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TECHNOLOGY FOR PRODUCING A FLOCCULATING-STABILIZING REAGENT FOR WATER PURIFICATION BASED ON AMPHOTERIC CARBOXYMETHYL CHITOSAN

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Abstract: This paper studies the technology of obtaining amphoteric carboxymethyl chitosan (ACC), soluble over a wide pH range, by carboxymethylation of chitosan and introduction of a cationic group, and its application as a flocculating and stabilizing reagent for turbidity removal from natural waters. The coexistence of anionic ($–COO^-$) and cationic ($–NH_3^+$ / quaternary ammonium) groups provides neutralization of negatively charged colloidal particles and interparticle bridging. The relationship between the degree of substitution, solubility, charge density of the reagent and turbidity removal efficiency was evaluated by jar tests; the structure was confirmed by FT-IR spectroscopy. As a natural, non-toxic and biodegradable reagent, ACC is an alternative to synthetic polyacrylamide-based flocculants.

Keywords: amphoteric carboxymethyl chitosan, cationic group, flocculant, turbidity removal, charge neutralization, bridging mechanism, water treatment, biopolymer.

Annotatsiya: Maqolada xitozanni karboksimetillash va kationli guruh kiritish orqali keng pH oralig‘ida eriydigan amfoter karboksimetilxitozan (AKX) olish hamda uni tabiiy suvlarni loyqalikdan tozalash uchun flokulyatsiyalovchi-stabillovchi reagent sifatida qo‘llash texnologiyasi o‘rganildi. Molekulada anionli ($–COO^-$) va kationli ($–NH_3^+$ / chorlamali ammoniy) guruhlarning birgalikda bo‘lishi reagentga manfiy zaryadli kolloid zarralarni neytrallash va makromolekulalararo ko‘prik hosil qilish qobiliyatini beradi. Reagentning almashinish darajasi, eruvchanligi va zaryad zichligi bilan loyqalikni yo‘qotish samaradorligi orasidagi bog‘liqlik jar-test usulida baholandi; tuzilish IK-Furye spektroskopiyasi bilan tasdiqlandi. Tabiiy, zaharsiz va biologik parchalanuvchan reagent sifatida AKX poliakrilamid asosidagi sintetik flokulyantlarga muqobil hisoblanadi.

Kalit so‘zlar: amfoter karboksimetilxitozan, kationli guruh, flokulyant, loyqalikni yo‘qotish, zaryadni neytrallash, ko‘prik mexanizmi, suv tozalash, biopolimer.

Аннотация: В статье изучена технология получения амфотерного карбоксиметилхитозана (АКХ), растворимого в широком диапазоне pH, путём карбоксиметилирования хитозана и введения катионной группы, а также его применение в качестве флокулирующего и стабилизирующего реагента для очистки природных вод от мутности. Совместное присутствие анионных ($–COO^-$) и катионных ($–NH_3^+$ / четвертичный

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аммоний) групп обеспечивает нейтрализацию заряда отрицательно заряженных коллоидных частиц и мостикообразование. Взаимосвязь между степенью замещения, растворимостью, плотностью заряда реагента и эффективностью удаления мутности оценивалась методом jar-test; строение подтверждено ИК-Фурье спектроскопией. Как природный, нетоксичный и биоразлагаемый реагент, АКХ является альтернативой синтетическим флокулянтам на основе полиакриламида.

Ключевые слова: амфотерный карбоксиметилхитозан, катионная группа, флокулянт, удаление мутности, нейтрализация заряда, мостикообразование, очистка воды, биополимер.

Kirish

Suv tozalash sifati ko‘p jihatdan muallaq va kolloid zarralarni qanchalik to‘liq cho‘ktirib olishga, ya’ni flokulyatsiya bosqichiga bog‘liq. Bu maqsadda an’anaviy ravishda poliakrilamid asosidagi sintetik flokulyantlar ishlatiladi; biroq ularning tabiatda to‘liq parchalanmasligi va qoldiq monomerlarning zaharliligi jiddiy ekologik e’tirozlarga sabab bo‘ladi. Mana shu bois so‘nggi yillarda tabiiy, zararsiz va biologik parchalanadigan biopolimer flokulyantlar diqqat markaziga chiqdi[1].

Xitozan xitinning deatsetillanishidan olinadigan kationli polielektrolit bo‘lib, protonlangan amino guruhlari hisobiga manfiy zaryadli muallaq zarralarni biriktiradi. Ammo uning suvda erishi faqat kislotali muhitda yuz berishi amaliy qo‘llanishni cheklaydi[2]. Karboksimetil guruhining kiritilishi eruvchanlikni keng pH oralig‘ida ta’minlaydi, biroq hosil bo‘lgan sof anionli karboksimetilxitozanda zaryadni neytrallash qobiliyati pasayadi: loyqalik zarralari ham manfiy zaryadli bo‘lgani uchun samarali flokulyatsiya uchun molekulada kationli markazlar bo‘lishi zarur[3]. Shu sababli ushbu ishda karboksimetil bilan birga kationli (chorlamali ammoniy) guruh kiritilib, zaryadni neytrallash va ko‘prik mexanizmlarini birlashtiruvchi amfoter xossali reagent olinadi[4].

Ichimlik va sanoat suvlarini tozalashda alyuminiy tuzlari hamda sintetik polielektrolitlarning o‘rnini bosadigan ekologik xavfsiz reagentlarga ehtiyoj kuchaymoqda. Xitin va xitozanning an’anaviy manbai suv mahsulotlarini qayta ishlash chiqindilari bo‘lsa-da, O‘zbekistonda ular pillachilik chiqindilaridan, aniqrog‘i tut ipak qurti (Bombyx mori) g‘umbagidan olinadi; bu esa mahalliy, qayta tiklanadigan xom ashyo bazasini ta’minlaydi[5]. Shu bois mahalliy hissa, avvalo, xitozanni kerakli

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[1]Application of chitosan and its derivatives (dialdehyde and carboxymethyl chitosan) as bioflocculants for iron and turbidity removal from filter backwash water // Water. 2023. Vol. 15, № 16. Article 2913. DOI: 10.3390/w15162913. Design of amphoteric chitosan flocculants for phosphate and turbidity removal in wastewater // Carbohydrate Polymers. 2018.

[2]Cationic content effects of biodegradable amphoteric chitosan-based flocculants (CMC-CTA) on the flocculation properties. 2013.

[3]Synthesis, characterization and sludge dewaterability evaluation of the chitosan-based flocculant CCPAD // Polymers. 2019. Vol. 11, № 1. Article 95. DOI: 10.3390/polym11010095. Turbidity reduction in drinking water by coagulation-flocculation with chitosan polymers // Journal of Water and Health. 2019. Vol. 17, № 2.

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[5]Rashidova S.Sh., Milusheva R.Yu. Xitin va xitozan Bombyx mori: sintez, xossalari va qo‘llanilishi. Toshkent: Fan, 2009.

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funksional reagentga aylantira olishda namoyon bo‘ladi. Shundan kelib chiqib, ishimizda karboksimetil va kationli guruhlar izchil kiritilib amfoter reagent olindi hamda uning almashinish darajasi va zaryad zichligi loyqalikni yo‘qotish samaradorligi bilan qanday bog‘lanishi kuzatildi; yakuniy maqsad amfoter karboksimetilxitozan sintezini optimallashtirish va flokulyatsiyalovchi samaradorligini baholashdan iborat.

Materiallar va usullar

Asosiy xom ashyo yuqori deatsetillanish darajasiga ega xitozan bo‘ldi. Karboksimetillash monoxlorsirka kislotasi (yoki uning natriy tuzi) bilan, kationli guruhni kiritish esa 3-xlor-2-gidroksipropiltrimetilammoniy xlorid (CTA) bilan amalga oshirildi; muhit natriy gidroksid ishtirokida ishqoriy qilinib, izopropanol-suv aralashmasidan iborat bo‘ldi. Sinov uchun ma’lum boshlang‘ich loyqalikka ega model suv namunalari (kaolin yoki bentonit suspenziyasi) tayyorlandi.

Reagent ikki bosqichda olindi: xitozan ishqoriy muhitda faollantirilib, monoxlorsirka kislotasi bilan karboksimetillandi; so‘ngra CTA bilan kationli guruh payvandlanib, amfoter karboksimetilxitozan hosil qilindi. Mahsulot neytrallandi, spirt bilan yuvilib tozalandi va quritildi. Almashinish darajasi va kationli guruh ulushi titrlash usulida, tuzilish IK-Furye spektroskopiyasida tasdiqlandi.

Flokulyatsiya samaradorligi standart jar-test usulida baholandi: reagentning turli dozalari namunaga qo‘shilib, aralashtirish va cho‘ktirishdan so‘ng qoldiq loyqalik turbidimetrda o‘lchandi. Optimal pH va reagent dozasi tajriba qatorida aniqlandi; loyqalikni yo‘qotish samaradorligi foizda hisoblandi.

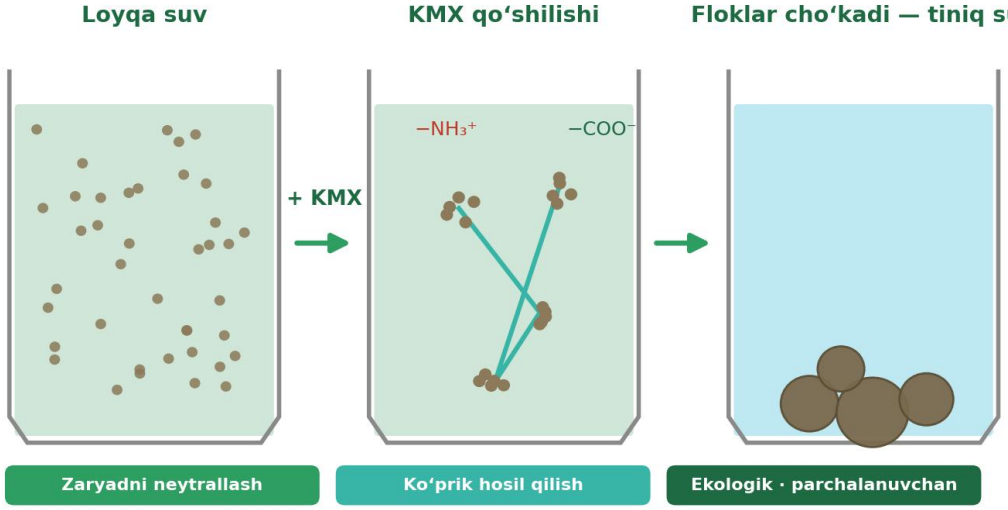
Tanlangan sharoitlar (namuna): karboksimetillash 60 °C da 4 soat, so‘ng CTA bilan kationlash 60 °C da 3 soat davomida olib borildi. Jar-test kaolin suspenziyasida (boshlang‘ich loyqalik ≈ 100 NTU) bajarildi: tez aralashtirish 1 daqiqa (≈120 ayl/daq), sekin aralashtirish 15 daqiqa (≈40 ayl/daq), cho‘ktirish 30 daqiqa. Reagent dozalari 1–8 mg/l, pH 6–8 oralig‘ida o‘rganildi; qoldiq loyqalik turbidimetrda o‘lchandi.

Natijalar

Karboksimetilxitozanning flokulyatsiyalovchi ta’sir mexanizmi 3-rasmda ko‘rsatilgan: reagent qarama-qarshi zaryadli kolloid zarralarni neytrallaydi va makromolekulalararo ko‘prik hosil qilib, ularni yirik floklarga birlashtiradi hamda cho‘kishini tezlashtiradi.

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3-rasm. Karboksimetilxitozan: zaryadni neytrallash va ko‘prik mexanizmi



IK-spektrda karboksil guruhiga (–COO^-) va kationli ammoniy markazlariga xos yutilish polosalari amfoter tuzilmani tasdiqladi. Tajribada sintez sharoitlarining almashinish darajasi (AD), kationli guruh ulushi va unumga, hamda reagent dozasi va pH ning loyqalikni yo‘qotish samaradorligiga ta’siri jar-test usulida o‘rganildi.

Tajriba hisob-kitobi

Namuna rejim: karboksimetillash 60 °C da 4 soat, so‘ng CTA bilan kationlash 60 °C da 3 soat. Olingan reagentda almashinish darajasi ≈ 0,72, kationli guruh ulushi ≈ 0,45.

Loyqalikni yo‘qotish samaradorligi (E) jar-test natijalari asosida quyidagicha hisoblanadi:

$E = (T_0 - T) / T_0 \cdot 100\ \%,$

bu yerda T_0 boshlang‘ich, T esa reagent ta’siridan keyingi qoldiq loyqalik (NTU).

boshlang‘ich loyqalik T_0 = 100 NTU, 4 mg/l dozada qoldiq loyqalik T = 8,5 NTU bo‘lsa, E = (100 − 8,5) / 100 · 100 = 91,5 %.

Optimal doza 4 mg/l atrofida qayd etildi. Dozani 8 mg/l gacha oshirilganda zaryadning qayta yuklanishi tufayli samaradorlik 82 % gacha pasaydi; pH ning 6–8 oralig‘ida u sezilarli o‘zgarmadi.

Muhokama

Amfoter karboksimetilxitozanning flokulyatsiyalovchi ta’sirini ikki mexanizm, ya’ni zaryadni neytrallash va ko‘prik hosil qilish, birgalikda izohlaydi. Reagentdagi kationli markazlar manfiy zaryadli kolloid zarralarning zaryadini so‘ndiradi, makromolekula zanjirlari esa ularni yirik flokulalarga bog‘lab, cho‘kishni tezlashtiradi[6]. Karboksimetil guruhi reagentni keng pH oralig‘ida

[6]Application of chitosan and its derivatives (dialdehyde and carboxymethyl chitosan) as bioflocculants for iron and turbidity removal from filter backwash water // Water. 2023. Vol. 15, № 16. Article 2913. DOI: 10.3390/w15162913. ;

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eruvchan saqlaydi, kationli guruh esa sof anionli karboksimetilxitozanga xos zaryad neytrallash cheklovini bartaraf etadi[7].

Reagent dozasining optimal qiymatdan oshishi zaryadning qayta yuklanishi tufayli kolloid tizimni qayta barqarorlashtirib, samaradorlikni pasaytirishi mumkin. Almashinish darajasi va molekulyar massa flokulyatsiya qobiliyatini belgilovchi muhim parametrlardir; ularni payvandlash (graft) kopolimerlash yo‘li bilan boshqarish samaradorlikni yanada oshirishi mumkinligi adabiyotda ko‘rsatilgan[8]. Reagentning tabiiyligi va biologik parchalanuvchanligi uni ekologik xavfsiz suv tozalash texnologiyalari uchun istiqbolli qiladi.

Xulosa

Xitozanga karboksimetil va kationli guruhlarni ketma-ket kiritish yo‘li bilan keng pH oralig‘ida eriydigan amfoter karboksimetilxitozan olindi va uning suv loyqaligini kamaytirishdagi imkoniyatlari ko‘rib chiqildi. Reagentdagi kationli markazlar manfiy zaryadli zarralarni neytrallaydi, makromolekula esa ularni ko‘prik orqali yiriklashtiradi. Tabiiyligi, zararsizligi va biologik parchalanuvchanligi amfoter karboksimetilxitozanni poliakrilamidli sintetik flokulyantlarga munosib, ekologik xavfsiz muqobil sifatida ko‘rsatadi. Flokulyatsiya samaradorligining miqdoriy ko‘rsatkichlari muallifning jar-test natijalari bilan keyinchalik to‘ldiriladi.

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Tadqiqot maxsus tashqi moliyalashtirishsiz bajarilgan.

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Foydalanilgan adabiyotlar

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