{0.3}Mn_{1.7}O_4$ va $LiAl_{0.3}Mn_{1.7}O_4$ shpinel namunalarining SEM tasvirlari 2-rasmda keltirilgan. SEM tasvirlardan ko'rinib turibdiki zarrachalar oktaedrik tuzilishga ega ekanligini ko'rsatdi. Ushbu morfologik xususiyat shpinel fazasining shakllanishi va uning kristall tuzilishiga bog'liq bo'lib, zol-gel usuli natijasida hosil bo'luvchi zarrachalarning nisbatan bir xil shaklga ega ekanligini tasdiqlaydi.
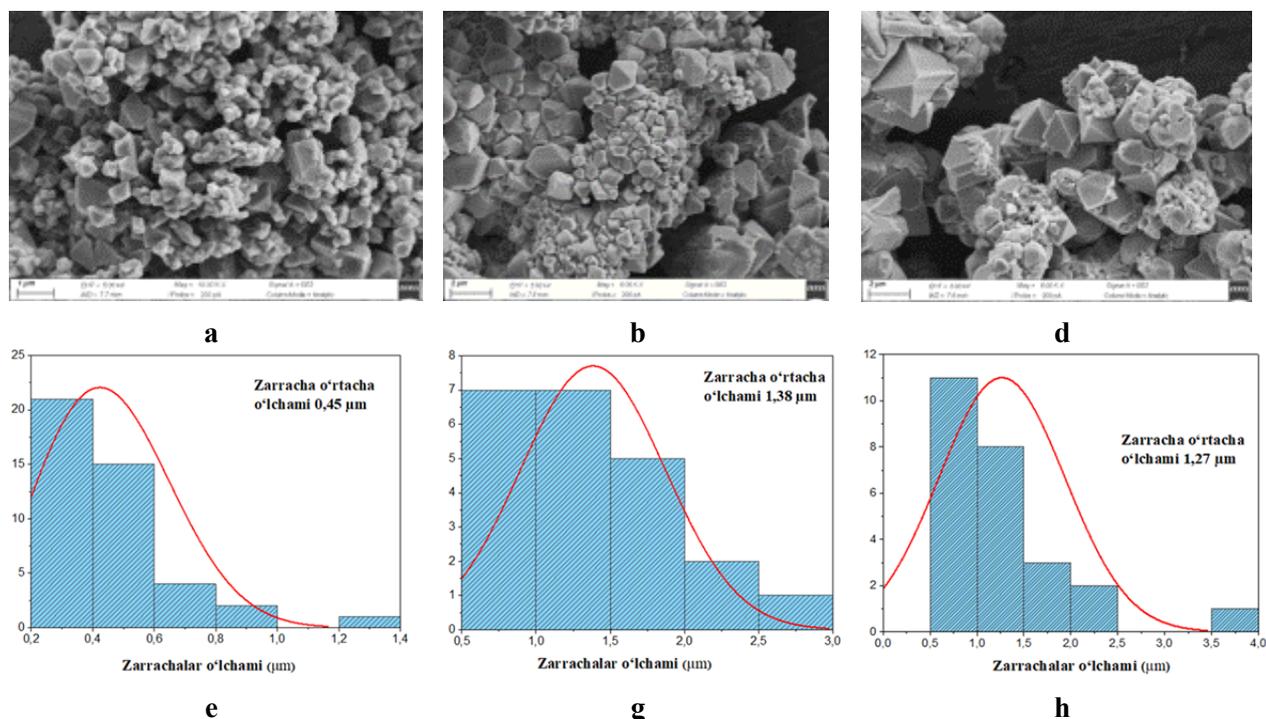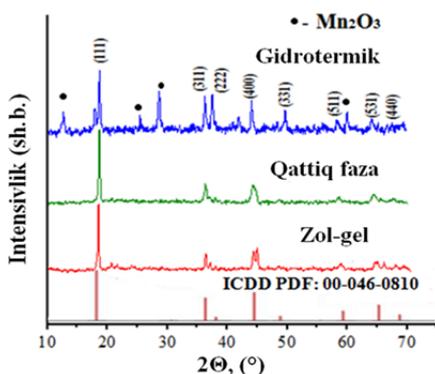


**2-rasm. Zol-gel usuli bilan olingan $LiMn_2O_4$ (a), $LiMg_{0.3}Mn_{1.7}O_4$ (b), $LiAl_{0.3}Mn_{1.7}O_4$ (d) shpinel namunasi yuzasining SEM tasvirlari va zarracha o'lchami taqsimoti (e, g, h, mos ravishda)**

Tasvir dasturi (ImageJ) yordamida zarracha o'lchami taqsimotini tahlil qilish natijasida $LiMn_2O_4$ shpinel zarrachalarining o'lchamlari 0,2 mkm dan 1,4 mkm gacha oraliqda ekanligi aniqlandi (2e-rasm.). 2e, g, h-rasmlardagi grafik ma'lumotlar asosida zarrachalarning o'rtacha o'lchami taxminan $LiMn_2O_4$ uchun 0,45 mkm, $LiMg_{0.3}Mn_{1.7}O_4$ va $LiAl_{0.3}Mn_{1.7}O_4$ shpinellar uchun bu qiymat mos ravishda 1,38 va 1,27 mkm ga teng ekanligi aniqlandi.
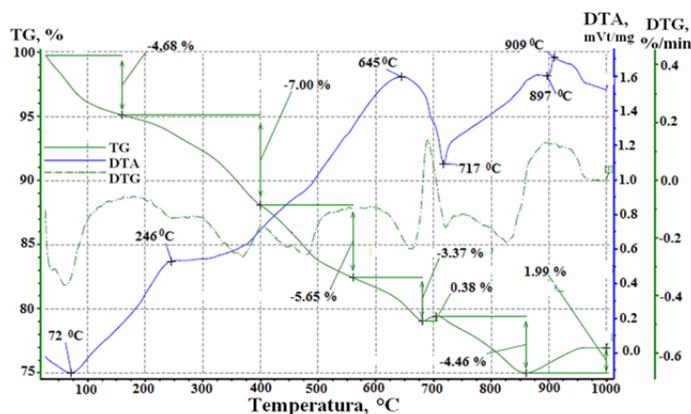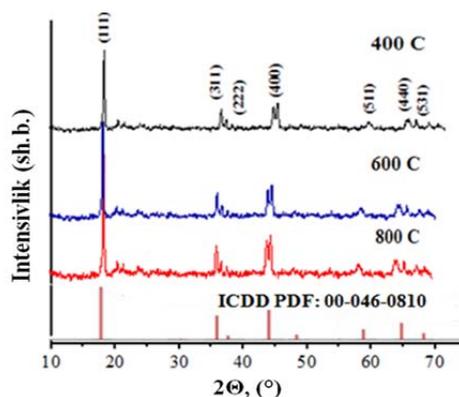


**3-rasm. Zol-gel usuli bilan olingan $LiMn_2O_4$ shpinel namunalarining DTA-TG egri chiziqlari**

Qattiq faza, zol-gel va gidrotermik usullarda sintez qilingan Li-Mn shpinel namunalari DTA-TG egri chizig'i 20-300 °C oralig'ida tahlil qilinishi 72-85 °C oralig'ida endotermik cho'qqining mavjudligini ko'rsatadi, natijada massa yo'qotilishi namunalarda mos ravishda 22,74, 4,68 va 15,88 % ga ega bo'lib, fizik va kimyoviy bog'langan suvning chiqib ketishi bilan izohlanadi. Qattiq fazali va zol-gel usulida sintez qilingan $LiMn_2O_4$ shpinelining shakllanishi 700-720 °C da endotermik cho'qqi va taxminan 8,29 va 4,46 % massa yo'qolishi bilan sodir bo'ladi. Gidrotermik usulda bu jarayon 850 °C da sodir bo'ladi, bu endotermik ta'sir orqali tasdiqlanadi va massa 2,85 % ga kamayishi bilan aniqlandi.



**4-rasm. Turli usullar bilan sintez qilingan Li-Mn asosidagi shpinel namunalarining rentgenogrammalari**

**5-rasm. Zol-gel usulida sintez qilingan $LiMn_2O_4$ shpinel namunalarining 400, 600 va 800 ° C da kalsinatsiya qilingan rentgenogrammalari**

4 va 5-rasmda keltirilgan rentgenogrammalar shuni ko'rsatadiki, barcha namunalar bir fazali Li-Mn shpineli bo'lib, $LiMn_2O_4$ strukturasiga ega. Bu 2θ burchakdagi tor va intensiv difraksion cho'qqilar hamda ularga mos keluvchi Miller indekslari – 18,9 (111), 36,7 (311), 44,5 (400), 58,8 (511) va 64,7 (404) orqali tasdiqlanadi. Gidrotermik sintez usulida olingan Li-Mn shpinel namunasi rentgenogrammasida $Mn_2O_3$ qo'shimcha fazasi mavjud, bu esa prekursorning to'liq reaksiyaga kirishmaganligi bilan izohlanadi. Qattiq fazali sintez usulida olingan $LiMn_2O_4$ shpineli kristall panjarasining *a* parametrining hisoblangan qiymati 8,197 Å ni tashkil etadi.

**2-jadval**

**Turli usullar bilan sintez qilingan va 600 °C da qayta ishlov berilgan $LiMn_2O_4$ shpinel namunalarining kristall panjara parametrlari**

| Sintez usuli | $D$, nm | $d$, Å | $a$, Å | $V$, Å³ |
|---|---|---|---|---|
| Qattiq fazali | 22,4 | 2,46 | 8,197* | 550,7 |
| Zol-gel | 17,3 | 2,43 | 8,120** | 535,3 |
| Gidrotermik | 27,0 | 3,07 | 8,167** | 544,7 |

*- $LiMn_2O_4$ uchun *a* parametri 8,190 Å(COD_96-402-9204);
** - $LiMn_2O_4$ uchun *a* parametri 8,145 Å (COD_96-151-4050).

Zol-gel va gidrotermik usullar bilan olingan namunalar uchun mos malumotlar qiymati bilan solishtirganda *a* parametrida biroz farq kuzatildi, uning qiymati 8.120 Å va 8.167 Å, mos ravishda (2-jadval). 2-jadvalda keltirilgan kristall

o‘lchamlari tahlili shuni ko‘rsatadiki, eng kichik qiymat (17,3 nm) zol-gel usuli bilan olingan bir fazali shpinel zarrachasiga xosdir.

Qayta ishlov berish haroratining 400 °C dan 800 °C gacha ko‘tarilishi natijasida olingan $LiMn_2O_4$ shpinel namunalarining kristall hajmining 12,1 dan 19,9 nm gacha tabiiy o‘sishi kuzatildi (3-jadval).

**3-jadval**

**Zol-gel usuli bilan olingan va turli xil haroratlarda issiqlik bilan ishlov berilgan $LiMn_2O_4$ shpinel namunalarining kristall panjara parametrlari**

| Qayta ishlash harorati, °C | $D$, nm | $d$, Å | $a$, Å | $V$, Å$^3$ |
|---|---|---|---|---|
| 400 | 12,1 | 2,45 | 8,157* | 542,7 |
| 600 | 17,3 | 2,43 | 8,120* | 535,3 |
| 800 | 19,9 | 2,45 | 8,171** | 545,6 |

*- $LiMn_2O_4$ uchun $a$ parametri 8,145 Å (COD_96-151-4050);
** - $LiMn_2O_4$ uchun $a$ parametri 8,177 Å (COD_96-151-4054).

Yuqoridagi jadval ma’lumotlaridan ko‘rinadiki 400 va 600 °C da termik ishlov berilgan Li-Mn shpinel namunalari uchun $a$ parametrining qiymati 8,157 Å va 8,120 Å ni tashkil qiladi va mos malumotlar qiymatidan bir oz farq qiladi. 800 °C da issiqlik bilan ishlov berilgan namuna uchun $a$ (8.171 Å) parametrining hisoblangan qiymati tegishli ma’lumotlar qiymatiga yaxshi mos keladi.

6-rasmda keltirilgan $LiMn_2O_4$ shpinel namunalarining IQ spektrlari tahlil qilinganda, 530-700 cm$^{-1}$ sohada Mn-O bog‘lanishiga tegishli polosalar aniqlandi.
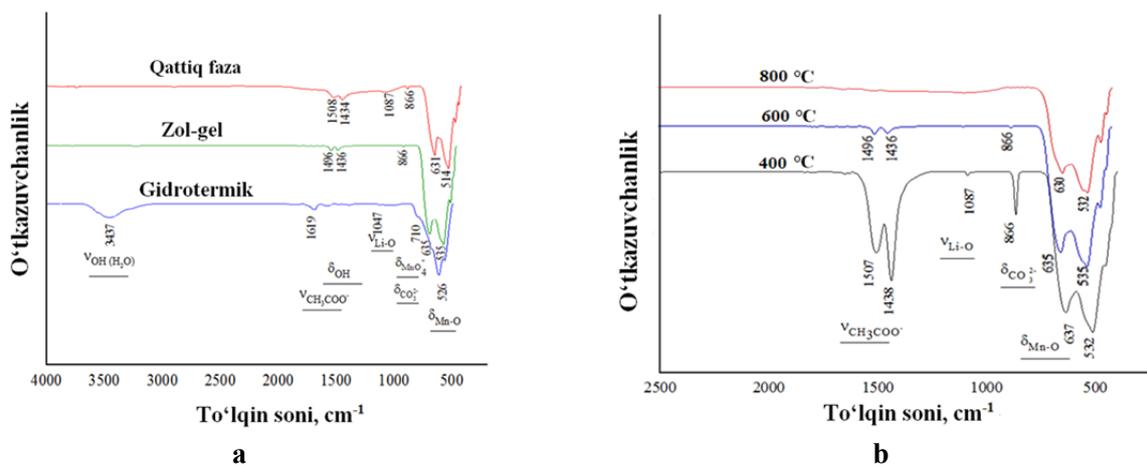


**6-rasm. 600 °C da turli usullar bilan (a) va turli haroratlarda kalsinatsiyalash (b) natijasida olingan $LiMn_2O_4$ shpinel namunalarining IQ spektrlari**

Bu esa shpinel strukturasidagi Mn-O bog‘lanishlarining mavjudligini va ularning tartiblangan holatda ekanligini ko‘rsatadi. Shuningdek, 1085 cm$^{-1}$ da kuzatilgan keng polosa Li-O tebranishlariga tegishli bo‘lib, bu litiy ionlarining shpinel strukturasida joylashganligini tasdiqlaydi.

$LiMg_xMn_{(2-x)}O_4$ tarkibli namunalarning fazaviy tuzilishi $LiMn_2O_4$ (PDF2 #35-0782) shpinel tuzilishiga mos ekanligi aniqlandi. Kuzatilgan cho‘qqilar (111), (311), (222), (400), (511) va (440) tekisliklar (hkl) ga mos keladi. Bu cho‘qqilar shpinel tuzilishli faza uchun xarakterli bo‘lib, kubik kristall panjarasi mavjud ekanligini tasdiqlaydi. 7-rasmdagi rentgenogrammalardan ko‘rish mumkinki,

barcha shpinel namunalarda asosiy choʻqqilar saqlanib qolgan, lekin ayrim namunalarda qoʻshimcha choʻqqilar paydo boʻlgan (masalan $2\theta$ = 28-32° oraligʻida). Bu $Mg^{2+}$ ioni kiritilganda biroz boʻlsada panjara buzilishi yuzaga kelganligini koʻrsatadi. $LiMg_xMn_{(2-x)}O_4$ (x=0.3, 0.5 va 0.7) namunalarda choʻqqilar biroz siljigan va intensivlik oʻzgargan. $Mg^{2+}$ miqdorining ortishi bilan choʻqqilar chap tomonga siljishi, bu $Mg^{2+}$ ionining $Mn^{3+}/Mn^{4+}$ ionlariga nisbatan biroz boʻlsada kattaroq ion radiusga ega ekanligi bilan izohlash mumkin.
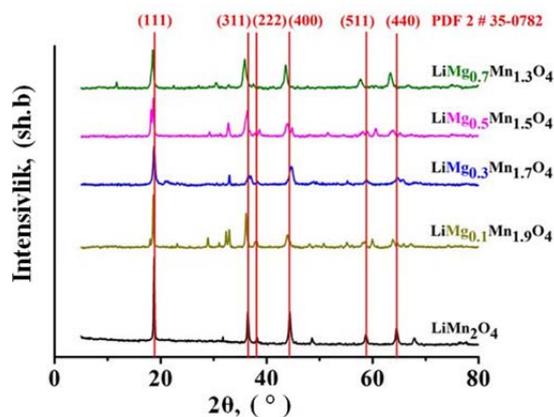


**7-rasm. $LiMn_2O_4$ va $LiMg_xMn_{(2-x)}O_4$ ($0 \le x \le 0.7$) shpinel namunalarining rentgenogrammalari**
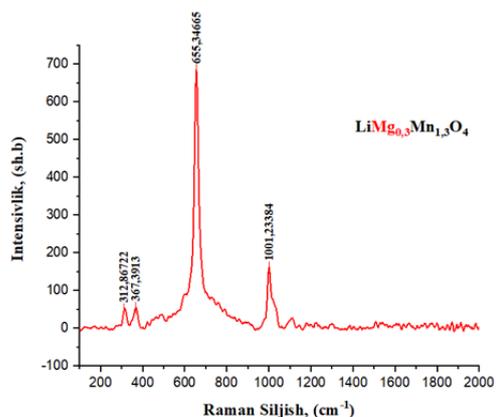
**8-rasm. $LiMg_xMn_{(2-x)}O_4$ shpinel namunasining Raman spektri**

4-jadvalda $Mg^{2+}$ ioni bilan modifikatsiyalangan Li-Mn shpinellarining kristall panjarasi parametrlari va oʻrtacha kristall oʻlchamlari keltirilgan boʻlib, $Mg^{2+}$ ionlari bilan modifikatsiyalash panjara parametri $a$ ning 8.253 Å (x = 0.1) dan 8.309 Å (x = 0.7) gacha oshishi kuzatildi, yaʼni kiritilgan magniy miqdori ortishi bilan bu parametr ham oshadi. $LiMg_{0.3}Mn_{1.7}O_4$ shpinel namunasi bu oʻzgarishga boʻysunmaydi, uning panjara parametri $a$ 8.253 Å ga teng.

**4-jadval**

**$LiMg_xMn_{(2-x)}O_4$ shpinel namunalarining kristall panjara parametrlari**

| Namuna | Panjara parametri $a$, Å | Elementar yacheykasining hajmi $V$, Å3 | Kristall hajmi $D$, nm |
|---|---|---|---|
| $LiMn_2O_4$ | 8,175 | 546,250 | 31,7 |
| $LiMg_{0.1}Mn_{1.9}O_4$ | 8,253 | 562,110 | 36,0 |
| $LiMg_{0.3}Mn_{1.7}O_4$ | 8,191 | 549,550 | 17,2 |
| $LiMg_{0.5}Mn_{1.5}O_4$ | 8,254 | 562,290 | 26,7 |
| $LiMg_{0.7}Mn_{1.3}O_4$ | 8,309 | 573,620 | 30,3 |
| $LiMn_2O_4$ (PDF 2 # 35-0782) | 8,248 | 561,030 | – |

8-rasmda $LiMg_xMn_{(2-x)}O_4$ shpinel namunalarining Raman siljishlari 200–1000 $cm^{-1}$ spektral sohada koʻrsatilgan. Ushbu spektrlarning umumiy xususiyati 550-750 $cm^{-1}$ diapazonidagi 650 $cm^{-1}$ atrofida yuqori intensivlikdagi Mn-O bogʻining tebranishiga tegishli. 800 $cm^{-1}$ dan yuqori sohada joylashgan oʻrtacha intensivlikdagi Raman siljishlar choʻqqisi $F_{2g}^{(3)}$ simmetriyaga ega. $F_{2g}^{(3)}$ rejimi Li-O bogʻi bilan bogʻliq boʻlib, yaʼni tetraedrik kation tuzilishiga ega. 330 $cm^{-1}$ da

intensivligi yuqori bo'lgan chiziq $Mg^{2+}$ ga tegishli bo'lib, simmetriyaning kation o'zgarishlariga olib keladigan Raman siljishi bo'lishi mumkin.

**Li-Mn shpinellari asosidagi nanotuzilishli materiallarning teksturaviy xususiyatlari.** Barcha tahlil qilingan $LiMg_xMn_{(2-x)}O_4$ shpinel namunalar uchun azotning adsorbsiya-desorbsiya izotermalari kapillyar-kondensatsiya gisterezis halqasiga ega bo'lib, IUPAC tasnifiga muvofiq IV turga mansubdir. Ushbu turdagi izotermalar, odatda, mezog'ovak materiallarga xos bo'lib, ularning rivojlangan g'ovaklik tizimiga egaligini ko'rsatadi. Tadqiqot natijalari shuni ko'rsatadiki, o'rganilgan oksidlarning izotermalari H3 tipidagi gisterezis halqasiga ega bo'lib, bu esa yoriqsimon g'ovaklarning mavjudligidan dalolat beradi (11-rasm).

5-jadval

**$LiMg_xMn_{(2-x)}O_4$ shpinel namunalarining teksturaviy xarakteristikalari**

| Namuna | $A_{BET}$, m²/g | $V_{sp\,des}$, cm³/g | $D_{BJH\,des}$, nm | Gisterezis halqa turi | G'ovaklik shakli |
|---|---|---|---|---|---|
| $LiMn_2O_4$ | 8,3 | 0,015 | 8,3 | | |
| $LiMg_{0.1}Mn_{1.9}O_4$ | 17,1 | 0,028 | 7,9 | H3 | yoriqsimon |
| $LiMg_{0.3}Mn_{1.7}O_4$ | 14,2 | 0,027 | 8,6 | | |
| $LiMg_{0.7}Mn_{1.3}O_4$ | 16,6 | 0,073 | 21,2 | | |

$Mg^{2+}$ ionlarining x ≥ 0,3 da kiritilishi g'ovak diametri qiymatlarining o'zgarishiga olib kelmaydi. G'ovaklarning eng katta hajmi (0,073 cm³/g) va o'rtacha hajmi (21,2 nm) x = 0,7 ga tegishli namunaga xos bo'lib, unda $Li_{0,5}Mg_{0,5}O_{1,5}$ va $Mn_{1,5}Mg_{0,5}O_{2,5}$ oksidlarining aralashmalari mavjud.
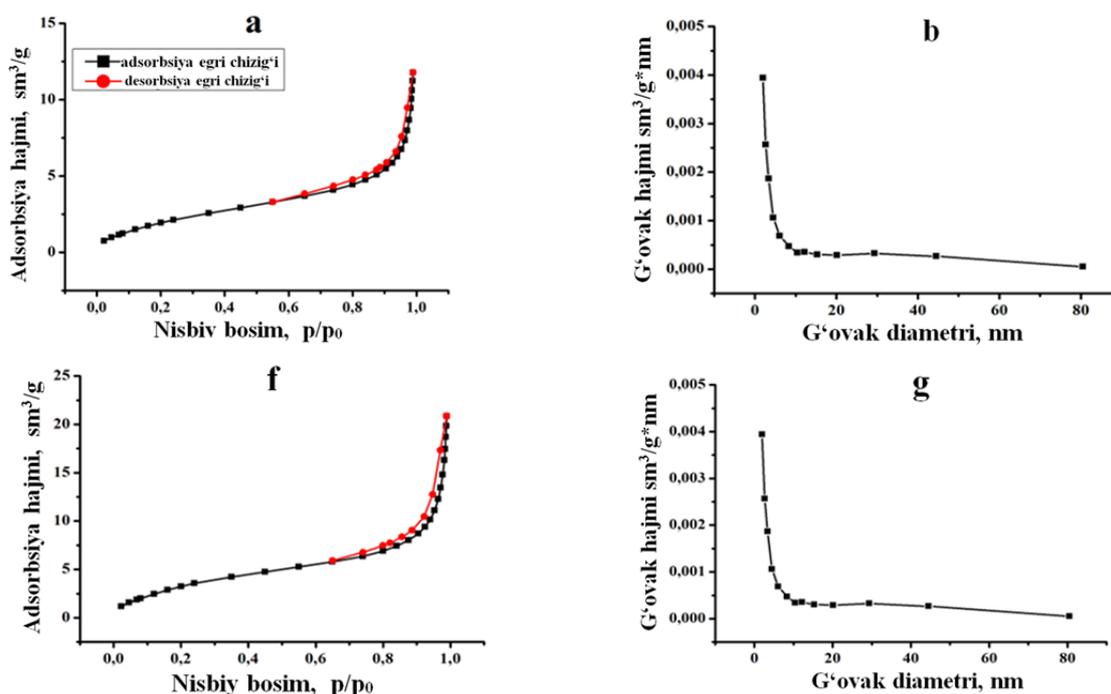


**11-rasm. $N_2$ (a, f,) va BJH g'ovak o'lchamlari taqsimotining (b, g) past haroratli adsorbsion-desorbsion izotermlari. $LiMn_2O_4$ (a, b) va $LiMg_{0.3}Mn_{1.7}O_4$ (f, g)**

Bunday holda, 0,1 ≤ x ≤ 0,3 oralig'ida, o'ziga xos sirt maydonida ~ 1,7-2,1 marta va g'ovak hajmida ~ 1,8 marta o'sishi kuzatildi. $Mg^{2+}$ ionlari tarkibining x=0,7 ga oshishi o'rtacha g'ovak hajmining 21,2 nm gacha sezilarli darajada oshishi bilan birga keladi (5-jadval).

Dissertatsiyaning "**Li-Mn shpinellari asosidagi nanotuzilishli materiallarning Li$^+$ ionlari sorbsiyasida qo'llanilishi**" deb nomlangan **to'rtinchi bobida** Li-Mn shpinellari asosidagi adsorbentlarning sorbsion xossalari, adsorbsiya izotermalari va kinetikasini tadqiq qilish bo'yicha olingan amaliy va nazariy ma'lumotlarning tahlili keltirilgan.

HMg$_x$Mn$_{(2-x)}$O$_4$ adsorbent namunalari 45 dan 79% gacha konversiya darajasini ko'rsatdi (12-rasm). HMg$_{0.3}$Mn$_{1.7}$O$_4$ va HAl$_{0.3}$Mn$_{1.7}$O$_4$ namunalari konversiyaning eng yuqori darajasini 79 va 74 % mos ravishda, HAl$_{0.7}$Mn$_{1.3}$O$_4$ namunasida 43% konversiyaning eng past darajasi aniqlandi (13-rasm).
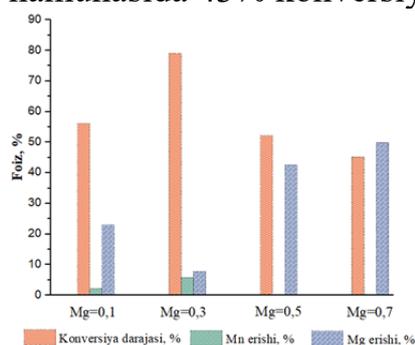


**12-rasm. LiMg$_x$Mn$_{(2-x)}$O$_4$ namunalarning H-shaklga o'tish va metall ionlarining erish foizi**
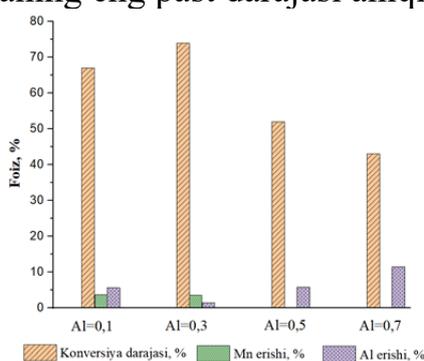
**13-rasm. LiAl$_x$Mn$_{(2-x)}$O$_4$ namunalarning H-shaklga o'tish va metall ionlarining erish foizi**
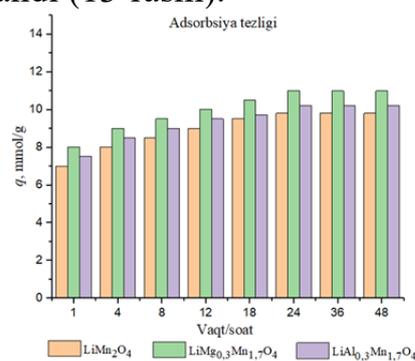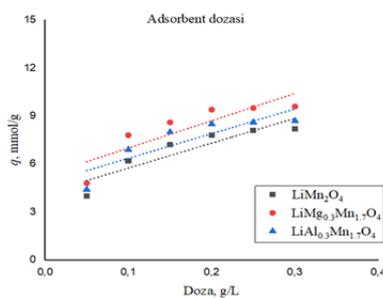
**14-rasm. Li-Mn asosidagi adsorbentlarning namunaviy eritmadagi Li$^+$ ion uchun adsorbsiya tezligi (pH=12, C$_0$=0,2)**

Kuzatishlarga ko'ra, adsorbsiya tezligi vaqt o'tishi bilan asta-sekin ortib borib, taxminan 24 soatda muvozanatga erishilgan. Dastlabki 1 soat ichida litiyning ajralishi biroz sekin kechib, LiMn$_2$O$_4$, LiMg$_{0.3}$Mn$_{1.7}$O$_4$ va LiAl$_{0.3}$Mn$_{1.7}$O$_4$ asosidagi adsorbentlar uchun sorbsiya sig'imi mos ravishda 7,20, 8,10 va 7,54 mmol/g larni tashkil qilgan. 24 soat o'tgach esa, bu qiymatlar 9,42, 10,65 va 9,63 mmol/g ga yetgan. Tajriba davom ettirib, 48 soatgacha kutilganda ham, litiy miqdori ortmagan (14-rasm).
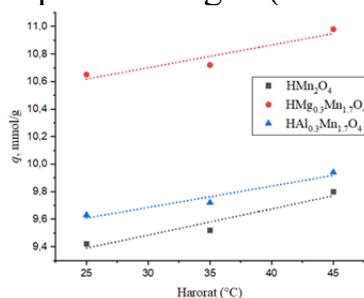


**15-rasm. Li-Mn asosidagi adsorbent namunalarning turli haroratlarda Li$^+$ ion uchun sorbsiya sig'imi**

**16-rasm. asosidagi adsorbentlarning adsorbsion faolligiga namunaviy eritmadagi adsorbent dozasi ta'siri**
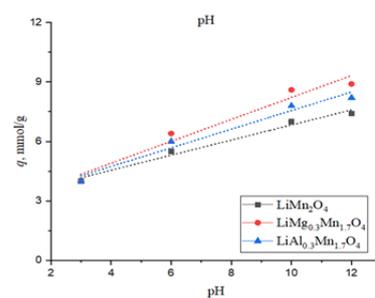
**17-rasm. Li-Mn asosidagi adsorbentlarning adsorbsion faolligiga namunaviy eritmaning pH ta'siri.**

15-rasmda esa turli haroratlarda HMn$_2$O$_4$, HMg$_{0.3}$Mn$_{1.7}$O$_4$ va HAl$_{0.3}$Mn$_{1.7}$O$_4$ adsorbentlar tomonidan Li$^+$ ionining adsorbsiyasi ko'rsatilgan. HMg$_{0.3}$Mn$_{1.7}$O$_4$ ning sorbsiya sig'imi haroratning oshishi tartibida 10,65, 10,72 va 10,98 mmol/g qiymatlarda aniqlandi.

LiMn$_2$O$_4$ asosidagi adsorbentning dozasini 0,05 dan 0,2 g/l gacha oshirish adsorbsiya sig'imining 4,0 dan 7,8 mmol/g gacha oshishiga olib keldi. Ushbu ko'rsatkich LiMg$_{0.3}$Mn$_{1.7}$O$_4$ va LiAl$_{0.3}$Mn$_{1.7}$O$_4$ asosidagi adsorbentlar uchun mos ravishda 4,8 dan 9,4 mmol/g ga va 4,4 dan 8,5 mmol/g ga oshib borishi kuzatildi (16-rasm). Biroq, adsorbentlar dozasini 0,3 va 0,4 g/l gacha oshirish adsorbsiya sig'imiga sezilarli ta'sir ko'rsatmaydi, bu esa adsorbentning to'yinganligi bilan bog'liq. Tadqiqot natijalari shuni ko'rsatdiki, tanlangan namunalar uchun adsorbsiya sig'imi pH 3,0 dan 13,0 gacha bo'lgan muhitda ortib boradi (17-rasm).
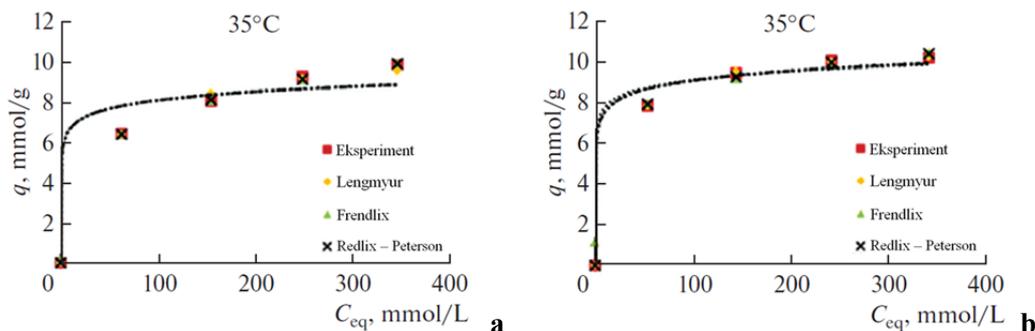


**18-rasm. LiMn$_2$O$_4$ (a) va LiMg$_{0.3}$Mn$_{1.7}$O$_4$ (b) ga asoslangan adsorbentlar namunalari bo'yicha Li$^+$ ionlarining adsorbsion izotermalari 35 °C model eritma haroratida**

18-rasmda adsorbsiya izotermalarining matematik modellashtirish natijalari Lengmyur, Frendlix va Redlix-Peterson izoterma modellariga asoslangan holda tahlil qilindi va ularning parametrlarining solishtirma ko'rinishi 6-jadvalda keltirilgan. Ushbu modellar yordamida olingan nazariy qiymatlar eksperimental natijalar bilan taqqoslandi.

**6-jadval**

**LiMn$_2$O$_4$ va LiMg$_{0.3}$Mn$_{1.7}$O$_4$ asosidagi adsorbent namunalari uchun 25, 35 va 45 °C namunaviy eritma haroratida adsorbsion izotermlarning matematik modellarining hisoblangan parametrlari.**

| Ko'rsatkich | LiMn$_2$O$_4$ | | | LiMg$_{0.3}$Mn$_{1.7}$O$_4$ | | |
|---|---|---|---|---|---|---|
| T$_{namunaviy eritma}$, °C | 25 °C | 35 °C | 45 °C | 25 °C | 35 °C | 45 °C |
| | Lengmyur izotermasi modeli | | | | | |
| q$_0^{max}$, mmol/g | 10,50 | 10,54 | 10,72 | 10,65 | 10,72 | 10,98 |
| K$_L$, L/mmol | 0,019 | 0,024 | 0,024 | 0,036 | 0,045 | 0,049 |
| $R^2$ | 1,000 | 0,978 | 0,997 | 0,992 | 0,971 | 0,999 |
| | Frendlix izoterma modeli | | | | | |
| n$_F$ | 3,600 | 3,990 | 4,140 | 5,390 | 6,890 | 6,120 |
| K$_F$, (mmol/g)/(l/mmol)$^{n_F}$ | 1,840 | 2,260 | 2,450 | 3,440 | 4,430 | 3,980 |
| $R^2$ | 0,974 | 0,998 | 0,961 | 0,992 | 0,962 | 0,995 |
| | Redlix-Peterson izoterma modeli | | | | | |
| g | 0,760 | 0,780 | 0,800 | 0,850 | 0,890 | 0,870 |
| a$_{RP}$, (mmol/l)$^{-g}$ | 0,560 | 0,570 | 0,430 | 0,420 | 0,310 | 0,380 |
| K$_{RP}$, l/mmol | 1,300 | 1,560 | 1,370 | 1,810 | 1,760 | 1,880 |
| $R^2$ | 0,976 | 0,997 | 0,962 | 0,991 | 0,975 | 0,993 |

Tahlillar shuni ko'rsatdiki, izotermalarning eksperimental ma'lumotlarga eng yaxshi mosligi Lengmyur modeli orqali aniqlangan bo'lib, ushbu model bo'yicha hisoblangan korrelatsiya koeffitsiyenti ($R^2$) boshqa modellar bilan solishtirganda eng yuqori bo'ldi.

Kinetik tahlil natijalari shuni ko'rsatadiki, adsorbsiya jarayoni dastlabki bosqichda, ya'ni vaqtning kichik qiymatlarida nisbatan sekin kechadi. Biroq, vaqt o'tishi bilan adsorbsiya jarayoni faollashadi va qisqa vaqt ichida taxminan 40–50 daqiqa davomida tizim adsorbsiya-muvozanat holatiga yetadi, bu esa $Li^+$ ionlarining adsorbsiya sirtlariga tezda taqsimlanishini anglatadi (19a, b-rasm).
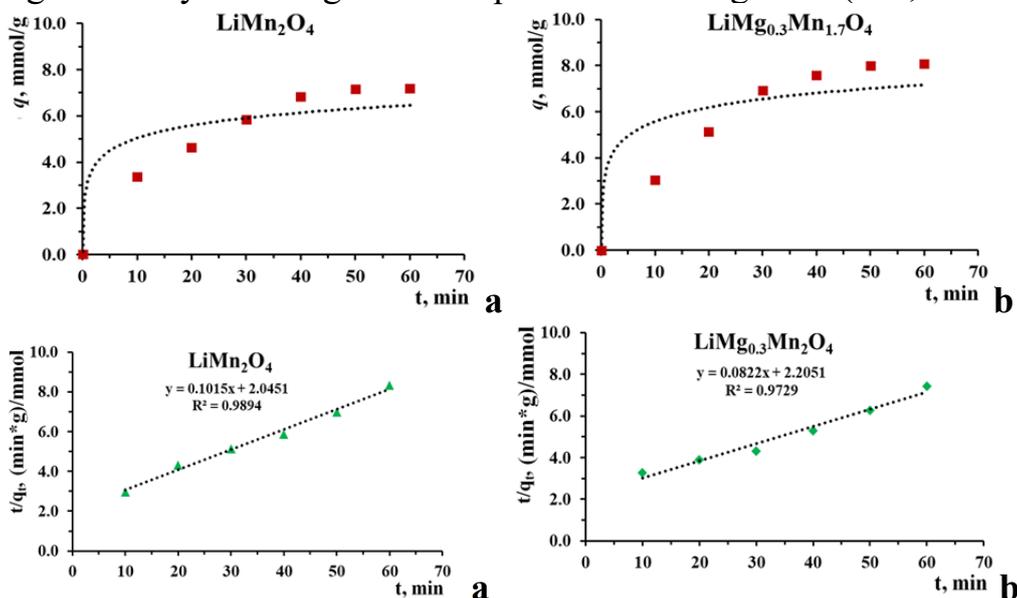


**19-rasm. LiMn$_2$O$_4$ va LiMg$_{0.3}$Mn$_{1.7}$O$_4$ asosidagi adsorbent namunalari bo'yicha (a, b) Li$^+$ ion adsorbsiyasining kinetik egri chiziqlari, shuningdek (d, e) psevdo-ikkinchi tartibli tenglamalarning yaqinlashish egri chiziqlari**

LiMn$_2$O$_4$ va LiMg$_{0.3}$Mn$_{1.7}$O$_4$ tarkibga ega adsorbent namunalari 298 dan 318 K haroratlar oraliqlarida namunaviy eritmalardan Li$^+$ ioni uchun sorbsiya jarayonlarida termodinamik ko'rsatkichlarining o'zgarishi 7-jadvalda keltirilgan.

**7-jadval**

**Adsorbsiya jarayoning termodinamik ko'rsatkichlari**

| Adsorbentlar | $\Delta H^\circ$ (J/mol) | $\Delta S^\circ$ (J/mol·K) | $\Delta G^\circ$ (J/mol) | | |
|---|---|---|---|---|---|
| | | | 298 K | 308 K | 318 K |
| LiMn$_2$O$_4$ | 17800 | 84,20 | -7294,3 | -8134,4 | -8401,2 |
| LiMg$_{0.3}$Mn$_{1.7}$O$_4$ | 17030 | 86,90 | -8881,2 | -9764,3 | -10277,8 |

Keltirilgan 7-jadval ma'lumotlaridan ko'rinib turibdiki Lengmyur muvozanat konstantasi asosida hisoblab topilgan $q_0^{max}$ qiymati 298, 308 va 318 K haroratlarda oshib borgan.

**8-jadval**

**LiMn$_2$O$_4$ va LiMg$_{0.3}$Mn$_{1.7}$O$_4$ asosidagi adsorbent namunalari bo'yicha Li$^+$ ionlari adsorbsiyasi uchun psevdo-birinchi va psevdo-ikkinchi tartibli kinetik modellarning hisoblangan parametrlari.**

| Ko'rsatkich | LiMn$_2$O$_4$ | LiMg$_{0.3}$Mn$_{1.7}$O$_4$ |
|---|---|---|
| | Psevdo-birinchi tartibli kinetik model | |
| K$_1$, min$^{-1}$ | 0,099 | 0,089 |
| q$_{eq}$, mmol/g | 12,200 | 12,200 |
| R$^2$ | 0,880 | 0,989 |
| | Psevdo-ikkinchi tartibli kinetik model | |
| K$_2$, g/(mmol*min) | 0,005 | 0,003 |
| q$_{eq}$, mmol/g | 9,900 | 12,200 |
| h, mmol/(min*g) | 0,500 | 0,500 |
| R$^2$ | 0,941 | 0,973 |

LiMn$_2$O$_4$ shpineli uchun adsorbsiya tezligi koeffitsienti 0,005 g/(mmol·min) ga teng bo'lib, LiMg$_{0.3}$Mn$_{1.7}$O$_4$ shpinel materiali uchun esa bu qiymat biroz pastroq 0,003 g/(mmol·min) bo'lgan (4.4-jadval). LiMn$_2$O$_4$ va LiMg$_{0.3}$Mn$_{1.7}$O$_4$ shpinel namunalarining adsorbsiya kinetikasidagi farqlar ularning tarkibiy tuzilmasi, ion radiuslar va elektron zichliklarining farqlanishi bilan bog'liq bo'lishi mumkin. Tajriba natijalari asosida olingan kinetik ma'lumotlar matematik modellashtirish orqali chuqur tahlil qilindi. Natijalar Li$^+$ ionlarining adsorbsiyasi uchun psevdo-ikkinchi tartibli kinetik model eng maqbul ekanini ko'rsatdi.

## XULOSALAR

1. Zol-gel, qattiq faza va gidrotermik usullaridan foydalangan holda Li-Mn shpinellari asosidagi nanotuzulishli sorbsion materiallar sintez qilishning asosiy parametrlari aniqlanib, Mg$^{2+}$ va Al$^{3+}$ ionlari modifikatsiyasi orqali LiMg$_x$Mn$_{(2-x)}$O$_4$ hamda LiAl$_x$Mn$_{(2-x)}$O$_4$ tarkibli shpinellar sintez qilindi. Shpinel fazasining shakllanishida, qayta ishlov berish harorati uchun 600-800 °C oralig'i maqbul ekanligi aniqlandi.

2. Sintez qilingan Li-Mn asosidagi shpinellar barqaror kubik shpinel strukturasi shaklida hosil bo'lishi bilan birga, modifikatsiyalangan Mg$^{2+}$ va Al$^{3+}$ ionlari miqdori kristall panjaraning *a* parametri, elementar yacheyka hajmi va o'rtacha kristallit o'lchamiga ta'sir ko'rsatishi hamda zarrachalar morfologiyasiga sezilarli ta'sir ko'rsatmasligi, biroq zarracha o'rtacha o'lchamining 0,45 dan 2,34 mkm gacha o'sishi aniqlandi.

3. Sintez qilingan Li-Mn asosidagi shpinellar H3 tipidagi gisterez halqasiga ega bo'lib, g'ovak shaklining yoriqsimon ekanligi aniqlandi. LiMn$_2$O$_4$ va LiMg$_{0.3}$Mn$_{1.7}$O$_4$ shpinel zarracha g'ovaklarining monomodal taqsimotiga va maksimum g'ovak diametri D ≤ 3 nm intervalida joylashgan.

4. Mg$^{2+}$ va Al$^{3+}$ ionlari bilan modifikatsiyalangan Li-Mn shpinellari asosida adsorbentlar hosil bo'lishida 43 % dan 79 % gacha konversiya darajasini ko'rsatdi. Optimal adsorbsion xususiyatlar adsorbent miqdori 0,2 g/L va pH 10,0-13,0 oralig'ida kuzatildi. Adsorbsiya tezligi vaqt o'tishi bilan asta-sekin ortib borib va taxminan 24 soatda muvozanatga erishishi aniqlandi. Tadqiqot natijalari asosida patentga talabnoma berilgan.

5. Adsorbsiya izotermalarining matematik tahlili amalga oshirildi va Lengmyur muvozanat konstantasi asosida hisoblab topilgan q$_0^{max}$ qiymati 298, 308 va 318 K haroratlarda oshib, eng yuqori qiymat LiMg$_{0.3}$Mn$_{1.7}$O$_4$ shpinel asosidagi adsorbent uchun 10,98 mmol/g ekanligi aniqlandi. ΔH$^°$ musbat qiymatga ega bo'lib, adsorbsiya jarayonining endotermik ekanligini tasdiqladi. Psevdo-ikkinchi tartibli kinetik tenglama konstantalari qiymatlari LiMn$_2$O$_4$ va LiMg$_{0.3}$Mn$_{1.7}$O$_4$ shpinellari uchun mos ravishda 0,005 va 0,003 g/(mmol·min) ga teng ekanligi aniqlandi.

6. LiMn$_2$O$_4$, LiMg$_x$Mn$_{(2-x)}$O$_4$ va LiAl$_x$Mn$_{(2-x)}$O$_4$ shpinellari "Navoiy kon-metallurgiya kombinati" AJ hamda "MOXSAR" MCHJ QK da sinovdan o'tkazildi va Li$^+$ ioni uchun adsorbent sifatida qo'llashga tavsiya berildi.

# SCIENTIFIC COUNCIL DSc.03/31.01.2023.K/T.78.01 FOR THE AWARD OF ACADEMIC DEGREES AT TERMEZ STATE UNIVERSITY

## SAMARKAND STATE UNIVERSITY NAMED AFTER SHAROF RASHIDOV

## BEGIMKULOVA SHAHNOZA AKBARJON QIZI

## SOL-GEL SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES OF NANOSTRUCTURED SORPTION MATERIALS BASED ON Li-Mn SPINELS

**02.00.01 – Inorganic chemistry**
**02.00.04 – Physical chemistry**

## DISSERTATION ABSTRACT FOR THE DOCTOR OF PHILOSOPHY (PhD) ON CHEMISTRY SCIENCES

**Termez – 2025**

The theme of the Doctor of Philosophy (PhD) dissertation in chemical sciences is registered in the Higher Attestation Commission under the Ministry of Higher Education, Science and Innovation of the Republic of Uzbekistan under the number B2024.2.PhD/K770.

The dissertation has been prepared at the Samarkand State University named after Sharof Rashidov.

The abstract of dissertation in three languages (Uzbek, English, Russian (resume)) is available online www.tersu.uz and on the website of "ZiyoNet" information-educational portal www.ziyonet.uz.

| | |
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| | **Bekchanov Davronbek**<br>Doctor of Chemical Sciences, Professor |
| **Leading organization:** | **Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan** |

The defense will take place on "11" X 2025 at "14⁰⁰" at the meeting of the Scientific Council for the Awarding of Sciences Degrees DSc.03/31.01.2023.K/T.78.01 at Termez State University at the address: 190111, Termez, district, pos. Barkamol Avlod, 43 tel: (+99876) 221-74-55; (+99876) 221-71-17, e-mail: termizdu@umail.uz

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# INTRODUCTION (abstract of PhD dissertation)

**The relevance and importance of the dissertation title.** Today, as a result of the widespread use of high-energy devices and lithium-ion batteries in the world, the global demand for lithium in industry has increased sharply. This, combined with the limited and decreasing lithium resources in the Earth's crust, estimated at around 16.7 million tons, further increases the need to extract lithium from alternative sources. Due to the environmental and economic complexity of the lithium extraction process from traditional mines, current scientific research is aimed at developing methods for the effective extraction of lithium from saline lake waters and seawater. In particular, the use of Li-Mn based sorption materials is considered one of the most promising technological solutions among such processes. This type of material has high selectivity and adsorption capacity, and is capable of selectively sorbing $Li^+$ ions over ions such as $Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$. Therefore, they are of high scientific importance for science and industry in recovering lithium not only from natural brines, but also from aqueous solutions generated during the processing of lithium-ion batteries.

Due to the background of limited natural reserves of lithium in the world, modern scientific research is being conducted on a large scale aimed at its selective extraction from saline natural and technological aqueous environments. In this regard, obtaining nanostructured sorption materials with high dispersion, structural stability and ion-selective properties, synthesis of nanomaterials with high sorption activity based on Li-Mn spinels modified with metal ions by the sol-gel method, in-depth analysis of their physicochemical, structural-state properties, as well as research into the ion exchange kinetics of these materials, increasing selectivity, application in the extraction of lithium from secondary and natural sources in terms of regeneration efficiency, and development of sorption materials with high adsorption properties are of great practical importance.

Research conducted in our republic shows the possibility of obtaining nanostructured sorption materials with special physicochemical properties. The study of relationships such as "structure-adsorption, properties-stability" in multiphase nanoscale systems of metal oxide-based adsorbents is the most important task of chemical technology and nanotechnology, opening up new prospects for their practical application. The Decree of the President of the Republic of Uzbekistan No. PF-60 dated January 28, 2022 "On the Development Strategy of New Uzbekistan for 2022-2026"[1] sets out important tasks aimed at "further development of the export potential of local industries, fully utilizing existing opportunities". In the development of the chemical industry, one of the main sectors of our economy, scientific and practical research aimed at synthesizing Li-Mn-based nanostructured sorption materials for lithium ions using modern methods and their effective use in adsorption processes, as well as obtaining new types of adsorbents to solve various problems related to alternative

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[1] Decree of the President of the Republic of Uzbekistan No. PF-60 dated January 28, 2022 :On the Development Strategy of New Uzbekistan for 2022-2026".

energy and production, is of great importance.

The results of this dissertation research will serve to a certain extent in the implementation of the tasks set out in the Decree of the President of the Republic of Uzbekistan No. PF-60 dated January 28, 2022 "On the Development Strategy of New Uzbekistan for 2022-2026", No. PQ-3983 dated October 25, 2018 "On measures for the accelerated development of the chemical industry in the Republic of Uzbekistan", No. PQ-4265 dated April 3, 2019 "On measures to further reform the chemical industry and increase its investment attractiveness", No. PQ-4992 dated February 13, 2021 "On measures to further reform and financial soundness of chemical industry enterprises, and develop the production of high-value-added chemical products", and other regulatory legal acts related to this activity.

**The conformity of research with priority directions of development of science and technologies of the Republic.** This work is related to the development of science and technology of the Republic, specifically under the VII plan. It is being carried out in accordance with the priorities of "Chemical Technology and Nanotechnology".

**The degree of study of the problem.** Leading scientists around the world have conducted research on the synthesis of nanostructured sorption materials based on Li-Mn spinels modified with various metal ions. In particular, Liyan Tian, Wei Ma, and Mei Han prepared nanostructured lithium-ion sieves by separating lithium and magnesium from spinel-structured lithium manganese oxides doped with magnesium ions. This research was the basis for initial studies aimed at better understanding the adsorption-desorption processes of $Li^+$. Also, in the scientific research on Li-Mn spinels, foreign scientists such as Ming-si Shen, Hai-bo Yuan, and Ya-Xin Su synthesized calcium-doped lithium manganese oxides $Li_{0.98}Ca_{0.02}Mn_2O_4$ by hydrothermal method, and studied their morphology and physicochemical properties. A.I.Ivanes and his team synthesized $Li_{1.33}Mn_{1.67}O_4$ spinel-structured oxides modified with $Al^{3+}$ ions and, as a result, using the low-temperature nitrogen adsorption-desorption method, determined the modification of spinel with ions.

Scientific research in the field of synthesis of sorption materials and adsorbents is also developing rapidly in our republic. In particular, our scientists M.G.Mukhamadiev, Kh.Kh.Turaev, D.A.Gafurova, D.J.Bekchanov, Kh.T.Trobov, O.N.Ruzimuradov, Sh.I.Mamatkulov and others studied in detail the synthesis of sorption materials, their physical, chemical and adsorption properties, as well as their areas of application in practice.

Great deal of data on the physicochemical properties of spinel-structured Li-Mn-based nanostructured materials synthesized by the sol-gel method is presented in the scientific literature, but the adsorption properties of these nanostructured oxides for $Li^+$ ions and the factors affecting them, solving the problem of insufficient stability of the Li-Mn spinel structure, and the processes of synthesizing nanostructured adsorbents by partially replacing $Mn^{3+}$ ions with $Mg^{2+}$ and $Al^{3+}$ cations, respectively, have not been fully studied. Therefore, this dissertation work is aimed at a systematic study of the above processes, as well as

obtaining Li-Mn based nanostructured spinels modified with $Mg^{2+}$ and $Al^{3+}$ ions and studying their physicochemical properties.

**The connection of investigation with plans of science-investigated works of the science-investigate institution where dissertation was carried out.** This dissertation research was carried out within the framework of the international scientific framework "Uzbekistan-Belarus" on the topic "Highly selective adsorbents for lithium ions based on modified Li-Mn spinels: sol-gel synthesis, adsorption properties and stability" (2021-2023) in accordance with the scientific direction of the Department of Inorganic Chemistry and Materials Science of the Sharof Rashidov Samarkand State University and the research plan of the Turin Polytechnic University No. MRB-2021-531.

**The purpose of the study** the aim of the study is to synthesize nanostructured sorption materials based on Li-Mn spinels modified with $Mg^{2+}$ and $Al^{3+}$ ions using the sol-gel method and to determine their physicochemical and adsorption properties to $Li^{+}$ ion.

**The tasks of the research work are:**

synthesis of nanostructured sorption materials based on Li-Mn spinel using various chemical methods;

determination of optimal conditions for the synthesis of spinel-structured Li-Me-Mn based adsorbents for $Li^{+}$ ions by modifying $Mg^{2+}$ and $Al^{3+}$ ions;

analysis of the structure and properties of synthesized Li-Mn and Li-Me-Mn spinels using modern physicochemical methods;

study of the textural properties of synthesized Li-Mn and Li-Me-Mn spinels;

determination of the adsorbent activity of synthesized spinel-structured Li-Mn based nanostructured sorption materials for $Li^{+}$ ions in the adsorption-desorption processes.

**The objects of the research work** are lithium, manganese, magnesium, and aluminum salts and some of their oxides, citric acid, hydrochloric acid, and brines.

**The subject of investigation** is the composition, structure, physicochemical, and sorption properties of nanostructured sorption materials synthesized based on Li-Mn spinels modified with $Mg^{2+}$ and $Al^{3+}$ ions.

**The methods of research.** In the course of the research, modern physical and chemical methods such as scanning electron microscopy (SEM), UV-vis spectroscopy, powder X-ray diffraction (XRD), IR spectroscopy, Raman spectroscopy, X-ray fluorescence spectroscopy (XRF), thermal analysis (TG and DTA), BET and BJH methods were used to determine the composition and structure of the sorption materials obtained. In addition, in the study of adsorption processes, analysis of isotherms using Langmuir, Freundlich and Redlich-Peterson models, and description of adsorption kinetics, pseudo-first and pseudo-second order kinetic models were used.

**The scientific novelty of the study consists of:**

for the first time, nanostructured sorption materials with high sorption capacity were synthesized using the sol-gel method based on Li-Mn spinels modified with $Mg^{2+}$ and $Al^{3+}$ ions;

the physicochemical properties of the synthesized sorption materials based on $LiMn_2O_4$, $LiMg_xMn_{(2-x)}O_4$ and $LiAl_xMn_{(2-x)}O_4$ spinels were analyzed, and it was found that the $LiMg_{0.3}Mn_{1.7}O_4$ spinel sample had the highest sorption capacity for $Li^+$ ions;

the adsorption isotherms for $Li^+$ ion on $LiMn_2O_4$ and $LiMg_{0.3}Mn_{1.7}O_4$ adsorbent samples were studied, and it was found that the course of the isotherms corresponds to the Langmuir model for the obtained results;

it has been proven that the adsorption kinetics of $Li^+$ ion on $LiMn_2O_4$ and $LiMg_{0.3}Mn_{1.7}O_4$ adsorbent samples conform to a pseudo-second order kinetic model.

**The practical results of the study include:**

optimal conditions for the synthesis of nanostructured adsorbents based on Li-Mn with spinel structure modified with $Mg^{2+}$ and $Al^{3+}$ ions were determined;

the degree of conversion to the H-form in the formation of adsorbents based on $LiMg_xMn_{(2-x)}O_4$ and $LiAl_xMn_{(2-x)}O_4$ spinels was in the range of 43-79 %, and the highest conversion level was determined for the sample with x=0.3 for Mg;

the maximum sorption capacity for the adsorbent based on $LiMg_{0.3}Mn_{1.7}O_4$ spinel was found to be 10.98 mmol/g in a $Li^+$ ion solution at 45 °C;

it has been shown that nanostructured adsorbents based on the obtained Li-Mn spinels have high efficiency in removing $Li^+$ ions from wastewater from hydrometallurgical enterprises.

**The reliability of obtained results.** The results obtained in the scientific research work were analyzed using modern physicochemical methods such as scanning electron microscopy (SEM), infrared spectroscopy (IR), UV-vis spectroscopy (UV-vis), Raman spectroscopy, thermogravimetric analysis (TGA), X-ray phase analysis (XRD), X-ray fluorescence spectrometry (XRF), BET and BJH analysis. The kinetics of ion equilibrium and adsorption processes were described based on pseudo-first and pseudo-second order kinetic models. Adsorption isotherms were calculated according to the Langmuir, Freundlich, and Redlich-Petersen models. Adsorption thermodynamics was analyzed based on experimental results using modern theories and relevant equations, processed using mathematical and statistical methods, and reasonable conclusions were drawn.

**The scientific and practical value of the results of the research.**

The scientific significance of the research results is explained by the development of the basis for obtaining nanostructured sorption materials based on spinel-structured Li-Mn using the sol-gel method, the mechanisms of spinel formation, and the study of nanostructured systems based on Li-Mn modified with $Mg^{2+}$ and $Al^{3+}$, as well as adsorbents for $Li^+$ ions based on them.

The practical significance of the research results is the synthesis of nanostructured sorption materials with improved textural properties based on Li-Mn spinels modified with $Mg^{2+}$ and $Al^{3+}$, and the determination of the adsorption activity of these nanostructured sorption materials in the collection of $Li^+$ ions from water basins rich in lithium salts in our Republic.

**Implementation of the research results.** Based on the scientific results obtained on the development of a technology for obtaining nanostructured sorption materials based on Li-Mn spinel modified with $Mg^{2+}$ and $Al^{3+}$ for $Li^+$ ion sorption:

adsorbents based on spinel structures synthesized by $LiMn_2O_4$, $Li_{1.33}Mn_{1.67}O_4$, $LiMg_xMn_{(2-x)}O_4$ and $LiAl_xMn_{(2-x)}O_4$ were put into practice at the Navoi Mining and Metallurgical Combine Joint Stock Company for the removal of Li+ ions from wastewater (Reference No. 23/01-01-07/687 of the Navoi Mining and Metallurgical Combine JSC dated November 6, 2024). As a result, it was possible to adsorb and extract up to 98% of $Li^+$ ions from the wastewater of hydrometallurgical enterprises.

Adsorbents with $LiMg_{0.3}Mn_{1.7}O_4$ and $LiAl_{0.3}Mn_{1.7}O_4$ compositions were used for the sorption separation of $Li^+$ ions from wastewater of the joint venture "MOXSAR" LLC (Reference No. 17/04-2 of JV "MOXSAR" LLC dated April 17, 2025). As a result, the sorption separation of $Li^+$ ions from wastewater allowed the use of spinels with $LiAl_{0.3}Mn_{1.7}O_4$ (60-62 mg/g) and $LiMg_{0.3}Mn_{1.7}O_4$ (70-74 mg/g) compositions synthesized on the basis of local raw materials with high sorption capacity as import-substituting sorbents.

**Approbation of the research results.** The results of this research were presented and discussed at 15 scientific and practical conferences, including 9 international and 6 national.

**The publication of results of investigation.** A total of 20 scientific works have been published on the topic of the dissertation, of which 5 articles have been published in scientific publications recommended for publication of the main scientific results of Doctor of Philosophy (PhD) dissertations by the Higher Attestation Commission of the Republic of Uzbekistan, including 3 articles in Republican and 2 articles in International journals and 9 in international scientific conferences, and 6 theses have been published in Republican scientific and practical conferences.

**The structure and volume of dissertation.** The dissertation consists of an introduction, 4 chapters, a conclusion, A list of used literature and an appendix. The volume of the dissertation is 119 pages.

## MAIN CONTENT OF DISSERTATION

**In the introduction** The part justifies the relevance and importance of the research conducted, sets out the goals and objectives, highlights the object and subject of the study, indicates the correspondence of the research to the priority areas of science and technology on a republican scale, describes the scientific novelty, scientific and practical significance of the research results, reveals the reliability, scientific and practical significance of the results achieved, and reveals the possibilities of their application in practice, and provides information on scientific works published within the scope of the dissertation topic and the composition of the dissertation.

The first chapter of the dissertation, entitled **"Scientific foundations and promising approaches to the formation of nanostructured sorption materials based on Li-Mn spinel",** justifies the goals and objectives of the research work based on a detailed analysis of literature data on nanostructured sorption materials

based on Li-Mn with a spinel structure and the main methods for their preparation, application prospects, the current state of preparation of sorption materials modified with metal ions for $Li^+$ ions, and development trends.

The second chapter of the dissertation, entitled **"Sol-gel synthesis of nanostructured sorption materials based on Li-Mn spinel",** describes the physicochemical methods used in the research and the models used for isotherms, the approach to choosing the synthesis methods of materials, the development of methods for obtaining nanostructured sorption materials based on spinel Li-Mn using the sol-gel method and modifying them with $Mg^{2+}$, $Al^{3+}$ ions in different ratios, obtaining materials by changing the concentration of metal ions and temperature, studying the structure of the obtained materials and their sorption properties for $Li^+$ ions.

Sorption materials based on $LiMn_2O_4$ with a spinel structure were synthesized using solid phase, hydrothermal and sol-gel methods. Modification of $Mg^{2+}$ and $Al^{3+}$ ions to Li-Mn based spinels was carried out using the sol-gel method. The properties of the synthesized materials were studied using physicochemical research methods. Figure 1 shows a scheme for the synthesis of $LiMn_2O_4$ spinel by the sol-gel method.
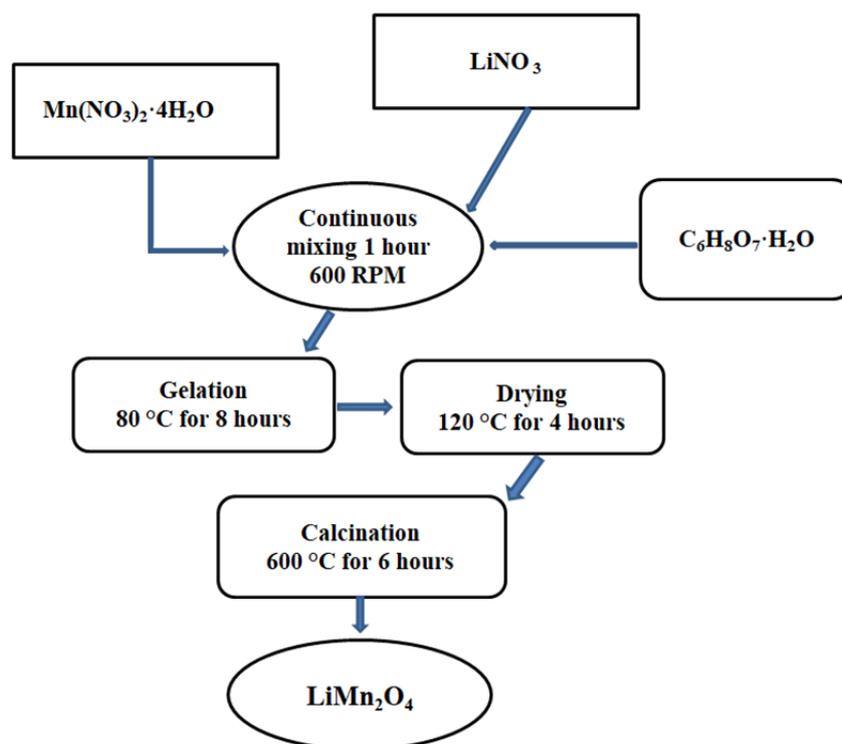


**Figure 1. Synthesis scheme of $LiMn_2O_4$ spinel by sol-gel method**

According to the scheme presented in Figure 1, the processing temperatures for the formation of $LiMn_2O_4$ spinel were 400 °C, 600 °C, and 800 °C.

To synthesize $LiMg_xMn_{(2-x)}O_4$ ($0 \leq x < 0.7$) spinel samples, aqueous solutions of lithium nitrate ($LiNO_3$), manganese (II) nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$) and magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$), and citric acid ($C_6H_8O_7 \cdot H_2O$) were mixed in a certain mass ratio (Table 1).

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**Table 1**
**Masses of initial precursors in the formation of $LiMg_xMn_{(2-x)}O_4$ spinel samples (g)**

| Sample | $LiNO_3$ | $Mn(NO_3)_2 \cdot 4H_2O$ | $Mg(NO_3)_2 \cdot 6H_2O$ | $C_6H_8O_7 \cdot H_2O$ |
|---|---|---|---|---|
| $LiMg_{0.1}Mn_{1.9}O_4$ | 0.552 | 3.8152 | 0.2048 | 5.04 |
| $LiMg_{0.3}Mn_{1.7}O_4$ | 0.552 | 3.4136 | 0.6144 | 5.04 |
| $LiMg_{0.5}Mn_{1.5}O_4$ | 0.552 | 3.0120 | 1.0240 | 5.04 |
| $LiMg_{0.7}Mn_{1.3}O_4$ | 0.552 | 2.6104 | 1.4336 | 5.04 |

According to the data in this table, it can be seen that the molar ratio of $(C_6H_8O_7 \cdot H_2O) : (Li^+ + Mg^{2+} + Mn^{2+}$ salts) was chosen to be 1 : 1 in the formation of $LiMg_xMn_{(2-x)}O_4$ spinels.

The third chapter, entitled **"Preparation and physicochemical properties of nanostructured sorption materials based on Li-Mn spinel",** presents the results of studying the formation, structure, physicochemical and textural properties of synthesized nanostructured sorption materials based on Li-Mn spinel.

In the formation of $LiMn_2O_4$ spinel by the sol-gel method, the precursors are first hydrolyzed in solution to form the corresponding metal and hydroxyl ions.
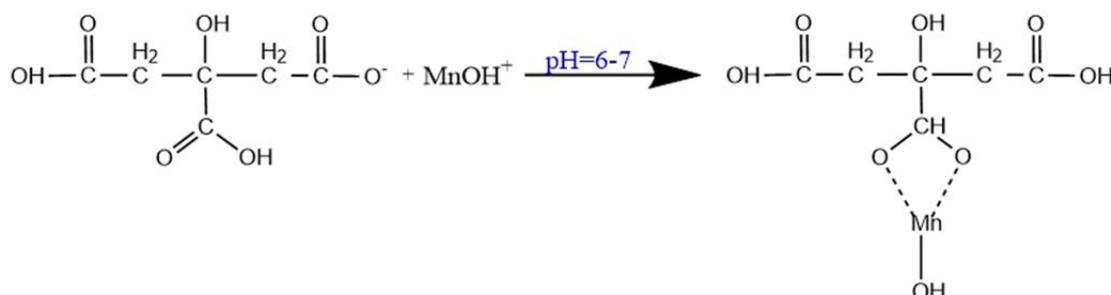


**Reaction 1. The reaction of formation of chelate complexes in the presence of $MnOH^+$ and citric acid**

For example, $Mn^{2+}$ ions are hydrolyzed to form $MnOH^+$, which forms chelate complexes with citric acid at pH=6-7 (Reaction 1). At 80 °C, the gelation process occurs and the $Li^+$ ions adsorbed by the gel combine with the Mn(II) complex, and the gel decomposes at high temperature. As a result, $LiMn_2O_4$ nanoparticles with a spinel structure are formed.
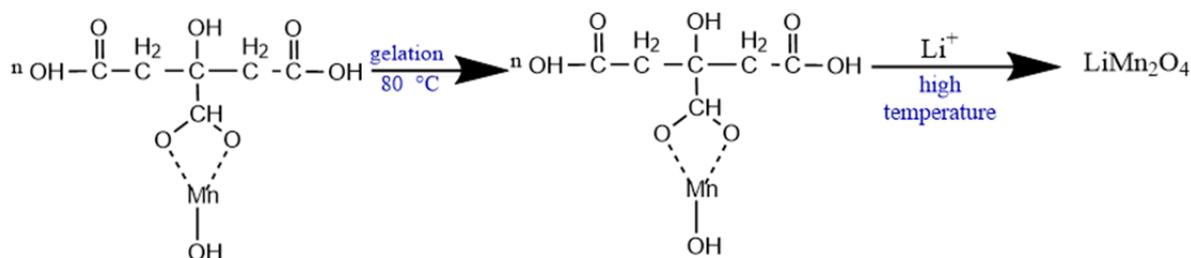


**Reaction 2. Formation reaction of spinel-structured $LiMn_2O_4$ nanoparticles**

SEM images of $LiMn_2O_4$, $LiMg_{0.3}Mn_{1.7}O_4$ and $LiAl_{0.3}Mn_{1.7}O_4$ spinel samples synthesized by the sol-gel method are shown in Figure 2. As can be seen from the SEM images, the particles have an octahedral structure. This morphological feature is related to the formation of the spinel phase and its crystal structure, confirming that the particles formed by the sol-gel method have a relatively uniform shape.
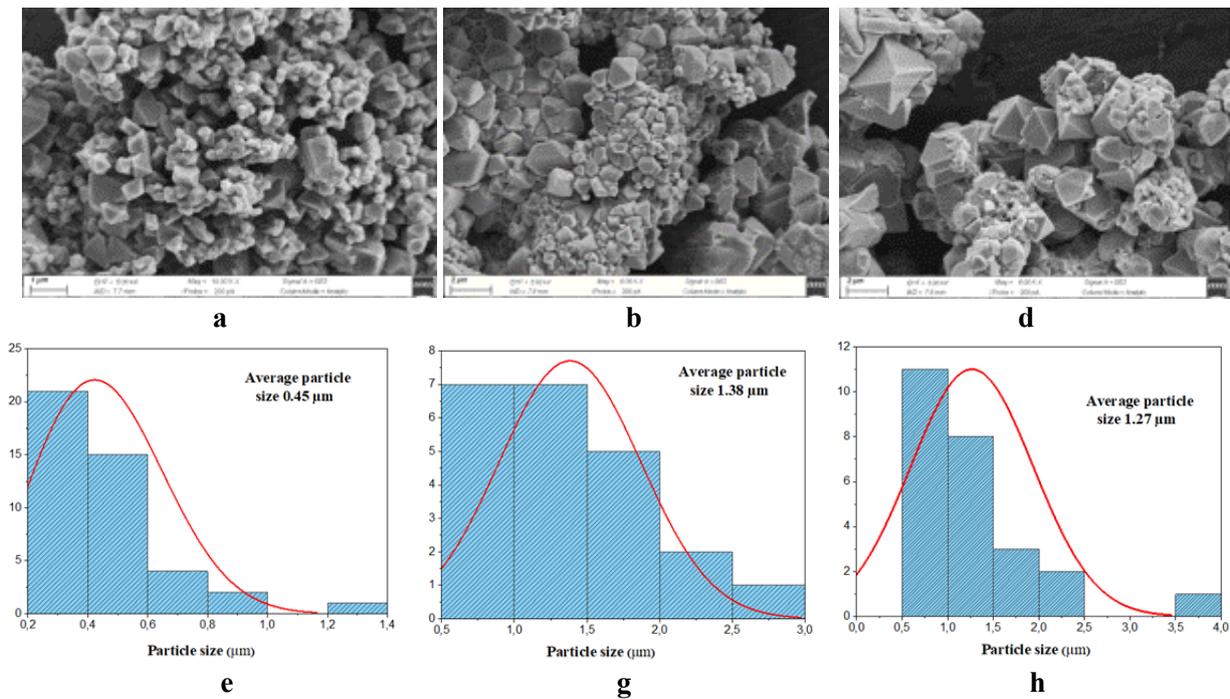
**Figure 2. SEM images of the surface LiMn$_2$O$_4$ (a), LiMg$_{0.3}$Mn$_{1.7}$O$_4$ (b), LiAl$_{0.3}$Mn$_{1.7}$O$_4$ (d) and particle size distribution (e, g, h, respectively) of spinel samples obtained by the sol-gel method.**

Analysis of the particle size distribution using ImageJ software revealed that the LiMn$_2$O$_4$ spinel particles ranged in size from 0.2 μm to 1.4 μm (Fig. 2e). Based on the graphical data in Figs. 2e, g, h, the average particle size was found to be approximately 0.45 μm for LiMn$_2$O$_4$, and 1.38 and 1.27 μm for LiMg$_{0.3}$Mn$_{1.7}$O$_4$ and LiAl$_{0.3}$Mn$_{1.7}$O$_4$ spinels, respectively.
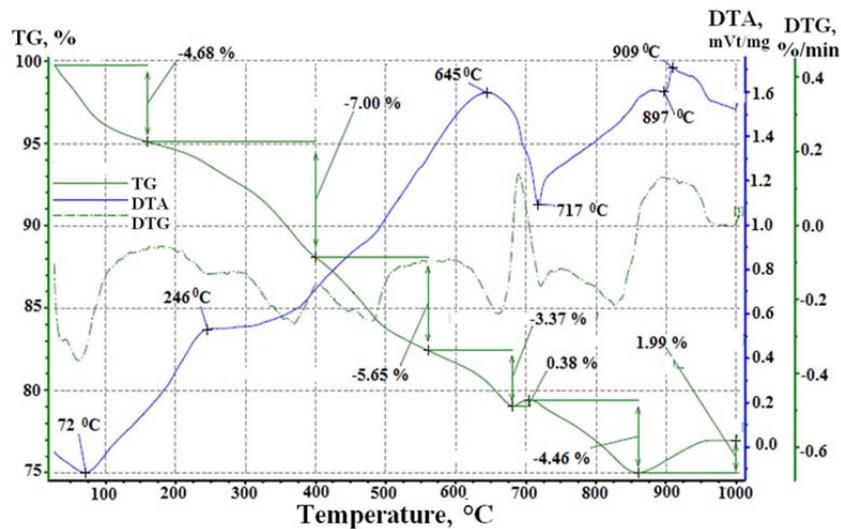


**Figure 3. DTA-TG curves of LiMn$_2$O$_4$ spinel samples obtained by the sol-gel method**

Analysis of the DTA-TG curves of Li-Mn spinel samples synthesized by solid-phase, sol-gel, and hydrothermal methods in the range of 20-300 °C shows the presence of an endothermic peak in the range of 72-85 °C, resulting in mass losses of 22.74, 4.68, and 15.88% in the samples, respectively, which is explained

by the release of physically and chemically bound water. The formation of $LiMn_2O_4$ spinel synthesized by solid-phase and sol-gel methods occurs at 700-720 °C with an endothermic peak and a mass loss of approximately 8.29 and 4.46%, respectively. In the hydrothermal method, this process occurs at 850 °C, which is confirmed by the endothermic effect and is determined by a mass loss of 2.85%.
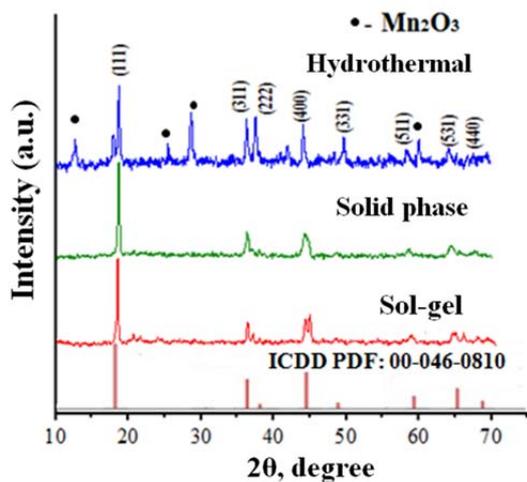


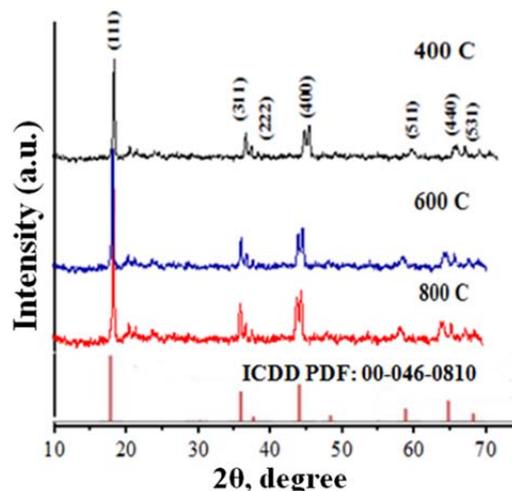**Figure 4. X-ray diffraction patterns of Li-Mn-based spinel samples synthesized by various methods**

**Figure 5. X-ray diffraction patterns of $LiMn_2O_4$ spinel samples synthesized by the sol-gel method calcined at 400, 600 and 800 ° C**

The X-ray diffraction patterns presented in Figures 4 and 5 show that all samples are single-phase Li-Mn spinel with the $LiMn_2O_4$ structure. This is confirmed by the narrow and intense diffraction peaks at 2θ angles and the corresponding Miller indices 18.9 (111), 36.7 (311), 44.5 (400), 58.8 (511) and 64.7 (404). The X-ray diffraction pattern of the Li-Mn spinel sample obtained by the hydrothermal synthesis method contains an additional $Mn_2O_3$ phase, which is explained by the incomplete reaction of the precursor. The calculated value of the α parameter of the $LiMn_2O_4$ spinel crystal lattice obtained by the solid-phase synthesis method is 8.197 Å.

**Table 2**

**Crystal lattice parameters of $LiMn_2O_4$ spinel samples synthesized by various methods and annealed at 600 °C**

| Synthesis method | $D$, nm | $d$, Å | $a$, Å | $V$, Å$^3$ |
|---|---|---|---|---|
| Solid phase | 22.4 | 2.46 | 8.197* | 550.7 |
| Sol-gel | 17.3 | 2.43 | 8.120** | 535.3 |
| Hydrothermal | 27.0 | 3.07 | 8.167** | 544.7 |

\*- Parameter $a$ for $LiMn_2O_4$ 8.190 Å(COD_96-402-9204);

\*\* - Parameter $a$ for $LiMn_2O_4$ 8.145 Å (COD_96-151-4050).

A slight difference in the α parameter was observed compared to the corresponding data values for the samples obtained by the sol-gel and hydrothermal methods, with values of 8.120 Å and 8.167 Å, respectively (Table 2). Analysis of the crystal sizes presented in Table 2 shows that the smallest value

(17.3 nm) is characteristic of the single-phase spinel particle obtained by the sol-gel method.

As the annealing temperature increased from 400 °C to 800 °C, a natural increase in the crystal size of the obtained $LiMn_2O_4$ spinel samples from 12.1 to 19.9 nm was observed (Table 3).

**Table 3**

**Crystal lattice parameters of $LiMn_2O_4$ spinel samples obtained by the sol-gel method and heat-treated at different temperatures**

| Processing temperature, °C | $D$, nm | $d$, Å | $a$, Å | $V$, Å$^3$ |
|---|---|---|---|---|
| 400 | 12.1 | 2.45 | 8.157* | 542.7 |
| 600 | 17.3 | 2.43 | 8.120* | 535.3 |
| 800 | 19.9 | 2.45 | 8.171** | 545.6 |

\*- Parameter $a$ for $LiMn_2O_4$ 8.145 Å(COD_96-151-4050);
\*\* - Parameter $a$ for $LiMn_2O_4$ 8.177 Å (COD_96-151-4054).

From the table above, it can be seen that the values of α for the Li-Mn spinel samples heat-treated at 400 and 600 °C are 8.157 Å and 8.120 Å, which are slightly different from the corresponding data. The calculated value of α (8.171 Å) for the sample heat-treated at 800 °C is in good agreement with the corresponding data.

When analyzing the IR spectra of the $LiMn_2O_4$ spinel samples presented in Figure 6, peaks corresponding to the Mn-O bond were detected in the 530-700 cm$^{-1}$ region.
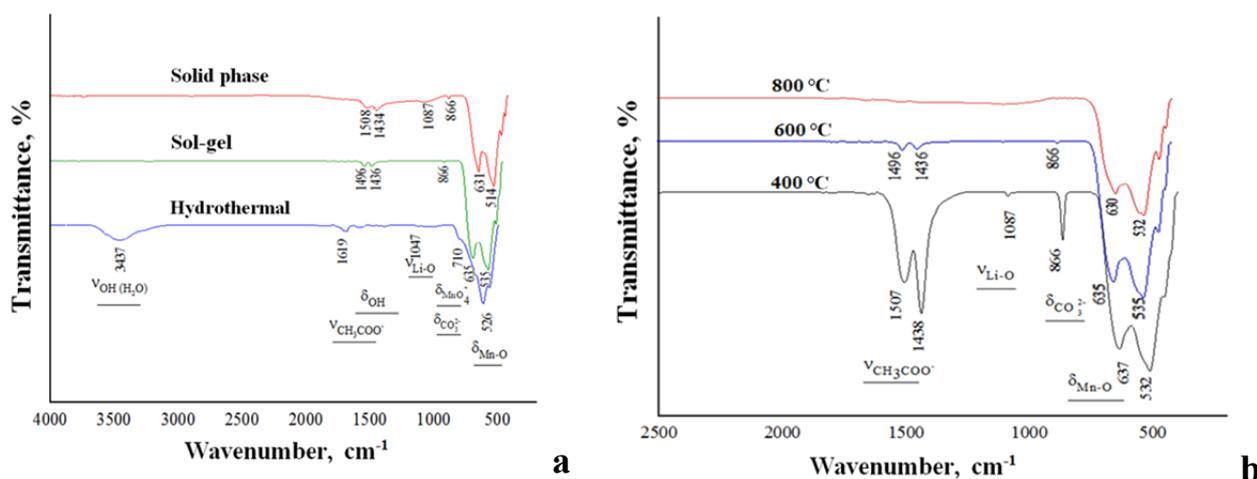


**Figure 6. IR spectra of $LiMn_2O_4$ spinel samples obtained by different methods at 600 °C (a) and calcination at different temperatures (b)**

This indicates the presence of Mn-O bonds in the spinel structure and their ordered state. Also, the broad band observed at 1085 cm$^{-1}$ is attributed to Li-O vibrations, which confirms the location of lithium ions in the spinel structure.

The phase structure of the $LiMg_xMn_{(2-x)}O_4$ samples was found to be consistent with the spinel structure of $LiMn_2O_4$ (PDF2 #35-0782). The observed peaks correspond to the (111), (311), (222), (400), (511) and (440) texels (hkl).

These peaks are characteristic of the spinel phase, confirming the presence of a cubic crystal lattice. It can be seen from the X-ray diffraction patterns in Figure 7 that the main peaks are preserved in all spinel samples, but additional peaks appear in some samples (for example, in the range of $2\theta = 28\text{-}32$ °). This indicates that a slight lattice distortion occurs when $Mg^{2+}$ ions are introduced. In the $LiMg_xMn_{(2-x)}O_4$ (x=0.3, 0.5 and 0.7) samples, the peaks are slightly shifted and the intensity changes. The shift of the peaks to the left with increasing $Mg^{2+}$ content can be explained by the fact that the $Mg^{2+}$ ion has a slightly larger ionic radius compared to the $Mn^{3+}/Mn^{4+}$ ions.



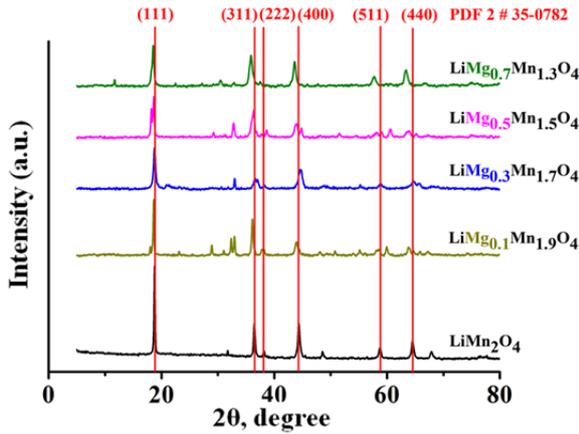**Figure 7. X-ray diffraction patterns of spinel samples of $LiMn_2O_4$ and $LiMg_xMn_{(2-x)}O_4$ ($0 \leq x \leq 0.7$)**

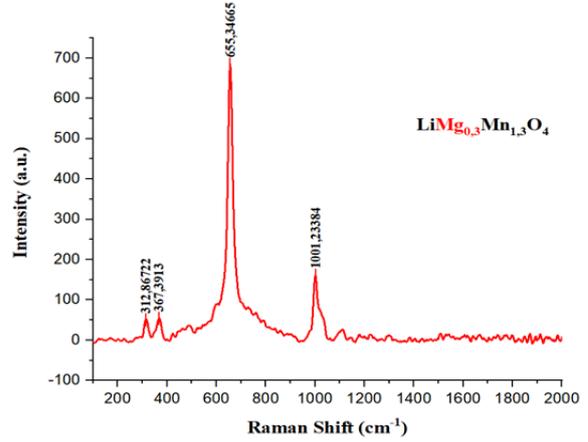**Figure 8. Raman spectra of $LiMg_xMn_{(2-x)}O_4$ spinel samples**

Table 4 presents the crystal lattice parameters and average crystal sizes of Li-Mn spinels modified with $Mg^{2+}$ ions. It was observed that the lattice parameter $\alpha$ increased from 8.253 Å (x = 0.1) to 8.309 Å (x = 0.7) upon modification with $Mg^{2+}$ ions, i.e., this parameter also increased with increasing magnesium content. The $LiMg_{0.3}Mn_{1.7}O_4$ spinel sample is not subject to this change, its lattice parameter $\alpha$ is equal to 8.253 Å.

**Table 4**

**Crystal lattice parameters of $LiMg_xMn_{(2-x)}O_4$ spinel samples**

| Sample | Lattice parameter $a$, Å | Unit cell volume $V$, Å3 | Crystallite size $D$, nm |
|---|---|---|---|
| $LiMn_2O_4$ | 8.175 | 546.250 | 31.7 |
| $LiMg_{0.1}Mn_{1.9}O_4$ | 8.253 | 562.110 | 36.0 |
| $LiMg_{0.3}Mn_{1.7}O_4$ | 8.191 | 549.550 | 17.2 |
| $LiMg_{0.5}Mn_{1.5}O_4$ | 8.254 | 562.290 | 26.7 |
| $LiMg_{0.7}Mn_{1.3}O_4$ | 8.309 | 573.620 | 30.3 |
| $LiMn_2O_4$ (PDF 2 # 35-0782) | 8.248 | 561.030 | – |

Figure 8 shows the Raman shifts of the $LiMg_xMn_{(2-x)}O_4$ spinel samples in the spectral region 200–1000 $cm^{-1}$. The common feature of these spectra is the high-intensity Mn-O bond vibration around 650 $cm^{-1}$ in the range 550–750 $cm^{-1}$. The medium-intensity Raman shift peak located above 800 $cm^{-1}$ has $F_{2g}^{(3)}$ symmetry. The $F_{2g}^{(3)}$ mode is associated with the Li-O bond, i.e., has a tetrahedral cation

structure. The high-intensity line at 330 cm$^{-1}$ is attributed to Mg$^{2+}$ and may be a Raman shift leading to cationic changes in symmetry.

**Textural properties of nanostructured materials based on Li-Mn spinels.** The nitrogen adsorption-desorption isotherms for all analyzed LiMg$_x$Mn$_{(2-x)}$O$_4$ spinel samples have a capillary-condensation hysteresis loop, which belongs to type IV according to the IUPAC classification. This type of isotherm is usually characteristic of mesoporous materials and indicates their developed porosity system. The results of the study show that the isotherms of the studied oxides have a hysteresis loop of type H3, which indicates the presence of crack-like pores (Fig. 11).

Table 5

**Textural characteristics of LiMg$_x$Mn$_{(2-x)}$O$_4$ spinel samples.**

| Sample | $A_{BET}$, m$^2$/g | $V_{sp\,des}$, cm$^3$/g | $D_{BJH\,des}$, nm | Hysteresis loop type | Porous shape |
|---|---|---|---|---|---|
| LiMn$_2$O$_4$ | 8.3 | 0.015 | 8.3 | | |
| LiMg$_{0.1}$Mn$_{1.9}$O$_4$ | 17.1 | 0.028 | 7.9 | H3 | fissured |
| LiMg$_{0.3}$Mn$_{1.7}$O$_4$ | 14.2 | 0.027 | 8.6 | | |
| LiMg$_{0.7}$Mn$_{1.3}$O$_4$ | 16.6 | 0.073 | 21.2 | | |

The introduction of Mg$^{2+}$ ions at x $\geq$ 0.3 does not lead to a change in the pore diameter values. The largest pore volume (0.073 cm$^3$/g) and average size (21.2 nm) are characteristic of the sample with x = 0.7, which contains admixtures of Li$_{0.5}$Mg$_{0.5}$O$_{1.5}$ and Mn$_{1.5}$Mg$_{0.5}$O$_{2.5}$ oxides.
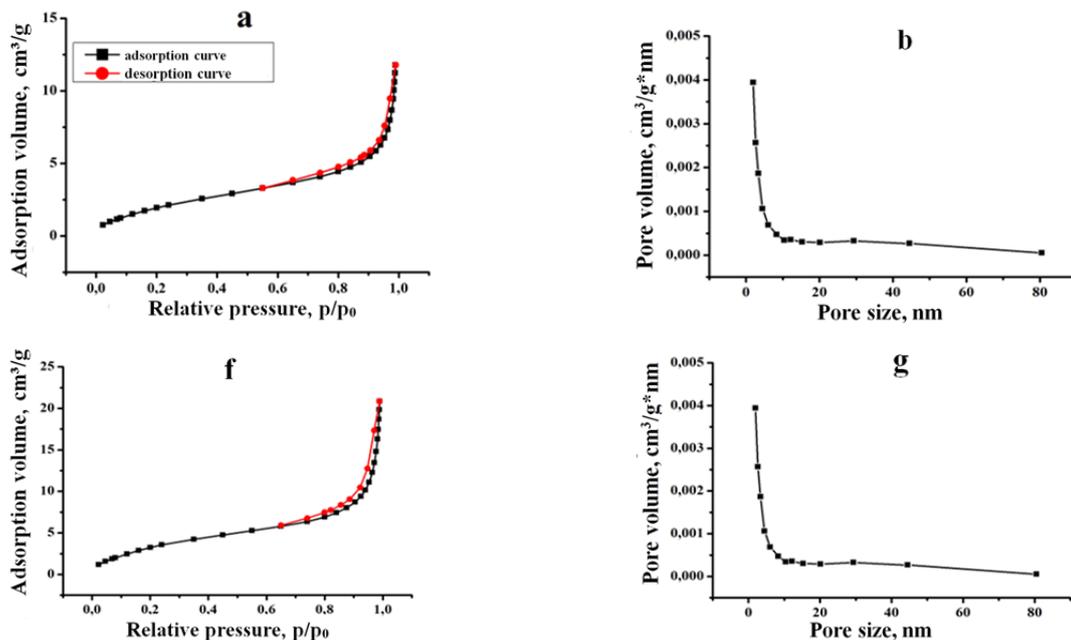


**Figure 11. Low-temperature adsorption-desorption isotherms of N$_2$ (a, f,) and BJH pore size distribution (b,g). LiMn$_2$O$_4$ (a,b) and LiMg$_{0.3}$Mn$_{1.7}$O$_4$ (f, g)**

In this case, in the range of 0.1 $\leq$ x $\leq$ 0.3, an increase in the specific surface area by ~ 1.7-2.1 times and in the pore volume by ~ 1.8 times was observed. An increase in the content of Mg$^{2+}$ ions to x=0.7 is accompanied by a significant increase in the average pore size to 21.2 nm (Table 5).

The fourth chapter of the dissertation, entitled **"Application of nanostructured materials based on Li-Mn spinel in the sorption of Li$^+$ ions"**,

presents an analysis of practical and theoretical data obtained from the study of the sorption properties, adsorption isotherms, and kinetics of adsorbents based on Li-Mn spinel.

The $HMg_xMn_{(2-x)}O_4$ adsorbent samples showed conversion levels ranging from 45 to 79 % (Figure 12). The $HMg_{0.3}Mn_{1.7}O_4$ and $HAl_{0.3}Mn_{1.7}O_4$ samples showed the highest conversion levels of 79 and 74%, respectively, while the $HAl_{0.7}Mn_{1.3}O_4$ sample showed the lowest conversion level of 43% (Figure 13).



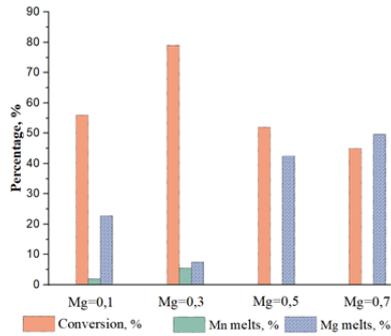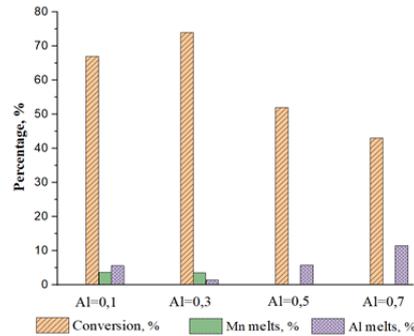**Figure 12. Percentage of H-formation and dissolution of metal ions in $LiMg_xMn_{(2-x)}O_4$ samples**

**Figure 13. Percentage of H-formation and dissolution of metal ions in $LiAl_xMn_{(2-x)}O_4$ samples**
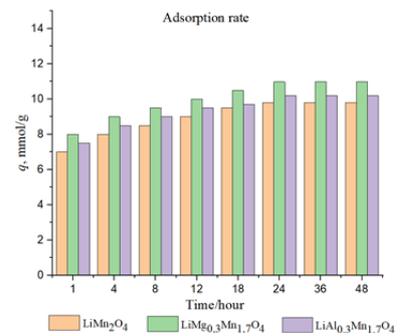
**Figure 14. Adsorption rate of Li-Mn-based adsorbents for $Li^+$ ion in a sample solution (pH=12, $C_0$=0.2)**

According to observations, the adsorption rate gradually increased over time, reaching equilibrium in about 24 hours. During the first 1 hour, the lithium release was somewhat slow, and the sorption capacities for adsorbents based on $LiMn_2O_4$, $LiMg_{0.3}Mn_{1.7}O_4$ and $LiAl_{0.3}Mn_{1.7}O_4$ were 7.20, 8.10 and 7.54 mmol/g, respectively. After 24 hours, these values reached 9.42, 10.65 and 9.63 mmol/g. Even when the experiment was continued and waited for up to 48 hours, the lithium content did not increase (Figure 14).
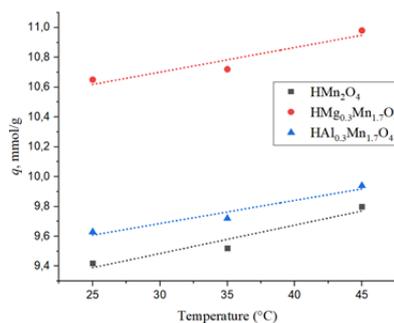


**Figure 15. Sorption capacity of $Li^+$ ion samples based on Li-Mn at different temperatures**
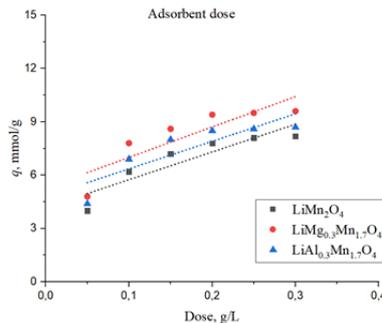
**Figure 16. Effect of adsorbent dosage in a sample solution on the adsorption activity of adsorbents based on**
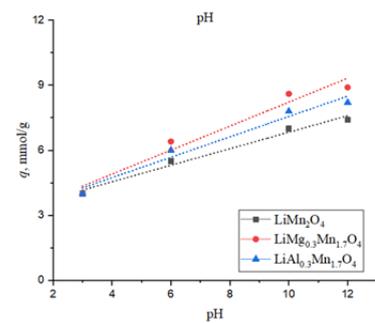
**Figure 17. Effect of pH of sample solution on adsorption activity of Li-Mn-based adsorbents**

Figure 15 shows the adsorption of $Li^+$ ion by $HMn_2O_4$, $HMg_{0.3}Mn_{1.7}O_4$ and $HAl_{0.3}Mn_{1.7}O_4$ adsorbents at different temperatures. The sorption capacity of $HMg_{0.3}Mn_{1.7}O_4$ was determined to be 10.65, 10.72 and 10.98 mmol/g in the order of increasing temperature. Increasing the dosage of $LiMn_2O_4$-based adsorbent from

0.05 to 0.2 g/l led to an increase in the adsorption capacity from 4.0 to 7.8 mmol/g. This indicator was observed to increase from 4.8 to 9.4 mmol/g and 4.4 to 8.5 mmol/g for $LiMg_{0.3}Mn_{1.7}O_4$ and $LiAl_{0.3}Mn_{1.7}O_4$ based adsorbents, respectively (Figure 16). However, increasing the adsorbent dose to 0.3 and 0.4 g/l does not significantly affect the adsorption capacity, which is due to the saturation of the adsorbent. The results of the study showed that the adsorption capacity for the selected samples increases in the pH range from 3.0 to 13.0 (Figure 17).
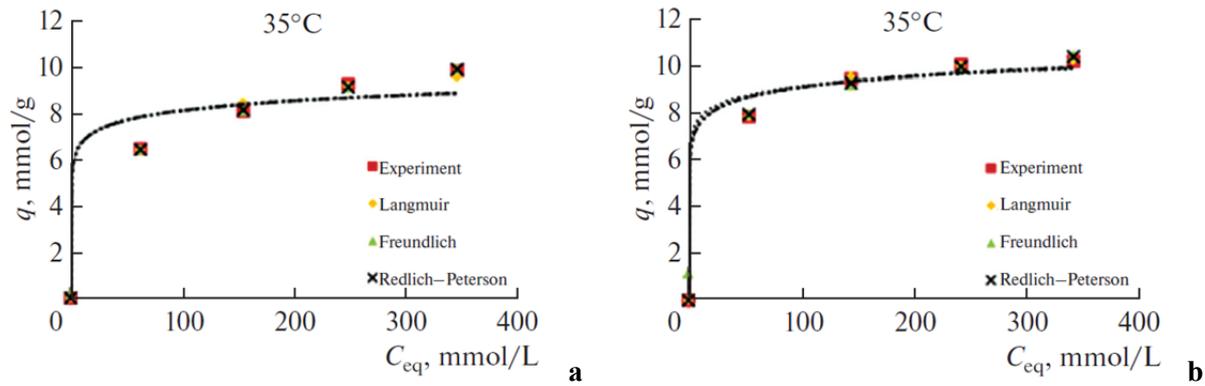


**Figure 18. Adsorption isotherms of Li$^+$ ions on samples of adsorbents based on LiMn$_2$O$_4$ (a) and LiMg$_{0.3}$Mn$_{1.7}$O$_4$ (b) at a model solution temperature of 35 °C**

In Figure 18, the results of mathematical modeling of adsorption isotherms were analyzed based on the Langmuir, Freundlich, and Redlich-Peterson isotherm models, and a comparative view of their parameters is given in table 6.

**Table 6**

**Calculated parameters of mathematical models of adsorption isotherms at sample solution temperatures of 25, 35 and 45 °C for adsorbent samples based on LiMn$_2$O$_4$ and LiMg$_{0.3}$Mn$_{1.7}$O$_4$.**

| Parameter | LiMn$_2$O$_4$ | | | LiMg$_{0.3}$Mn$_{1.7}$O$_4$ | | |
|---|---|---|---|---|---|---|
| $T_{\text{model solution,}}$ °C | 25 °C | 35 °C | 45 °C | 25 °C | 35 °C | 45 °C |
| | Langmuir isotherm model | | | | | |
| $q_0^{\text{max}}$, mmol/g | 10.50 | 10.54 | 10.72 | 10.65 | 10.72 | 10.98 |
| $K_L$, L/mmol | 0.019 | 0.024 | 0.024 | 0.036 | 0.045 | 0.049 |
| $R^2$ | 1.000 | 0.978 | 0.997 | 0.992 | 0.971 | 0.999 |
| | Freundlich isotherm model | | | | | |
| $n_F$ | 3.600 | 3.990 | 4.140 | 5.390 | 6.890 | 6.120 |
| $K_F$, (mmol/g)/(l/mmol)$^{n_F}$ | 1.840 | 2.260 | 2.450 | 3.440 | 4.430 | 3.980 |
| $R^2$ | 0.974 | 0.998 | 0.961 | 0.992 | 0.962 | 0.995 |
| | Redlich-Peterson isotherm model | | | | | |
| g | 0.760 | 0.780 | 0.800 | 0.850 | 0.890 | 0.870 |
| $a_{RP}$, (mmol/l)$^{-g}$ | 0.560 | 0.570 | 0.430 | 0.420 | 0.310 | 0.380 |
| $K_{RP}$, l/mmol | 1.300 | 1.560 | 1.370 | 1.810 | 1.760 | 1.880 |
| $R^2$ | 0.976 | 0.997 | 0.962 | 0.991 | 0.975 | 0.993 |

The theoretical values obtained using these models were compared with the experimental results. The analysis showed that the best fit of the isotherms to the experimental data was determined by the Langmuir model, and the coefficient of fit ($R^2$) calculated by this model was the highest compared to other models.

The results of the kinetic analysis show that the adsorption process is relatively slow at the initial stage, i.e. at small values of time. However, with time, the adsorption process becomes active and in a short time, approximately 40–50 minutes, the system reaches an adsorption-equilibrium state, which indicates a rapid distribution of $Li^+$ ions on the adsorption surfaces (Fig. 19a, b).
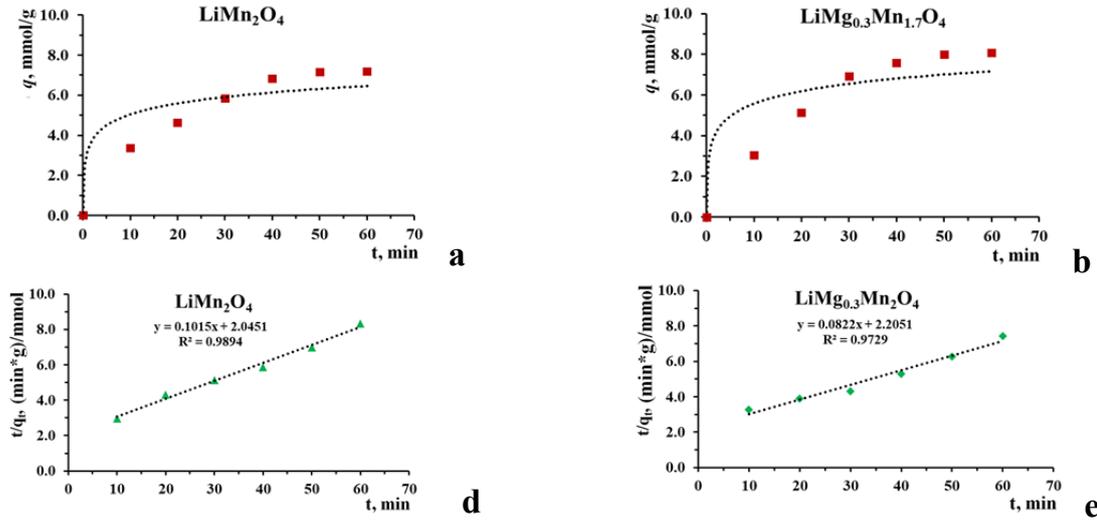


**Figure 19. (a, b) kinetic curves of $Li^+$ ion adsorption on adsorbent samples based on $LiMn_2O_4$ and $LiMg_{0.3}Mn_{1.7}O_4$, as well as (d, e) approximation curves of pseudo-second-order equations**

The changes in thermodynamic parameters of adsorbent samples with $LiMn_2O_4$ and $LiMg_{0.3}Mn_{1.7}O_4$ composition during the sorption processes for $Li^+$ ions from sample solutions at temperatures ranging from 298 to 318 K are presented in table 7.

**Table 7.**

**Thermodynamic parameters of the adsorption process**

| Adsorbents | $\Delta H^{\circ}$ (J/mol) | $\Delta S^{\circ}$ (J/molK) | $\Delta G^{\circ}$ (J/mol) | | |
|---|---|---|---|---|---|
| | | | 298 K | 308 K | 318 K |
| $LiMn_2O_4$ | 17800 | 84.20 | -7294.3 | -8134.4 | -8401.2 |
| $LiMg_{0.3}Mn_{1.7}O_4$ | 17030 | 86.90 | -8881.2 | -9764.3 | -10277.8 |

As can be seen from the data in Table 7, the value of q0max calculated based on the Langmuir equilibrium constant increased at temperatures of 298, 308, and 318 K.

**Table 8**

**Calculated parameters of pseudo-first and pseudo-second order kinetic models for $Li^+$ ion adsorption on $LiMn_2O_4$ and $LiMg_{0.3}Mn_{1.7}O_4$ based adsorbent samples.**

| Parameter | $LiMn_2O_4$ | $LiMg_{0.3}Mn_{1.7}O_4$ |
|---|---|---|
| | Pseudo-first-order kinetic model | |
| $K_1$, $min^{-1}$ | 0.099 | 0.089 |
| $q_{eq}$, mmol/g | 12.200 | 12.200 |
| $R^2$ | 0.880 | 0.989 |
| | Pseudo-second-order kinetic model | |
| $K_2$, g/(mmol*min) | 0.005 | 0.003 |
| $q_{eq}$, mmol/g | 9.900 | 12.200 |
| h, mmol/(min*g) | 0.500 | 0.500 |
| $R^2$ | 0.941 | 0.973 |

The adsorption rate coefficient for $LiMn_2O_4$ spinel was 0.005 g/(mmol·min), while for $LiMg_{0.3}Mn_{1.7}O_4$ spinel material this value was slightly lower at 0.003 g/(mmol·min) (Table 8). The differences in the adsorption kinetics of $LiMn_2O_4$ and $LiMg_{0.3}Mn_{1.7}O_4$ spinel samples may be due to the differences in their structural structure, ionic radii, and electron densities. The kinetic data obtained based on the experimental results were analyzed in depth by mathematical modeling. The results showed that the pseudo-second-order kinetic model fits for the adsorption of $Li^+$ ions.

## CONCLUSION

1. The main parameters for the synthesis of nanostructured sorption materials based on Li-Mn spinel using sol-gel, solid phase, and hydrothermal methods were determined, and spinels with $LiMg_xMn_{(2-x)}O_4$ and $LiAl_xMn_{(2-x)}O_4$ compositions were synthesized by modification of $Mg^{2+}$ and $Al^{3+}$ ions. It was found that the range of 600-800 °C is optimal for the formation of the spinel phase.

2. While the synthesized Li-Mn based spinels are formed in the form of a stable cubic spinel structure, the amount of modified $Mg^{2+}$ and $Al^{3+}$ ions affects the α parameter of the crystal lattice, the unit cell size, and the average crystallite size, and does not significantly affect the particle morphology, but increases the average particle size from 0.45 to 2.34 μm.

3. It was found that the synthesized Li-Mn based spinels have a hysteresis loop of the H3 type, and the pore shape is slit-like. $LiMn_2O_4$ and $LiMg_{0.3}Mn_{1.7}O_4$ have a monomodal distribution of spinel pores and a maximum pore diameter in the range of D ≤ 3 nm.

4. The formation of adsorbents based on Li-Mn spinels modified with $Mg^{2+}$ and $Al^{3+}$ ions showed a conversion level of 43% to 79%. The optimal adsorption properties were observed at an adsorbent content of 0.2 g/L and pH in the range of 10.0-13.0. It was found that the adsorption rate gradually increased with time and reached equilibrium in about 24 hours. A patent application was filed based on the research results.

5. The mathematical analysis of the adsorption isotherms was performed and it was found that the q0max value calculated based on the Langmuir equilibrium constant increased at temperatures of 298, 308 and 318 K, with a maximum value of 10.98 mmol/g. $\Delta H°$ had a positive value, confirming that the adsorption process was endothermic. The pseudo-second-order kinetic equation constants were 0.005 and 0.003 g/(mmol min) for $LiMn_2O_4$ and $LiMg_{0.3}Mn_{1.7}O_4$, respectively.

6. $LiMn_2O_4$, $LiMg_xMn_{(2-x)}O_4$ and $LiAl_xMn_{(2-x)}O_4$ spinels were tested at Navoi Mining and Metallurgical Combine JSC and MOXSAR LLC JV and recommended for use as adsorbents for $Li^+$ ions.

**НАУЧНЫЙ СОВЕТ DSc.03/31.01.2023.К/Т.78.01
ПО ПРИСУЖДЕНИЮ УЧЁНОЙ СТЕПЕНИ ДОКТОРА НАУК
ПРИ ТЕРМЕЗСКОМ ГОСУДАРСТВЕННОМ УНИВЕРСИТЕТЕ**

**САМАРКАНДСКИЙ ГОСУДАРСТВЕННЫЙ УНИВЕРСИТЕТ ИМЕНИ
ШАРОФА РАШИДОВА**

**БЕГИМКУЛОВА ШАХНОЗА АКБАРЖОН КИЗИ**

**СИНТЕЗ МЕТОДОМ ЗОЛЬ-ГЕЛЬ И ФИЗИКО-ХИМИЧЕСКИЕ
СВОЙСТВА НАНОСТРУКТУРИРОВАННЫХ СОРБЦИОННЫХ
МАТЕРИАЛОВ НА ОСНОВЕ Li-Mn ШПИНЕЛЕЙ**

02.00.01 – Неорганическая химия
02.00.04 – Физическая химия

**АВТОРЕФЕРАТ ДИССЕРТАЦИИ
ДОКТОРА ФИЛОСОФИИ (PhD) ПО ХИМИЧЕСКАМ НАУКАМ**

**Термез – 2025**

Тема диссертации доктора философии (PhD) зарегистрирована в Высшей аттестационной комиссии при Министерстве высшего образования, науки и инноваций Республики Узбекистан за номером B2024.2.PhD/K770.

Диссертация выполнена в Самаркандском государственном университете имени Шарофа Рашидова.

Автореферат диссертации на трех языках (узбекский, русский, английский (резюме)) размещен на веб-странице научного совета www.tersu.uz и на информационно-образовательном портале «ZiyoNet» по адресу www.ziyonet.uz.

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# ВВЕДЕНИЕ (аннотация диссертации доктора философии (PhD))

**Цель исследования** - синтез наноструктурированных сорбционных материалов на основе Li-Mn шпинелей, модифицированных ионами $Mg^{2+}$ и $Al^{3+}$ золь-гель методом, и определение их физико-химических и адсорбционных по отношению к ионам $Li^+$ свойств.

**Объектом исследования** были соли лития, марганца, магния и алюминия, а также некоторые их оксиды, лимонная кислота, соляная кислота и рассолы.

**Научная новизна исследования** заключается в следующем:

впервые золь-гель методом синтезированы сорбционные материалы с высокой сорбционной емкостью и наноструктурой на основе шпинелей Li-Mn, модифицированных ионами $Mg^{2+}$ и $Al^{3+}$;

определены физико-химические свойства синтезированных сорбционных материалов на основе шпинелей $LiMn_2O_4$, $LiMg_xMn_{(2-x)}O_4$ и $LiAl_xMn_{(2-x)}O_4$, при этом образец шпинели $LiMg_{0.3}Mn_{1.7}O_4$ обладал наибольшей сорбционной емкостью по отношению к ионам $Li^+$;

изучены изотермы адсорбции ионов $Li^+$ на образцах адсорбентов $LiMn_2O_4$ и $LiMg_{0.3}Mn_{1.7}O_4$, и установлено, что ход изотерм соответствует модели Ленгмюра для полученных результатов;

доказано, что кинетика адсорбции иона $Li^+$ на образцах адсорбентов $LiMn_2O_4$ и $LiMg_{0,3}Mn_{1,7}O_4$ соответствует кинетической модели псевдовторого порядка.

**Внедрение результатов исследования.** На основе полученных научных результатов по разработке технологии получения наноструктурированных сорбционных материалов на основе шпинелей Li-Mn, модифицированных $Mg^{2+}$ и $Al^{3+}$ и сорбция ионов $Li^+$.

на АО «Навоийском горно-металлургическом комбинате» для извлечения ионов $Li^+$ из сточных вод внедрены в эксплуатацию адсорбенты на основе синтезированных шпинельных структур $LiMn_2O_4$, $Li_{1,33}Mn_{1,67}O_4$, $LiMg_xMn_{(2-x)}O_4$ и $LiAl_xMn_{(2-x)}O_4$ (справка АО «Навоийский горно-металлургический комбинат» №23/01-01-07/687 от 06.11.2024 г.), в результате чего стало возможным адсорбировать и извлечь до 98% ионов $Li^+$ из сточных вод гидрометаллургических предприятий.

Для сорбционного выделения ионов $Li^+$ из сточных вод совместного предприятия ООО «МОКСАР» (Справка №17/04-2 СП ООО «МОКСАР» от 17.04.2025 г.) использованы сорбенты составов $LiMg_{0,3}Mn_{1,7}O_4$ и $LiAl_{0,3}Mn_{1,7}O_4$. В результате сорбционного выделения ионов $Li^+$ из сточных вод стало возможным использовать синтезированные на основе местного сырья с высокой сорбционной емкостью шпинели составов $LiAl_{0,3}Mn_{1,7}O_4$ (60-62 мг/г) и $LiMg_{0,3}Mn_{1,7}O_4$ (70-74 мг/г), обладающие высокой сорбционной емкостью, в качестве импортозамещающих сорбентов.

**Структура и объем диссертации.** Диссертация состоит из введения, четырех глав, заключения, списка использованной литературы и приложений. Объем диссертации составляет 119 страниц.

# E'LON QILINGAN ISHLAR RO'YXATI
# LIST OF PUBLISHED WORKS
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