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POLIETILENGLIKOL (PEG) BILAN MODIFIKATSIYALANGAN XITIN VA XITOZAN HOSILALARI

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Abstract: Chitin and chitosan are the most naturally abundant polymers after cellulose. Several types of products can be obtained from chitin and chitosan since they possess some exciting properties, such as biodegrad- ability, biocompatibility, nontoxicity, nonimmunogenicity, and noncarci- nogenicity. These biological and physicochemical properties, along with their abundance, make chitin and chitosan strong candidates for ubiquitous application in pharmaceutical and medical applications, paper production, textile wastewater treatment, biotechnology, cosmetics, food processing, and agriculture.

Annotatsiya: Xitin va xitozan sellyulozadan keyin tabiatda eng ko'p uchraydigan tabiiy polimerlar hisoblanadi. Ular biologik parchalanishi (biodegradatsiyalanishi), biokompatibilligi, toksik emasligi, immun tizim tomonidan rad etilmasligi (nonimmunogenligi) hamda kanserogen emasligi kabi muhim biologik va fizik-kimyoviy xususiyatlarga ega. Aynan ushbu xususiyatlari hamda tabiatda keng tarqalganligi sababli xitin va xitozan farmatsevtika, tibbiyot, qog'oz sanoati, to'qimachilik korxonalarining oqova suvlarini tozalash, biotexnologiya, kosmetologiya, oziq-ovqat sanoati va qishloq xo'jaligi kabi ko'plab sohalarda istiqbolli biomaterial sifatida e'tirof etilmoqda .

Xitin tabiatda eng ko'p tarqalgan tabiiy polisaxaridlardan biri bo'lib, sellyulozadan keyin ikkinchi o'rinda turadi. U azot saqlovchi chiziqli polisaxarid bo'lib, β-(1→4) bog'lari orqali o'zaro birikkan N-atsetil-D-glyukozamin monomerlaridan tashkil topgan. Xitinning molekulyar tuzilishi yuqori darajada tartiblangan bo'lib, uning molekulalari orasida ko'plab vodorod bog'lari hosil bo'ladi. Shu sababli xitin yuqori mexanik mustahkamlik, kimyoviy barqarorlik va kristallik darajasiga ega.

Xitin va xitozandan yangi funksional materiallar olish jarayonida ayrim muammolar mavjud. Ularning asosiy kamchiligi suyultirilgan kislotalarda cheklangan eruvchanlikka ega ekanligidir. Ushbu xususiyat xitin va xitozanning ko'plab texnologik jarayonlarda qo'llanilishini sezilarli darajada cheklaydi [1–11].

Xitozanning turli erituvchilarda eruvchanligini oshirish maqsadida uning molekulasidagi amin va gidroksil guruhlarini kimyoviy modifikatsiyalash istiqbolli yo'nalish hisoblanadi. Bunday yondashuv sellyuloza hosilalarini olish texnologiyalariga o'xshash tarzda amalga oshiriladi. Xususan, polietilenglikol (PEG) bilan graft-kopolimerlash usuli xitozanning eruvchanligi va funksional xususiyatlarini yaxshilashda samarali hisoblanadi.

Polietilenglikol (PEG) suvda hamda ko‘pgina organik erituvchilarda yaxshi eriydigan, toksikligi past, biokompatibil va biologik parchalanadigan poliefir polimeridir. U tibbiyot, biologiya, farmatsevtika va sanoatning ko‘plab yo‘nalishlarida keng qo‘llaniladi. PEG suv, metanol, etanol, atsetonitril, benzol va dixlormetanda yaxshi eriydi, biroq dietil efir hamda geksanda deyarli erimaydi [12,13].

Xitozanning eruvchanligi bilan bog‘liq muammolarni bartaraf etishda PEG eng samarali graft-polimerlardan biri sifatida qaraladi. Xususan, PEGilash (PEGylation) texnologiyasi xitozanning suvda eruvchanligini sezilarli darajada oshirish imkonini beradi. Ilmiy tadqiqotlarda PEG molekulalarini xitozan zanjiriga biriktirish orqali uning suvda eruvchanligi, termik barqarorligi va fizik-kimyoviy xossalari yaxshilanishi isbotlangan [14–16].

Mazkur bobda PEG bilan modifikatsiyalangan xitin va xitozan hosilalarini sintez qilish usullari, ularning fizik-kimyoviy tavsifi hamda tibbiyot, farmatsevtika, biotexnologiya va boshqa sohalardagi istiqbolli qo‘llanilish yo‘nalishlari tahlil qilinadi.

Xitin va xitozanning umumiy tavsifi

Xitin oq rangli, qattiq, elastikligi past va azot saqlovchi tabiiy polisaxarid hisoblanadi. U qayta tiklanuvchi biopolimer bo‘lib, asosan krevetka, qisqichbaqa, omar kabi qisqichbaqasimonlar qobig‘idan olinadi. Bundan tashqari, xitin mollyuskalar va hasharotlarning tashqi skeleti hamda ayrim zamburug‘lar hujayra devori tarkibida ham uchraydi. Tabiatda tarqalishi bo‘yicha u sellyulozadan keyingi ikkinchi eng ko‘p uchraydigan polisaxarid hisoblanadi [17–19].

Sanoatda xitin odatda qisqichbaqasimonlar qobig‘iga dastlab ishqor bilan ishlov berish orqali oqsillarni eritib ajratish, so‘ngra kislota yordamida mineral moddalarni eritish yo‘li bilan olinadi. Keyinchalik yuqori konsentratsiyali ishqor eritmasida deatsetillash reaksiyasi o'tkazilib, xitozan olinadi. Mahsulotning rangini yaxshilash maqsadida texnologik jarayonga ko‘pincha rangsizlantirish bosqichi ham kiritiladi. Natijada yuqori tozalikdagi oq rangli xitin yoki xitozan olinadi [20].

Kimyoviy tuzilishiga ko‘ra xitin β-(1→4) glikozid bog‘lari orqali o‘zaro bog‘langan 2-atsetamido-2-deoksi-β-D-glyukoza (N-atsetil-D-glyukozamin) qoldiqlaridan tashkil topgan chiziqli polisaxarid hisoblanadi (3.1-rasm).

Tuzilishi jihatidan xitin sellyulozaga juda o‘xshash bo‘lib, asosiy farqi glyukoza molekulasining ikkinchi uglerod atomida gidroksil guruhi o‘rniga atsetamid (–$NHCOCH_3$) guruhining mavjudligidir. Shu sababli xitin ko‘pincha sellyulozaning azot saqlovchi hosilasi sifatida qaraladi, biroq u sellyuloza hosil qiluvchi organizmlarda uchramaydi.

Xitozan esa N-atsetil-D-glyukozamin va D-glyukozamin birliklaridan tashkil topgan kopolimer bo‘lib, uning asosiy qismini β-(1→4) bog‘lari orqali bog‘langan 2-amino-2-deoksi-D-glyukopiranoza qoldiqlari tashkil etadi (3.2-rasm). Xitozan xitinning turli darajada deatsetillanishi natijasida hosil bo‘ladi va uning xossalari deatsetillanish darajasiga bevosita bog‘liq.

Xitinning deatsetillanish darajasi va kimyoviy faolligi

Xitinni xitozanga aylantirish jarayonida polimer zanjiridagi barcha atsetil guruhlari to'liq ajralib chiqmaydi. Shu sababli hosil bo'lgan xitozan tarkibida ma'lum miqdorda atsetamid guruhlari saqlanib qoladi. Boshqacha aytganda, xitozan qisman deatsetillangan xitin hisoblanadi. Deatsetillanish darajasi (Degree of Deacetylation, DD) xitozanning eng muhim tavsiflaridan biri bo'lib, uning fizik-kimyoviy va biologik xossalarini belgilaydi. Deatsetillanish darajasi ortishi bilan molekuladagi erkin amin guruhlari soni ham ortadi.

Xitin tarkibida azot miqdori odatda 5–8 % ni tashkil etadi va u asosan atsetillangan amin guruhlari ko'rinishida mavjud bo'ladi. Xitozanda esa azot birlamchi alifatik amin guruhlari shaklida uchraydi. Mazkur funksional guruhlarning mavjudligi xitin va xitozanning turli kimyoviy reaksiyalarda faol ishtirok etishiga imkon yaratadi. Ayniqsa, xitozan molekulasida amin guruhlari sonining ortishi uning kimyoviy reaktivligini sezilarli darajada oshiradi.

Har bir takrorlanuvchi monomer birligida birlamchi va ikkilamchi gidroksil guruhlari mavjud bo'lib, qisman deatsetillangan bo'g'inlarda amin guruhi ham uchraydi. Ushbu funksional guruhlar xitozanni xitinga nisbatan ancha faol polimerga aylantiradi. Natijada xitozan molekulasi turli xil kimyoviy modifikatsiyalarga oson uchraydi, bu esa uning fizik, kimyoviy va mexanik xossalarini maqsadli ravishda o'zgartirish imkonini beradi.

Ayniqsa, amin guruhlarining mavjudligi xitozanning ahamiyatini yanada oshiradi. Deatsetillanish darajasi yuqori bo'lgan sari erkin amin guruhlari soni ortadi va polimerning adsorbsion, ion almashinish hamda kompleks hosil qilish qobiliyati kuchayadi. Shu sababli xitozan og'ir metall ionlari, organik bo'yoqlar va boshqa ifloslantiruvchi moddalarni bog'lab olishda yuqori samaradorlik namoyon etadi.

Xitin va xitozan tarkibidagi amin guruhlari ularning xelatlovchi (chelating) xususiyatini ta'minlaydi. Amin hamda gidroksil guruhlari metall ionlari bilan koordinatsion bog' hosil qilib, barqaror kompleks birikmalarni shakllantiradi. Mazkur xossa xitozandan oqova suvlarni tozalash, og'ir metall ionlarini ajratish, katalizator tashuvchilari tayyorlash va biosorbentlar ishlab chiqarishda keng foydalanish imkonini beradi.

Xitinning polimorf shakllari

Xitin tabiiy manbasiga qarab uch xil kristall modifikatsiyada uchraydi. Bular α-xitin, β-xitin va γ-xitin allomorflaridir. γ-xitin ko'pincha α-xitinning modifikatsiyalangan shakli sifatida qaraladi.

α-xitin tabiatda eng keng tarqalgan va termodinamik jihatdan eng barqaror shakl hisoblanadi. Unda polimer zanjirlari antiparallel joylashgan bo'lib, ular orasida kuchli vodorod bog'lari hosil bo'ladi. Natijada α-xitin yuqori kristallik darajasiga, mexanik mustahkamlikka va kimyoviy barqarorlikka ega bo'ladi.

β-xitinda esa polimer zanjirlari parallel yo'nalishda joylashgan. Bunday tuzilish molekulalararo bog'lanishlarning nisbatan kuchsiz bo'lishiga olib keladi. Shu sababli β-xitin reaktivligi yuqoriroq bo'lib, kimyoviy modifikatsiyalarga osonroq uchraydi. Bundan tashqari, β-xitin erituvchilarni va boshqa molekulalarni o'z tuzilmasiga osonroq singdira oladi.

γ-xitin esa α- va β-xitin tuzilmalarining kombinatsiyasidan iborat bo'lib, uning kristall tuzilishi oraliq xususiyatlarga ega. Ushbu shakl ayrim zamburug'lar va boshqa biologik manbalarda uchraydi.

Xitinning eruvchanlik xususiyatlari

α- va β-xitin oddiy organik erituvchilarda deyarli erimaydi. Xitinning eruvchanligi past bo'lishining asosiy sababi uning yuqori kristallik darajasi hamda molekulalar orasida hosil bo'ladigan kuchli vodorod bog'lari hisoblanadi. Aynan shu bog'lanishlar polimer zanjirlarini juda zich joylashtirib, erituvchi molekulalarning polimer ichiga kirib borishini qiyinlashtiradi.

Xitinni eritish uchun odatda maxsus erituvchi tizimlardan foydalaniladi. Jumladan, dimetilatsetamid/litiy xlorid (DMAc/LiCl) aralashmasi, geksaftoroizopropanol, geksaftoroatseton seskigidrati, konsentrlangan fosfor kislotasi, litiy tiosiyanatning to'yingan eritmasi hamda past haroratdagi natriy gidroksid eritmalari xitinni eritishda samarali hisoblanadi.

Ba'zi sharoitlarda xitin suvda ham erishi mumkin, biroq bunda molekulyar massaning kamayishi va qisman deatsetillanish sodir bo'ladi. Tadqiqotlar shuni ko'rsatadiki, deatsetillanish darajasi 50 % dan yuqori bo'lganda polimerning eruvchanligi sezilarli darajada ortadi.

Bugungi kunda xitinning past eruvchanligi uni qayta ishlash va amaliy qo'llashdagi eng muhim muammolardan biri hisoblanadi. Shu sababli zamonaviy ilmiy tadqiqotlarda xitinni kimyoviy modifikatsiyalash, xususan suvda yaxshi eriydigan hosilalarini sintez qilish bo'yicha keng ko'lamli izlanishlar olib borilmoqda.

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