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Cu (II) IONINI SORBSION-SPEKTROFOTOMETRIK ANIQLASH**СОРБЦИОННО-СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ИОНОВ CU(II)****SORPTION-SPECTROPHOTOMETRIC DETERMINATION OF CU(II) ION****Kosimova Xurshida Rajabboyovna¹**¹O'zbekiston-Finlandiya pedagogika instituti, o'qituvchi**Bozorboyeva Ozoda Abdurajab qizi²**²Mirzo Ulug'bek nomidagi O'zbekiston Milliy universiteti, magistrant**Malikova Nodiraxon Komiljon qizi³**³Mirzo Ulug'bek nomidagi O'zbekiston Milliy universiteti, talaba**Raximov Samariddin Boxodirovich⁴** ⁴Mirzo Ulug'bek nomidagi O'zbekiston Milliy universiteti, PhD, dotsent**Yangibayev Azim Eshmurodovich⁵**⁵Mirzo Ulug'bek nomidagi O'zbekiston Milliy universiteti, (PhD)**Turg'unboyev Shavkatjon Shuhratjon o'g'li⁶** ⁶Farg'ona davlat universiteti, PhD, dotsent**Annotatsiya**

Tabiiy tola bo'lgan ipak fibroin sorbentga immobilangan nitrozin sarig'i bilan mis (II) ionini o'zaro kompleks hosil qilishi o'rganildi. Ushbu ishda mis (II) ionini aniqlashda tanlab ta'sir etuvchan, yuqori samarali bo'lgan analitik reagent tavsiya etilgan. Dastlab nitrozin sarig'ini ipak fibroinga immobilash xususiyatlari, so'ngra metall ionini bilan kompleks hosil qilishining analitik xossalari spektrofotometrik usulda o'rganilgan. Hosil bolgan kompleks turli spektroskopik va elektrokimyoviy usullar bilan o'rganildi. Ipak fibroin tolasiga immobilangan nitrozin sarig'i yordamida mis (II) ionini aniqlash jarayoni o'zining seliktivligi, quyi aniqlanish qiymatining kichikligi, natijalarning takrorlanuvchanligi, tezkorligi va regeneratsiya qulayligi bilan afzalliklarga ega. Immobilangan nitrozin sarig'i bilan mis (II) ionini kompleks hosil qilishida reagent va kompleksning spektr signallari mos ravishda 480 va 540 nm hosil bo'lgan, shuningdek ishlab chiqilgan usulda mis (II) ni quyi aniqlanish chegarasi 0,2 mg/ml oshmagan holda olingan natijalarda nisbiy standart chetlanish qiymati 0,033 dan kichikligi namoyon bo'lgan.

Аннотация

Изучено взаимодействие ионов меди (II) с иммобилизованным нитрозиновым желтым на натуральном волокне шелкового фиброина в качестве сорбента. В данной работе представлен селективный и высокоэффективный аналитический реагент для определения ионов меди (II). Сначала были изучены свойства иммобилизации нитрозинового желтого на шелковом фиброине, а затем аналитические характеристики образования комплекса с металлическим ионом с использованием спектрофотометрического метода. Полученный комплекс был изучен с помощью различных спектроскопических и электрохимических методов. Процесс определения ионов меди (II) с использованием иммобилизованного нитрозинового желтого на волокнах шелкового фиброина имеет преимущества, такие как селективность, низкий предел обнаружения, воспроизводимость результатов, быстрота и легкость регенерации. Спектроскопические сигналы реагента и образованного комплекса с ионами меди (II) были зарегистрированы на 480 нм и 540 нм соответственно. Кроме того, в разработанном методе предел нижнего обнаружения меди (II) был определен не более чем 0,2 мг/мл, при этом значение относительного стандартного отклонения оказалось менее 0,033.

Abstract

The interaction of copper (II) ions with immobilized nitrozin yellow on natural fiber silk fibroin as a sorbent was studied. This work presents a selective and highly efficient analytical reagent for the determination of copper (II) ions.

Initially, the properties of immobilizing nitrozin yellow onto silk fibroin were explored, followed by the analytical characteristics of complex formation with the metal ion using a spectrophotometric method. The resulting complex was studied using various spectroscopic and electrochemical methods. The process of determining copper (II) ions using immobilized nitrozin yellow on silk fibroin fibers has advantages such as selectivity, low detection limit, reproducibility of results, rapidity, and ease of regeneration. The spectroscopic signals of the reagent and the complex formed with copper (II) ions were found at 480 nm and 540 nm, respectively. Additionally, in the developed method, the lower detection limit of copper (II) was determined to be no more than 0.2 µg/ml, with the relative standard deviation value shown to be less than 0.033.

Kalit so'zlar: mis, nitrozin sarig'i, ipak fibroin, spektrofotometr, Kubelka-Munk funksiyasi, Buger-Lambert-Ber qonuni, korrelyatsiya koeffitsienti

Ключевые слова: медь, нитрозиновый желтый, шелковый фиброин, спектрофотометр, функция Кубелки-Мунка, закон Бугера-Ламберта-Бера, коэффициент корреляции.

Key words: copper, nitrozin yellow, silk fibroin, spectrophotometer, Kubelka-Munk function, Beer-Lambert-Bert law, correlation coefficient.

INTRODUCTION

Environmental pollution of many parts of the Earth becomes a serious problem last years. Some of these problems are related to pollution of the natural water with heavy metals. Due to the presence of metals in low concentration in water, it is not possible to detect them directly by various available methods. The use of the hybrid methods of detection by using immobilization of the organic reagents on various sorbents, in the order of the determination exact metal and extract them from complex mixture allows to ensure the selectivity of the method [1,2].

Copper is one of the most valuable and widely used metals in industry, and demand for this metal remains high due to its electrical conductivity, corrosion resistance, and antimicrobial properties. For this reason, mining and processing of the copper have huge ecology impact, as a water and soil pollution, releasing harmful gases into the atmosphere and loss of biodiversity. This contributes to the sustainable development of the industry and its long-term economic and ecological stability [3-5].

MATERIALS AND METHODS

The disodium salt of 2,4-dinitrobenzene-azo-1-naphthol-3,6-disulfoacid (nitrazine yellow) was used as an analytical reagent. Figure 1 shows the molecular structure of nitrazine yellow. As a functionally active group in nitrazine yellow, -OH and azo groups take part in forming a complex with a metal ion, while sulfo groups take part in binding with the matrix.

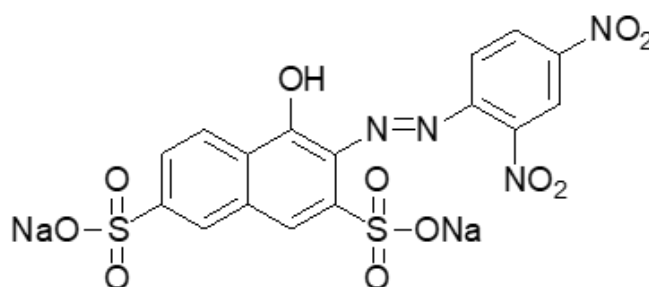
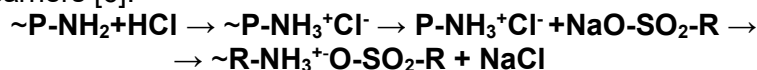


Figure 1. Molecular structure of nitrazine yellow

We use silk fibroin natural fibers, a waste raw material left over from silk fiber processing, as a solid phase.

Used equipment. The solution medium was measured using a pH meter "Mettler-Toledo LE438" (Switzerland) and "210 pH meter" (China). The reflection properties of the elements were analyzed in the "X-Rite eye-one-pro minispectrophotometer" (Switzerland) and the light absorption properties in the "EMC-30PC-UV Spectrophotometer" (Germany). To check the complex formation of the Cu (II) and nitrazine yellow were used conductometer "Mettler-Toledo LE703" (Switzerland). During the research, an organic reagent, which was initially selected as a carrier, was immobilized on silk fibroin. Below is the mechanism of immobilization of nitrazine yellow obtained as an analytical reagent to carriers [6]:



Immobilization increases the resistance of organic reagent layers to leaching and prevents photochemical degradation. Ion exchange fibrous sorbents differ from other granular sorbents by their surface area. This feature helps the sorption-desorption process to go well on its surface and to absorb ions of very small concentration [7].

Results and discussion

During the research, the optimal conditions (concentration, time, influence of environment) were studied for organic reagent immobilization on initially fibrous carriers. The optimal conditions for the formation of a copper ion complex with nitrazine yellow immobilized on a fibrous carrier were studied. The best results were achieved when the components were in the order of fiber+reagent+buffer+metal ion from a solution of universal buffer pH=2.12.

It is known that each substance absorbs or reflects electromagnetic rays at a certain wavelength. In order to study the immobilization of nitrazine yellow on the fiber, before and after the fiber is immobilized with a reagent, and Cu (II) ion with the immobilized nitrazine yellow the reflectance intensities of the complex formation with, was measured in "X-Rite eye-one-pro mini-spectrophotometer". The obtained results are presented in Figures 2 and 3.

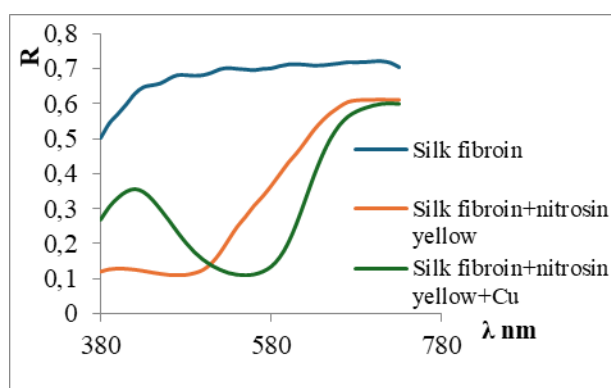


Figure 2. Silk fibroin fiber, nitrazine yellow immobilized on the fiber and the formed complex reflectance spectrums

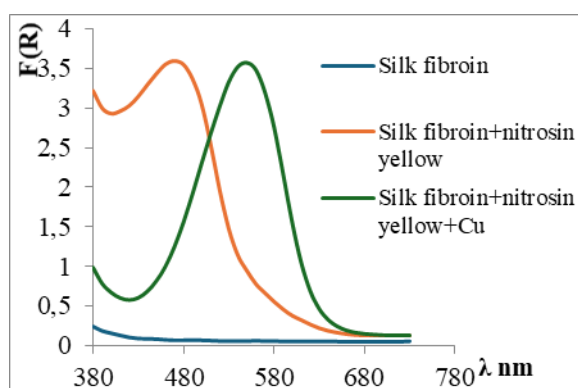


Figure 3. Silk fibroin fiber, expression of nitrazine yellow immobilized on the fiber and the formed complex reflectance spectrums in the Kubelka-Munk function

From the reflectance spectra in Figures 2 and 3, we conclude that nitrazine yellow is immobilized in silk fibroin fiber and its reflection area is $\lambda=480$ nm, bathochromic shift in the reflection spectrum of the complex formed from immobilized nitrazine yellow and Cu(II) observed. An ion with a wavelength of $\lambda=540$ nm. There is a contrast of $\Delta\lambda=60$ nm between the obtained spectra, which indicates the formation of a complex.

In order to verify the accuracy of the analysis results, the complex formation process was also studied in solution, where the process was carried out in solution and analyzed in an absorption spectrophotometer (Figure 4).

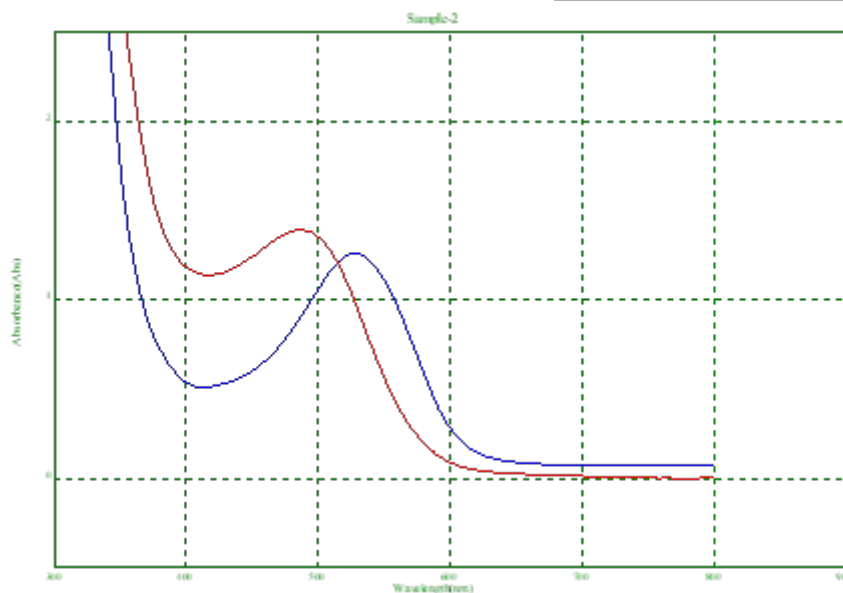


Figure 4. Absorption spectra of nitrazine yellow (red) and complex (blue).

The results in figure 4 show that the immobilized reagent and its complex have a 10 nm larger bathochromic shift than that in solution. This shift can be explained by the fact that rotational and vibrational energies are not spent in the fiber compared to the solution, and the molecular structure is rigid in the fiber.

Obedience to the Bouguer-Lambert-Beer law in the detection of Cu (II) ion with immobilized nitrazine yellow was studied. The obtained results are presented in Figure 5.

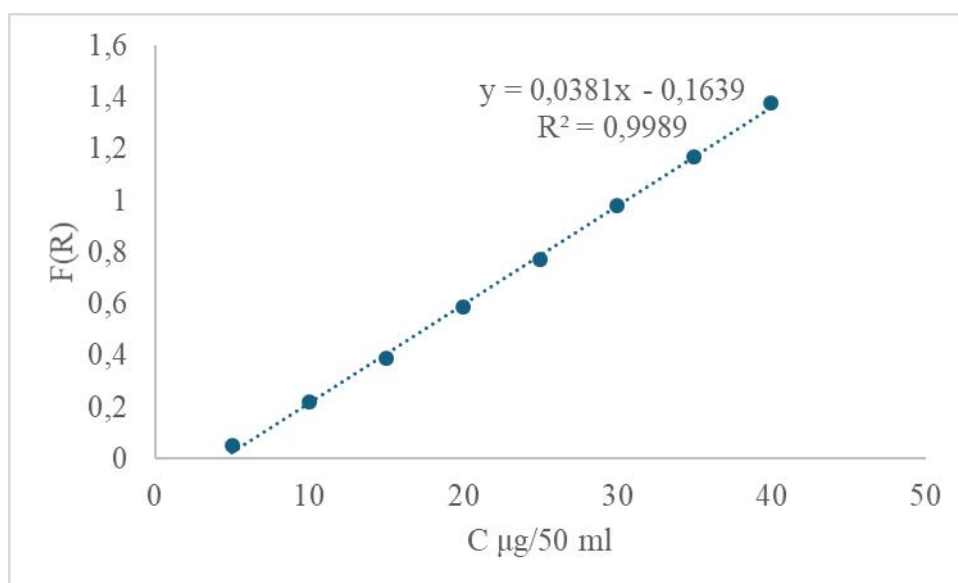


Figure 5. Graph of the complex obeying Beer's law.

The figure shows that the region of subordination to Beer's law is observed in the range of 0,16-1,6 µg/ml, with deviations from the straight line occurring at higher concentrations. It is evident that the value of the correlation coefficient tends to 1 ($R^2=0,9989$) with a direct connection of the graph, which indicates the reliability of the results obtained.

Table 1**Comparison of analytical properties of copper (II) complex formation with nitrazine yellow in solution and in solid phase**

Phase	pH	Λ_{\max} , R	Λ_{\max} , MeR.	$\Delta\lambda$	ϵ , 10^4	S.s., 10^{-4} $\mu\text{g}/\text{sm}^2$
Solution	2,12	480	530	50	2,24	1,0
Solid phase	2,12	480	540	60	7,46	0,53

The obtained results show that the reaction has enough contrast ($\Delta\lambda$) and high sensitivity. Copper (II) ion forms a stable complex compound with nitrazine yellow at pH=2,12. In this environment, several ions can interfere with the detection of copper (II) ion. Therefore, the effect of other ions was studied in the study of the selectivity of the developed method.

Therefore, in the experimental part of the work, the optimal conditions for the detection of copper (II) ion with nitrazine yellow were selected, the effect of neighboring ions was studied, and interfering ions were eliminated using masking and precipitation methods. The method of determining copper (II) ion with nitrosin yellow immobilized on silk fibroin fiber was used to analyze the composition of artificial compounds. The obtained results are presented in Table 2.

Table 2**Results of sorption-spectrophotometric determination of copper (II) ion from complex model compounds (P=0,95; n=4)**

Composition of the analyzed mixture, $\mu\text{g}/50$ ml	Found Cu, μg ($\bar{x} \pm \Delta X$)	S	S_r
Cu(10,0)+Fe(20,0)+Zn(20,0);	10,03 \pm 0,32	0,228	0,023
Cu(10,0)+Fe(20,0)+Ni(10,0);	10,09 \pm 0,29	0,210	0,021
Cu(10,0)+Co(10,0)+Cr(10,0)+Zn(20,0);	9,98 \pm 0,23	0,168	0,017
Cu(10,0)+Fe(10,0)+Pb(10,0)+Co(10,0);	10,12 \pm 0,32	0,229	0,023
Cu(10,0)+Cd(10,0)+Zn(10,0)+Mg(10,0)+Hg(10,0)	10,02 \pm 0,34	0,246	0,025

The data presented in the table show that the value of the relative standard deviation (S_r) in determining copper from the composition of secondary, tertiary and complex model compounds by the sorption-spectrophotometric method did not exceed 0.025, which indicates the accuracy and reproducibility of the developed methods. A conclusion was also made about the possibility of using the developed method to determine the copper (II) ion in the composition of natural objects with nitrazine yellow immobilized on silk fibroin.

CONCLUSION

Nitrosine yellow was used as an analytical reagent in the determination of copper (II) ion by sorption-spectrophotometric method. Silk fibroin fibrous sorbent, a local raw material, was proposed as a carrier for the immobilization of nitrazine yellow. The immobilization of the reagent to the fiber and the formation of a complex with copper (II) ion were studied by spectroscopic methods, in which the reflection spectra of the reagent and the complex had maximum values at 480 and 540 nm, respectively. The developed method made it possible to determine copper (II) from the composition of artificial mixtures with a lower detection limit of 0.16 $\mu\text{g}/\text{ml}$ with nitrazine yellow immobilized on silk fibroin, and the error did not exceed 0.025.

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