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Nigora YUNUSOVA,
O‘zbekiston Milliy universiteti magistranti
Mehrinigor MUXAMMADIYEVA
O‘zbekiston Milliy universiteti magistranti
Uchqun RO‘ZMETOV,
O‘zbekiston Milliy universiteti dotsenti, k.f.d
Maqsud SAYFIYEV,
Kimyo fanlari bo‘yicha falsafa doktori, PhD
E-mail: unigora098@gmail.com

O‘zMU professori, k.f.d N. Qutlimurotova taqrizi asosida

**A SENSITIVE SORPTION–SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF CU(II) IONS
IN NATURAL WATERS USING PYROCATECHOL BINAFFSHA IMMOBILIZED ON A POLYETHYLENE
POLYAMINE–POLYACRYLONITRILE (PPF-1) MATRIX**

Annotation

The contamination of natural waters with Cu(II) ions is a pressing environmental problem. The aim of this study is to develop a sensitive sorption–spectrophotometric method for the determination of Cu(II) ions using pyrocatechol violet reagent immobilized on a PPF-1 matrix. As a scientific novelty, for the first time, pyrocatechol violet reagent was immobilized onto a modified PPF-1 matrix to create a new polymer-based system for the efficient determination of Cu(II) ions. The studies were carried out using spectrophotometric and spectroscopic techniques. The absorption spectrum for Cu(II) ion determination was observed at a wavelength of 610 nm, with an optimal pH range of 5.0. The immobilization efficiency of pyrocatechol violet onto the polymer matrix was 96%. The developed method is a sensitive and effective approach for the determination and preconcentration of Cu(II) ions in various types of samples.

**MATRITSASIDA IMMOBILLANGAN PIROKATEXIN BINAFFSHA YORDAMIDA TABIIY SUVLARDA CU(II)
IONINI YUQORI SEZGIRLIKDA SORBSION-SPEKTROFOTOMETRIK ANIQLASH USULINI ISHLAB CHIQUISH**

Annotatsiya

Tabiiy suvlarning Cu(II) ionlari bilan ifloslanishi dolzarb ekologik muammodir. Ushbu tadqiqotning maqsadi PPF-1 matritsasida immobillangan pirokatixol binaffsha reagenti yordamida Cu(II) ionini aniqlash uchun sezgir sorbsion-spektrofotometrik usulni ishlab chiqishdan iborat. Ilmiy yangilik sifatida, Cu(II) ionini samarali aniqlash uchun birinchi marta pirokatexin binaffsha reagenti modifikatsiyalangan PPF-1 matritsasiga immobillanib, yangi polimer asosli tizim yaratildi. Tadqiqotlar spektrofotometriya va spektroskopiya usullari yordamida amalga oshirildi. Cu(II) ionini aniqlashning yutilish spektri 610 nm to‘lqin uzunligida va optimal pH 5.0 oralig‘ida kuzatildi. Pirokatixol binaffshaning polimer matritsasiga immobillanish samaradorligi 96% ni tashkil etdi. Ishlab chiqilgan ushbu usul turli obyektlar tarkibidan Cu(II) ionini aniqlash va konsentrlash uchun sezgir va samarali usul hisoblanadi.

Kalit so‘zlar: Cu(II) ionini, Pirokatexin binaffsha, PPF-1 matritsasi, immobillash, sorbsion–spektrofotometriya.

Kirish. So‘nggi yillarda tabiiy suvlarning og‘ir metall ionlari, xususan Cu(II) bilan ifloslanishi atrof-muhit va inson salomatligi uchun dolzarb muammolarni yuzaga keltirmoqda. Shu sababli Cu(II) ionlarini aniqlash, ajratish va oldindan konsentratsiyalash usullarini qo‘llash talab qilinadi. Ushbu tadqiqotda Cu(II)ni atrof-muhit obyektlaridan aniqlash uchun gibril sorbsion-spektrofotometrik usul taqdim etilgan. Ishlab chiqilgan usulda pirokatexin binaffshasi reagentini PPF-1 polimer matritsasiga immobillash hamda ushbu sistema yordamida turli obyektlar tarkibidan Cu(II) ionini aniqlash haqida so‘z boradi. Ushbu yondashuv aniqlash chegaralarini, selektivlik va aniqlikni oshiradi, shu bilan birga namunani tayyorlashni soddalashtiradi va matritsa qarshiligini yaxshilaydi. Pirokatexin binaffshaning immobillanishi Cu(II) ni selektiv tarzda bog‘lash imkonini beradi va samarali oldindan konsentratsiyani ta‘minlaydi. Ushbu ishlab chiqilgan usulni turli suv namunalari tarkibini tahlil qilishda va qattiq obyektlarni ham eritma holatiga o‘tkazib tahlil qilishda samarali qo‘llash mumkin.

Mavzuga oid adabiyotlar tahlili. Ko‘pchilik tirik organizmlar xrom, rux, nikel, temir va molibden kabi og‘ir metallarning kam miqdorlarini talab etadi. Lekin ko‘pgina og‘ir metallar hatto juda past konsentratsiyalarda ham organizmlarga zarur yetkazishi mumkin. Zarrali havo ifloslanishi (partikulyar ifloslanish) jahon miqyosida yurak-qon tomir kasalliklari bilan bog‘liq o‘lim va kasallanishning asosiy atrof-muhit xavfi hisoblanadi. Atrof-muhitning ifloslanishi va oziq-ovqatning og‘ir metall ionlari bilan zararlaniishi turli ekologik hamda inson salomatligiga oid xavflarni samarali nazorat qilish va kamaytirish uchun doimiy monitoringni talab etuvchi jiddiy muammolardir. Shu bois, atrof-muhit namunalariidagi og‘ir metall ionlari miqdorini o‘lchash va monitoring qilish - ularning inson organizmiga ijobiy yoki salbiy ta‘sirini inobatga olgan holda - analitik kimyo sohasining muhim yo‘nalishlaridan biridir [1–5].

Juda past konsentratsiyadagi og‘ir metall elementlar inson salomatligida muhim rol o‘ynaydi: ularning ayrimlari zarur bo‘lsa, boshqalari esa juda oz miqdorlarda ham toksik ta‘sir ko‘rsatadi. Misning past konsentratsiyadagi miqdorlarini aniqlash zamonaviy analitik kimyoning eng muhim yo‘nalishlaridan biridir. Biroq ko‘plab atrof-muhit namunalariini bevosita tahlil qilish matritsa ta‘silari va analitning juda past konsentratsiyasi sababli murakkab hisoblanadi [6].

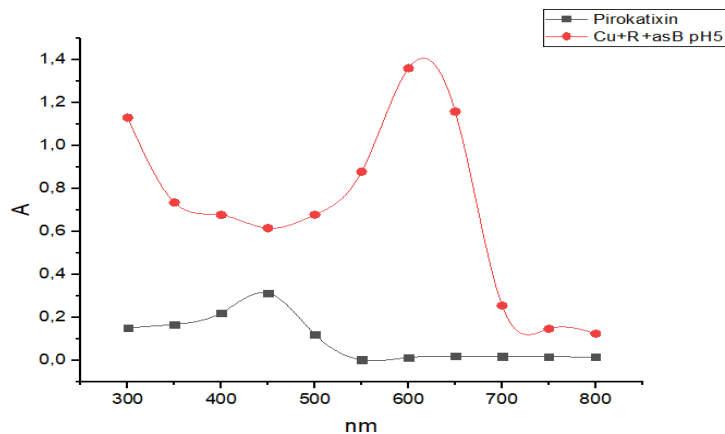
Atrof-muhitda metall ionlari miqdorining ortib borishi suv manbalarida ularning konsentratsiyasini kuzatish uchun tezkor va yuqori sezgirlikka ega analitik usullarga bo'lgan ehtiyojni yanada kuchaytirmoqda [7]. Odamlar, hayvonlar va o'simliklarning sog'lig'i uchun muhim metall bo'lgan mis ko'plab oziq-ovqat mahsulotlarida har xil miqdorda bo'ladi. O'tmishdan hozirgi kungacha, hunarmandchilikdan zargarlik buyumlariga, musiqa asboblardan qoplama materiallariga qadar ko'plab sohalarda qo'llanilib kelinayotgan mis rivojlangan mamlakatlarda odam boshiga 10 kilogrammgacha ko'tarildi. Mis sanoat, sanoat va mashinasozlik uchun ajralmas metall sifatida mavjud bo'lib kelmoqda [8]. Ayniqsa, ichimlik suvi tarkibida tabiiy ravishda mis elementining ionlari mavjud bo'lishi mumkin, chunki suv quvurlar, ayniqsa mis quvurlar orqali oqib o'tganda metallar suvga erishadi. U inson salomatligi uchun zarur mikroelement hisoblanadi. Cu(II) ionlarini aniqlashning aniq va sezgir usullari suv sifatini baholash va atrof-muhitni monitoring qilishda muhim ahamiyatga ega [9]. Imobilizatsion pirokatexin binafsha bilan PPF-1 sorbentining Cu(II) ionlarini aniqlash uchun qo'llanilishi an'anaviy atom yutilish jarayoniga nisbatan bir qator afzalliklarga ega, jumladan: soddaligi, Cu(II) ionlarini aniqlashning yuqori sezuvchanligi va selektivligi aniqlangan [10]. Cu(II) ionlarini aniqlashning aniqligi ularning atrof-muhitga ta'siri va salomatlikka bo'lgan oqibatlarini tushunish uchun juda muhimdir.

Tadqiqot metodologiyasi. Cu(II) ionini aniqlash tahlillari spektrofotometriya, IQ spektroskopiya va rentgen-fluoresent tahlili yordamida o'rganildi. Namunalarning og'irligi ABS 120-4N analitik tarozilar (Xitoy) yordamida o'lchandi; Eritma muhitini aniqlash uchun "PHS-3E" pH-metr (Xitoy) va "MS7-H550-S" aralashtirgich ishlatildi. IQ spektrlari Bruker Invenio S-2021 Fourier-spektrometrida 4000 - 400 cm^{-1} diapazonda ATR usulida yozib olindi. Reagent va komplekslarning imobilizatsion miqdori EMC-30PC-UV (Germaniya) va "Eye-One Pro" (Xitoy) nur qaytarish spektroskopiyasi yordamida o'rganildi.

Analitik reagent sifatida $5 \cdot 10^{-4}$ M konsentratsiyadagi standart Pirokatexin binafsha eritmasi, Cu(II) ioni eritmasidan esa $1 \cdot 10^{-3}$ M konsentratsiyadagi $\text{Cu}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ standart eritmalarini tanlandi. Tadqiqot tizimlarining kislotali va ishqoriy muhitini saqlash uchun atsetat bufer eritmalaridan foydalanildi. Bufer eritma tayyorlash uchun 0,2 M li $\text{CH}_3\text{COONa} \cdot \text{H}_2\text{O}$ va CH_3COOH eritmalaridan tayyorlangan.

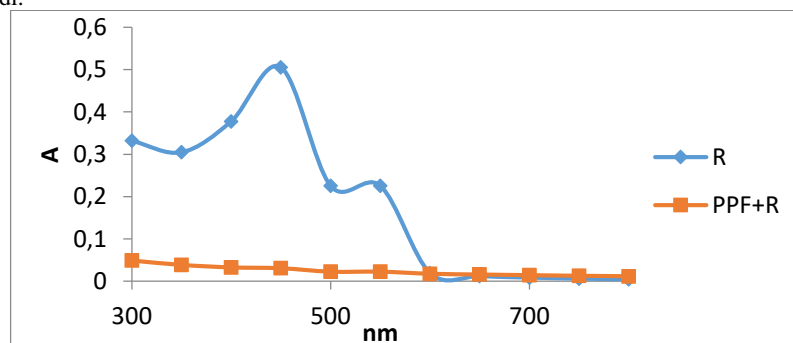
Imobilizatsion maqsadi - reagentlarning analitik parametrlarini yaxshilash va Cu(II) aniqlash sezgirlikni 10-100 baravar oshirish, shuningdek, imobilizatsion Pirokatexin binafsha bilan tayyorlangan substratlar orqali tahlilni samarali qilishdir.

Tahlil va natijalar. Pirokatexin binafshaning PPF-1 matritsada imobilizatsion samaradorligi spektrofotometrik xususiyatlarini o'rganish orqali baholandi. Spektrofotometrik o'lchovlar natijalariga ko'ra, Pirokatexin binafsha reagentining maksimal nur yutish to'lqin uzunligi 440 nm da kuzatildi, Cu(II) ionlari bilan hosil qilgan kompleksi esa 610 nm da maksimal signal berdi. Cu(II) ionlarini aniqlashda optimal pH 5,0 diapazonida bo'lib, aynan shu sharoitda analitik signal eng yuqori darajaga yetadi.



1-rasm: Pirokatexin binafsha reagentining suvli muhitdagi spektrlari

O'lchovlar atsetat bufer eritmasi yordamida amalga oshirildi, bu tizimning pH barqarorligini ta'minladi va natijalarning takrorlanuvchi hamda ishonchli bo'lishini kafolatlad. Tanlangan matritsada Pirokatexin binafsha reagentining imobilizatsion samaradorligi o'rganildi.



2-rasm: Pirokatexin binafsha reagentining PPF-1 toli sorbentiga imobilizatsion oldingi va keyingi yutilish spektrlari

Pirokatexin binafsha reagentining maksimal analitik signali 440 nm da kuzatildi, va optik zichlik keskin kamaydi. Shundan xulosa qilish mumkinki, imobilizatsion jarayoni Pirokatexin binafsha reagentining sulfo guruhi bilan PPF-1 matritsada sulfo guruhlarini o'rtasidagi o'zaro ta'sir hisobiga sodir bo'lgan.

Olingan natijalar shuni tasdiqladiki, Pirokatexin binafsha eritmasining optik zichligi 1,3614 ni tashkil etadi. Matritsada immobillashdan keyingi optik zichlik keskin kamayib 0.0131 ga yetdi. Optik zichlikning bunday keskin kamayishining sababi shundaki, pirokatexin binafsha PPF-1 matritsada samarali tarzda immobillandi.

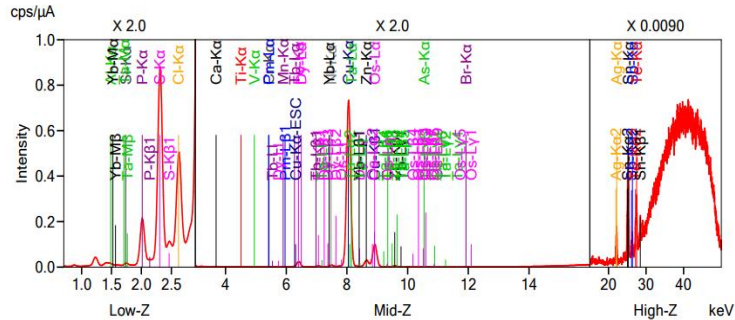
PPF-1 matritsada Pirokatexin binafshaning immobillash samaradorligini aniqlash uchun quyidagi 1-formula ishlatildi:

$$R\% = 1 - \frac{A}{A_0} = 1 - \frac{1.3614}{0.0131} = 0.96 \quad (1)$$

Bu yerda: A_0 – Pirokatexin binafsha reagent eritmasining immobillashdan oldingi optik zichligi, A – immobillashdan keyingi optik zichlik.

PPF-1 matritsada Pirokatexin binafshaning samarali immobillanishi 96% ni tashkil qildi. Bu barcha reagentlarning polimer sorbentga to'liq sorbsiya qilinganligini ko'rsatadi.

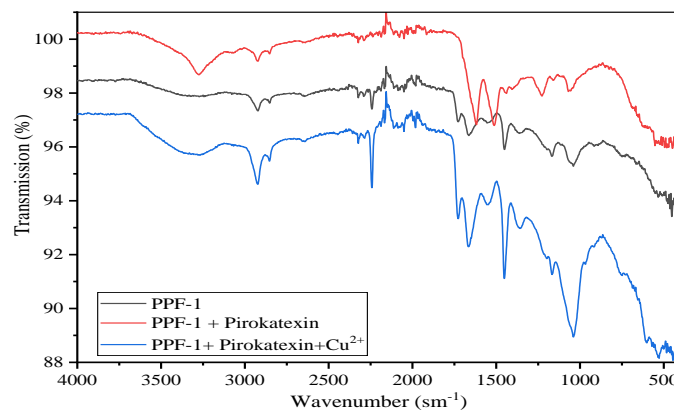
Tadqiqot davomida immobillangan va metall ion sorbsiyalangan tolali sorbentlar rengen-fluoresset tahlili yordamida tahlil qilindi.



3-rasm. PPF-1/pirokatexol binafshasi/Cu(II) matritsasining rengen fluorescent tahlili

Yuqoridagi tasvirdan ko'rinib turibdiki, metall ion sorbsiyasidan keyin Cu(II) ionining foiz ko'rsatgichi 27,6 % ni tashkil qilgan hamda ushbu ko'rsatgich Cu(II) ionining immobillangan sorbentga yaxshi sorbsiyalanganligini tasdiqlaydi.

PPF-1 sorbentining avval, immobillashdan keying va metall ion sorbsiyasidan keyingi IQ-spektrlardagi o'zgarishlar tahlil qilindi. PPF-1 polimerining IQ spektrlari o'rganilganda, polimer tuzilishiga xos bo'lgan funksional va analitik guruhlariga tegishli bir qator xarakterli yutilish chiziqlari aniqlandi. PPF-1 matritsasini Cu(II) ion bilan modifikatsiyalanishidan oldin va keyin olingan IQ-spektroskopiy natijalari FTIR spektrlarda bir nechta tor diapazonlarda sezilarli o'zgarishlarga olib kelgani qayd etildi. Xususan, $\sim 1621 \text{ cm}^{-1}$ da paydo bo'lgan yutilish chizig'i ferronga xos C=O valent tebranishini ko'rsatib, Cu(II) bilan koordinatsiyalanish jarayonida uning intensivligi ortdi va biroz siljidi. $1620\text{--}1650 \text{ cm}^{-1}$ diapazonidagi yangi chiziqlar aromatik halqa tebranishlari hamda C=N, C=C valent tebranishlariga tegishli bo'lib, Pirokatexin binafsha molekulasi bilan polimer sorbenti o'rtasida o'zaro ta'sir mavjudligini ko'rsatadi. 600 cm^{-1} dan pastda aniqlangan aniq yutilish chizig'i Cu-N koordinatsion bog'lariga xos bo'lib, metal-ligand kompleksining hosil bo'lganini tasdiqlaydi. Shu bilan birga, $1550\text{--}1400 \text{ cm}^{-1}$ oralig'idagi yangi cho'qqilar N-O va C-N tebranishlariga tegishli bo'lib, ularning koordinatsion muhit ta'sirida o'zgarishini bildiradi. Ushbu spektral o'zgarishlar PPF-1 polimerining muvaffaqiyatli funktsionallanishi va Pirokatexin binafsha bilan Cu(II) o'rtasida koordinatsion kompleksning shakllanganini isbotlaydi.



2-rasm. PPF-1 sorbentining, PPF-1 sorbentida Pirokatexin binafshaning immobillanishi hamda sorbentda Pirokatexin binafshaning Cu(II) ion bilan hosil qilgan kompleksining IQ spektrlari

Avval ta'kidlanganidek, reagent molekulasi tarkibida –OH va –S=N– funksional guruhlar mavjud bo'lib, unda kislorod atomlari akseptor, azot atomlari esa donor sifatida ishtirok etadi va Cu(II) ion bilan bog'lanish hosil qiladi. Natijada, 2-rasm qismida ko'rsatilganidek, rangining sariqdan yashilga o'tishi kuzatiladi.

Xulosa. Ushbu tadqiqotda Cu(II) ionlarini aniqlash uchun PPF-1 matritsasiga immobillangan analitik reagent sifatida Pirokatexin binafsha reagenti tanlangan va ushbu reagentning qattiq fazadagi komplekslari o'rganildi. Reagentning analitik xususiyatlari saqlab qolinganda PPF-1 sorbentida immobillandi. Pirokatexin binafshaning immobillanishi samaradorligi 96 % ni tashkil qilib, reagentning deyarli to'liq matritsaga birikganini ko'rsatdi. Cu(II) ionini aniqlashda optimal pH qiymati atsetatli bufer eritmada pH-5,0 - 5,5 bo'lib, aynan shu sharoitda analitik signal maksimal darajaga erishadi. Shuningdek, Cu(II) aniqlashda reagent va metall ion hosil qilgan kompleks 610 nm ekanligi aniqlangan. Ushbu natijalar PPF-1/Pirokatexin binafsha tizimini

Cu(II) ionlarini aniqlashda yuqori sezgirlik va aniqlik bilan ajralib turadigan, suv sifatini monitoring qilish va analitik tahlillar uchun samarali va ishonchli vosita sifatida ko'rsatadi.

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