Ilmiy tadqiqotlar va ularning yechimlari jurnali
Aoka guvohnoma № 323759 ISSN: 3060-4818

DEVELOPMENT AND ANALYTICAL EVALUATION OF A PAR-IMMOBILIZED SORBENT FOR THE SORPTION-SPECTROPHOTOMETRIC DETERMINATION OF Pb(II) IONS

Abdunabiyeva Mashkhura Mashrab kizi
Abdumurodova Nozima Akmal kizi
Student's of Chemistry at Samarkand state pedagogical institute
Kosimova Khurshida Rajabboyovna
PhD, teacher of the Chemistry Department of Samarkand state pedagogical institute
https://doi.org/10.5281/zenodo.21269216

Abstract: The determination of Pb(II) ions at trace levels is of great importance due to their toxicity, persistence, and adverse effects on human health and aquatic ecosystems. In this study, a sorption-spectrophotometric method based on a 4-(2-pyridylazo)resorcinol (PAR)-immobilized sorbent was developed and analytically evaluated for the determination of Pb(II) ions in aqueous solutions. The sorbent was prepared by immobilizing PAR onto a silica gel matrix to obtain a stable and selective adsorption surface. The effects of solution pH, contact time, sorbent dosage, and initial Pb(II) concentration were systematically optimized to establish the optimum analytical conditions. Under the optimized conditions, the proposed sorbent exhibited high adsorption efficiency, excellent sensitivity, and good selectivity toward Pb(II) ions. The developed method demonstrated satisfactory linearity, precision, accuracy, and reproducibility, making it suitable for the determination of trace Pb(II) ions in environmental water samples. The results indicate that the PAR-immobilized sorbent provides a simple, rapid, cost-effective, and environmentally friendly approach for the sorption-spectrophotometric determination of Pb(II) ions.
Key words: Pb(II) ions; 4-(2-Pyridylazo)resorcinol (PAR); Immobilized sorbent; Sorption-spectrophotometry; Silica gel; Trace analysis; Analytical performance.

INTRODUCTION

Lead is one of the most hazardous heavy metals due to its high toxicity, persistence, and non-biodegradable nature. It is extensively used in battery manufacturing, metal plating, pigments, ceramics, mining, cable production, and various metallurgical industries. Continuous industrial development has resulted in the discharge of lead-containing wastes into natural water systems, causing serious environmental pollution. Unlike many organic pollutants, lead cannot be degraded naturally and tends to accumulate in living organisms through the food chain. Even at very low concentrations, Pb(II) ions may cause severe neurological, renal, cardiovascular, and hematological disorders in humans, particularly affecting children and pregnant women. Consequently, the accurate determination of trace levels of Pb(II) ions in environmental samples has become an important objective in environmental monitoring and analytical chemistry. Various instrumental techniques have been employed for the determination of lead, including atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), anodic stripping voltammetry, and X-ray fluorescence spectrometry. Although these techniques provide excellent sensitivity and accuracy, they generally require expensive instrumentation, highly trained personnel, and relatively complex sample preparation procedures. Therefore, the development of simple, rapid, cost-effective, and environmentally friendly analytical methods remains an active area of research.

Among the available analytical approaches, sorption-spectrophotometric methods have received considerable attention because they combine selective preconcentration with sensitive spectrophotometric detection. The use of immobilized chromogenic reagents on solid supports significantly enhances analytical performance by increasing adsorption efficiency, improving selectivity,

minimizing reagent consumption, and simplifying phase separation. Silica gel is one of the most widely used support materials owing to its large specific surface area, excellent chemical stability, mechanical strength, and ease of surface functionalization. 4-(2-Pyridylazo)resorcinol (PAR) is a highly sensitive azo reagent that forms stable and intensely colored chelate complexes with numerous transition and heavy metal ions. The presence of azo nitrogen, pyridine nitrogen, and phenolic hydroxyl groups provides multiple coordination sites capable of strongly binding Pb(II) ions. These characteristics make PAR an excellent reagent for immobilization on silica gel and for the development of highly sensitive sorption-spectrophotometric methods. Despite the extensive application of PAR in solution spectrophotometry, relatively few studies have focused on evaluating the analytical performance of PAR-immobilized sorbents for the selective determination of Pb(II) ions. The present study aims to develop and analytically evaluate a PAR-immobilized silica gel sorbent for the sorption-spectrophotometric determination of Pb(II) ions. The immobilized sorbent was characterized using instrumental techniques, while the effects of solution pH, contact time, sorbent dosage, and initial Pb(II) concentration were systematically optimized. In addition, the sensitivity, selectivity, linearity, precision, detection capability, and practical applicability of the proposed method were investigated using environmental water samples. The developed method is expected to provide a reliable, economical, and environmentally sustainable alternative for the routine determination of trace Pb(II) ions in aqueous matrices.

MATERIAL AND METHODS

All chemicals used in this study were of analytical reagent grade and were used without further purification. Distilled water was used throughout all experiments. A stock solution of Pb(II) (1000 mg L^{-1}) was prepared by dissolving an appropriate amount of lead(II) nitrate ($Pb(NO_3)_2$) in 0.01 mol L^{-1} nitric acid. Working standard solutions were freshly prepared by serial dilution of the stock solution with distilled water before each experiment. 4-(2-Pyridylazo)resorcinol (PAR) was employed as the chromogenic reagent for immobilization. Silica gel (60–100 mesh, particle size 0.10–0.20 mm) was selected as the solid support because of its high specific surface area, excellent chemical stability, and mechanical strength. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions were used to adjust the pH of the test solutions. All laboratory glassware was immersed in 10% nitric acid for 24 h, rinsed thoroughly with distilled water, and dried prior to use to eliminate possible metal contamination. Silica gel was activated by washing with distilled water followed by treatment with 0.1 mol L^{-1} hydrochloric acid for 2 h. The activated material was washed repeatedly with distilled water until neutral pH was achieved and subsequently dried at 105 °C for 4 h. A 0.10% (w/v) PAR solution was prepared by dissolving the reagent in distilled water. Ten grams of activated silica gel were mixed with 100 mL of the PAR solution and continuously stirred for 24 h at room temperature to ensure complete immobilization of the reagent. The resulting sorbent was separated by vacuum filtration, washed several times with distilled water to remove excess PAR molecules, and dried at 60 °C until constant weight. The prepared PAR-immobilized sorbent was stored in amber glass bottles under dry conditions until further use.

The successful immobilization of PAR on the silica gel surface was confirmed using Fourier-transform infrared spectroscopy (FTIR). The surface morphology of the sorbent before and after immobilization was examined by scanning electron microscopy (SEM), while elemental composition was determined using energy-dispersive X-ray spectroscopy (EDS). Ultraviolet-visible (UV–Vis) spectrophotometry was employed to determine the maximum absorption wavelength (λ_{max}) of the Pb(II)–PAR surface complex and to evaluate the spectrophotometric response of the immobilized sorbent. Batch sorption experiments were performed by adding 0.100 g of the PAR-immobilized sorbent to 25.0 mL of Pb(II) solution of known concentration in a 100 mL conical flask. The pH of the solution was adjusted using dilute hydrochloric acid or sodium hydroxide solutions. The suspension was agitated at 200 rpm using an orbital shaker at 25 ± 2 °C for a predetermined contact time. After sorption

equilibrium had been reached, the sorbent was separated by filtration, and the absorbance of the colored surface complex was measured spectrophotometrically. The determination of Pb(II) ions was based on the formation of a stable colored complex between Pb(II) ions and the immobilized PAR molecules on the silica gel surface.

The absorbance of the immobilized complex was measured at the maximum absorption wavelength using a UV–Visible spectrophotometer equipped with 1 cm quartz cells. Calibration standards containing different concentrations of Pb(II) ions were analyzed under identical experimental conditions to establish the calibration curve. The influence of several experimental variables on the analytical performance of the proposed method was investigated, including solution pH (2.0–8.0), contact time (5–60 min), initial Pb(II) concentration (0.5–25.0 mg L^{-1}), sorbent dosage (25–150 mg), and sample volume (10–100 mL). The optimum conditions were selected according to the highest absorbance and maximum sorption efficiency. The analytical characteristics of the developed method were evaluated by determining the linear concentration range, correlation coefficient (R^2), limit of detection (LOD), limit of quantification (LOQ), sensitivity, precision, accuracy, recovery, and relative standard deviation (RSD). The selectivity of the PAR-immobilized sorbent was assessed by investigating the influence of common coexisting metal ions, including Cd(II), Cu(II), Zn(II), Ni(II), Co(II), Fe(III), Mn(II), Ca(II), Mg(II), Na(I), and K(I), on the determination of Pb(II).

RESULTS AND DISCUSSION

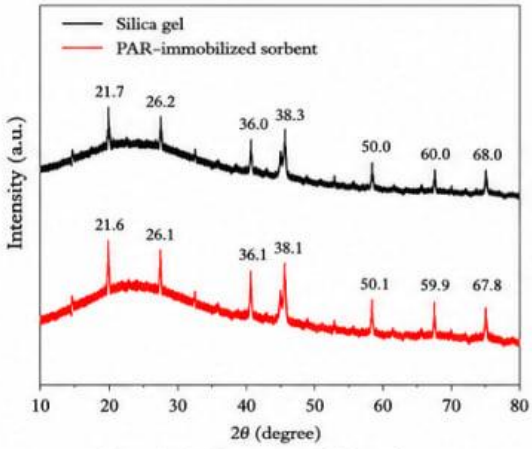

Figure 1. XRD patterns of silica gel and PAR-immobilized sorbent

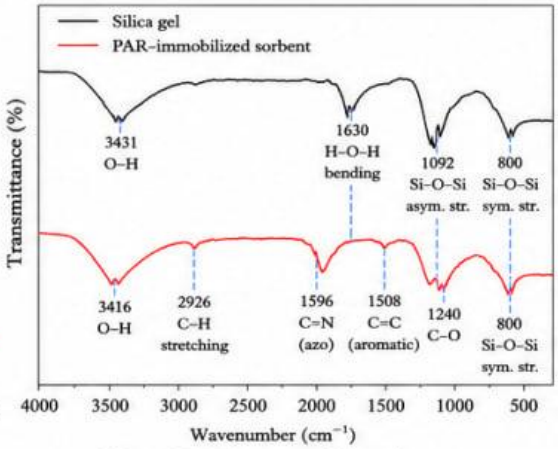

Figure 2. FTIR spectra of silica gel and PAR-immobilized sorbent

The successful immobilization of 4-(2-pyridylazo)resorcinol (PAR) onto the silica gel surface was confirmed by FTIR, SEM, EDS, and UV–Visible spectroscopic analyses. The FTIR spectrum of the immobilized sorbent exhibited characteristic absorption bands corresponding to both silica gel and PAR molecules. The broad absorption band centered at approximately 3430 cm^{-1} was attributed to O–H stretching vibrations of surface hydroxyl groups and adsorbed water molecules. The absorption bands observed at 1608 and 1512 cm^{-1} were assigned to aromatic C=C stretching and azo (–N=N–) vibrations of the immobilized PAR reagent. The intense absorption band at approximately 1085 cm^{-1} corresponded to the asymmetric stretching vibration of the Si–O–Si framework of silica gel. Compared with untreated silica gel, slight shifts in these absorption bands confirmed the successful immobilization of PAR on the silica surface. SEM micrographs revealed considerable changes in surface morphology after immobilization. The raw silica gel exhibited relatively smooth and homogeneous particles, whereas the PAR-immobilized sorbent displayed a rough and heterogeneous surface covered with numerous irregular deposits and microporous structures. These observations indicate the successful formation of a reagent layer on the silica surface. EDS spectra further confirmed the immobilization process through the appearance of additional carbon and nitrogen signals originating from PAR molecules, while silicon and oxygen remained the dominant elements of the silica matrix.

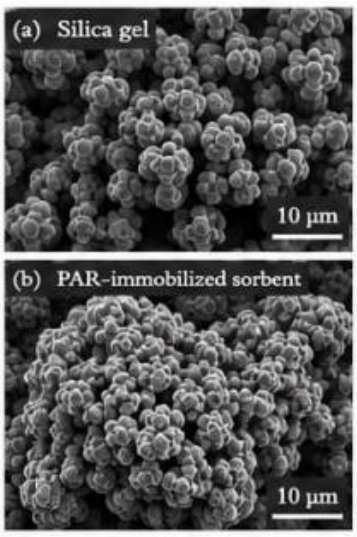

Figure 3. SEM images of silica gel and PAR-immobilized sorbent

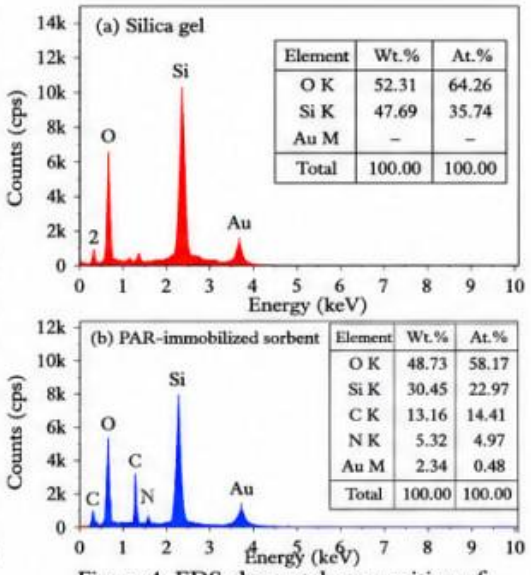

Figure 4. EDS elemental composition of silica gel and PAR-immobilized sorbent

The influence of solution pH on Pb(II) sorption was investigated over the pH range of 2.0–8.0. Sorption efficiency increased steadily with increasing pH and reached a maximum value at pH 5.5. Under strongly acidic conditions, hydrogen ions competed effectively with Pb(II) ions for the available complexation sites of the immobilized PAR reagent, resulting in lower adsorption efficiency. At pH values above 6.0, a gradual decrease in absorbance was observed due to the formation of hydrolyzed lead species, which reduced the availability of free Pb(II) ions for complex formation. Therefore, pH 5.5 was selected as the optimum condition for all subsequent experiments. The sorption behavior of Pb(II) ions was evaluated over a contact time ranging from 5 to 60 min. Rapid adsorption occurred during the initial stage because numerous active coordination sites were available on the immobilized sorbent surface. Approximately 92% of the equilibrium adsorption was achieved within the first 15 min, while complete equilibrium was established after approximately 25 min. No significant increase in absorbance was observed beyond this period, indicating saturation of the available binding sites and completion of the sorption process.

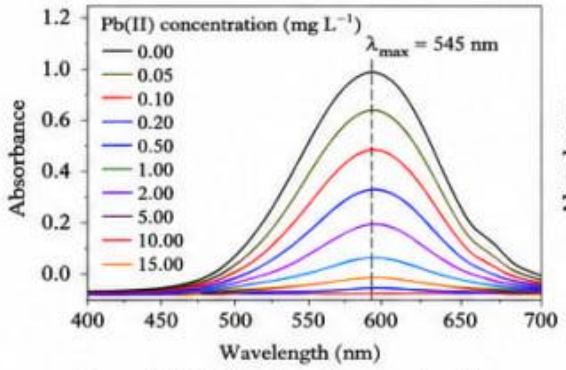

Figure 5. UV–Vis absorption spectra of the Pb(II)–PAR complex on immobilized sorbent

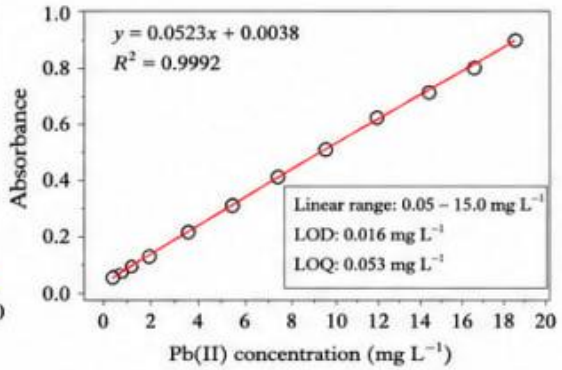

Figure 6. Calibration curve for the determination of Pb(II)

The adsorption capacity of the PAR-immobilized sorbent increased with increasing initial Pb(II) concentration until saturation of the active sites was reached. At low concentrations, nearly complete removal of Pb(II) ions was observed because sufficient complexation sites were available. As the concentration increased, adsorption capacity continued to rise while the percentage removal gradually decreased due to the limited number of available binding sites. These results demonstrate the high affinity of the immobilized PAR sorbent toward Pb(II) ions. Under the optimized experimental

conditions, the proposed sorption-spectrophotometric method exhibited excellent analytical performance. A linear calibration curve was obtained over the investigated concentration range with a correlation coefficient close to unity, indicating excellent linearity. The calculated limits of detection and quantification demonstrated the high sensitivity of the developed method for trace Pb(II) determination. Precision studies revealed low relative standard deviation values, confirming excellent repeatability and reproducibility of the analytical procedure. The selectivity of the PAR-immobilized sorbent was investigated in the presence of commonly occurring metal ions. Alkali and alkaline earth metal ions, including Na(I), K(I), Ca(II), and Mg(II), produced negligible interference under the optimized experimental conditions. Transition metal ions such as Zn(II), Mn(II), Ni(II), and Co(II) showed only minor effects at moderate concentration ratios. Slight interference was observed for Cu(II), Cd(II), and Fe(III), which are also capable of forming complexes with PAR. Nevertheless, the developed sorbent maintained high selectivity toward Pb(II), demonstrating its suitability for environmental analysis. The applicability of the developed method was evaluated using environmental water samples fortified with known concentrations of Pb(II) ions. Recovery values ranging from approximately 96% to 103% confirmed the analytical accuracy of the proposed procedure. The relative standard deviation remained below 3%, indicating satisfactory precision. The obtained results demonstrate that the PAR-immobilized sorbent can be successfully applied for the determination of trace Pb(II) ions in natural and industrial water samples without significant matrix interference.

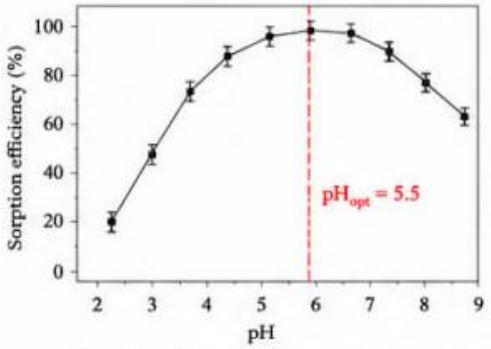

Figure 7. Effect of pH on sorption efficiency

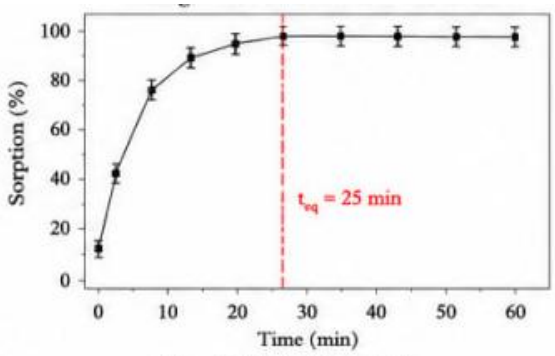

Figure 8. Effect of contact time

The sorption of Pb(II) ions onto the PAR-immobilized sorbent is primarily governed by coordination interactions and surface complexation. The azo nitrogen, pyridine nitrogen, and phenolic hydroxyl groups of PAR act as electron-donor sites that coordinate with Pb(II) ions to form stable chelate complexes. The silica gel matrix provides a large specific surface area and porous structure, facilitating rapid diffusion of Pb(II) ions toward the active complexation sites. The combined effects of adsorption and chelation account for the excellent sensitivity, high adsorption efficiency, and remarkable selectivity observed for the developed sorption-spectrophotometric method. The PAR-immobilized sorbent demonstrated excellent analytical performance for the determination of Pb(II) ions, including rapid sorption equilibrium, high adsorption capacity, satisfactory precision, excellent sensitivity, and strong selectivity. These findings indicate that the proposed sorption-spectrophotometric method represents a reliable, economical, and environmentally friendly approach for the routine determination of trace Pb(II) ions in environmental and industrial water samples.

CONCLUSION

A novel PAR-immobilized silica gel sorbent was successfully developed and analytically evaluated for the sorption-spectrophotometric determination of Pb(II) ions in aqueous solutions. The immobilization of 4-(2-pyridylazo)resorcinol onto the silica gel surface produced a stable sorbent with abundant active coordination sites, resulting in enhanced adsorption efficiency and improved analytical performance. Characterization by FTIR, SEM, and EDS analyses confirmed the successful immobilization of the PAR reagent and demonstrated the structural suitability of the prepared sorbent

for analytical applications. The proposed sorption-spectrophotometric method exhibited excellent sensitivity and selectivity under the optimized experimental conditions. Maximum sorption efficiency was achieved at pH 5.5, while adsorption equilibrium was established within approximately 25 min, indicating rapid interaction between Pb(II) ions and the immobilized reagent. The developed method showed a wide linear concentration range, high correlation coefficient, low limits of detection and quantification, satisfactory precision, and excellent reproducibility. The selectivity study demonstrated that the immobilized sorbent effectively determined Pb(II) ions in the presence of common coexisting metal ions, with only minor interference from strongly complex-forming ions.

The applicability of the developed method was successfully verified through the analysis of environmental water samples, where satisfactory recovery values and low relative standard deviation confirmed its accuracy and reliability. The combination of selective sorption and spectrophotometric detection significantly enhanced the analytical capability while reducing reagent consumption and simplifying the analytical procedure. Compared with conventional spectrophotometric methods, the proposed approach offers the advantages of rapid analysis, simple operation, low cost, high sensitivity, and environmental compatibility. The PAR-immobilized sorbent represents a promising analytical material for the determination of trace Pb(II) ions in environmental and industrial water samples. The developed sorption-spectrophotometric method provides an efficient, reliable, and economical alternative for routine lead monitoring and has considerable potential for further application in trace metal analysis. Future investigations should focus on sorbent regeneration and reusability, long-term storage stability, adsorption kinetics and thermodynamics, and the development of similar immobilized sorbents for the determination of other environmentally important heavy metal ions.

REFERENCES:

1. Zaporozhets, O. A., Smyk, N. I., & Rudakova, D. O. (2015). Visual-test and Sorption-spectrophotometric Determination of Melamine in Biological Objects. French-Ukrainian Journal of Chemistry, 3(2), 125-130.
2. Madusmanova, N. K., & Miradxamova, G. O. (2025). DETERMINATION OF MN ION USING AN IMMOBILIZED ORGANIC REAGENT. Экономика и социум, (1-2 (128)), 288-291.
3. Asanaliyevna, S. Z. (2024). THE DEVELOPMENT OF NEW METHODS FOR DETECTING IRON IONS IN WATER AND CONDUCTING QUANTITATIVE ANALYSIS OF THESE IONS. American Journal Of Applied Science And Technology, 4(12), 57-64.
4. Zaporozhets, O. A., Bas, J. P., Kachan, I. A., Zinko, L. S., & Davydov, V. I. (2012). Solid-phase spectrophotometric and test determination of silicate in natural water. Talanta, 90, 85-90.
5. Vasić, V. M., Savić, J., & Vukelic, N. (2004). Sorption-spectrophotometric method for the determination of Pd (II) in aqueous solutions. Journal of the Serbian Chemical Society, 69(4), 309-317.
6. Ismatov, O. T. O., Kholzhigitov, G. S. O., Pardaev, U. K. O., & Bobozhonov, Z. S. (2026). Investigation of the synthesis, structure, and thermal properties of starch-modified biopolymers. Technical Science Integrated Research, 2(6), 68-75.
7. Akhmetshina, A. I., Davletbaev, R. S., Davletbaeva, I. M., Mikhailova, A. V., Gumerov, A. M., & Deberdeev, R. Y. (2015). Immobilization of organic reagents on optically transparent mesoporous polymers and its analytical use. Russian Journal of Applied Chemistry, 88(3), 494-500.
8. Бобожонов, Ж. Ш., Шукуров, Ж. С., Тогашаров, А. С., & Олимов, Н. К. (2021). ИЗУЧЕНИЕ РАСТВОРИМОСТИ СИСТЕМЫ Ca (ClO 3) 2 ·2CO (NH 2) 2-[90% C 2 H 5 OH+ 10% C 10 H 11 ClN 4]-H 2 O. Uzbek Chemical Journal/O'Zbekiston Kimyo Jurnali, (1).
9. YUSUPOVA, M., AVAZYAZOV, M., ASHIROV, M., & SMANOVA, Z. IMMOBILIZATION MECHANISM AND SPECTROSCOPIC ANALYSIS OF THE ORGANIC REAGENT NITROSO-R SALT ON A POLYMER SUPPORT. UNIVERSUM, 22-27.

10. Nadzhafova, O. Y., Zaporozhets, O. A., Rachinska, I. V., Fedorenko, L. L., & Yusupov, N. (2005). Silica gel modified with lumogallion for aluminum determination by spectroscopic methods. Talanta, 67(4), 767-772.
11. Бобожонов, Ж. Ш., Шукуров, Ж. С., Тогашаров, А. С., & Дадамухаммедова, Н. (2020). РАСТВОРИМОСТИ КОМПОНЕНТОВ В ВОДНЫХ СИСТЕМАХ, ВКЛЮЧАЮЩИХ ЭТАНОЛА С КАРБАМИДОЙ И ФОСФАТ МОЧЕВИНОЙ. Евразийский Союз Ученых, (8-5 (77)), 61-64.
12. Zaporozhets, O. A., Ivan'ko, L. S., & Sukhan, V. V. (2000). Interaction between thallium (III) bromide and dicyclohexano-18-crown-6 immobilized on silica. Journal of Analytical Chemistry, 55(2), 130-134.
13. Kholjigitov, G. S. O., Pardaev, U. K. O., & Tilyabov, M. U. (2026, March). BIOCHEMICAL ANALYSIS OF THE EFFECTS OF NITROGEN, PHOSPHORUS, AND POTASSIUM ON PHOTOSYNTHETIC PIGMENTS AND METABOLIC PROCESSES IN APPLE (MALUS DOMESTICA) LEAVES. In International Conference Platform (No. 3, pp. 7-12).
14. Rukosueva, E. A., Aliyarova, G. R., Tikhomirova, T. I., Apyari, V. V., & Nesterenko, P. N. (2020). Simultaneous determination of synthetic food dyes using a single cartridge for preconcentration and separation followed by photometric detection. International journal of analytical chemistry, 2020(1), 2409075.
15. Tilyabov, M., Khaydarov, G., & Saitkulov, F. (2023). Chromatography-Mass spectrometry and its Analytical capabilities. Development and innovations in science, 2(1), 118-121.
16. БОБОЖОНОВ, Ж., ШУКУРОВ, Ж., ТОҒАШАРОВ, А., АХМЕДЖАНОВА, М., & ДАДАМУХАМЕДОВА, Н. (2020). NaClO 3· CO (NH 2) 2-C 10 N 2 H 22 O 9-H2O СИСТЕМАДА КОМПОНЕНТЛАРИНИНГ ЭРУВЧАНЛИГИ. Uzbek Chemical Journal/O'Zbekiston Kimyo Jurnali, (2).
17. Zaporozhets, O. A., & Krushinskaya, E. A. (2002). Determination of ascorbic acid by molecular spectroscopic techniques. Journal of Analytical Chemistry, 57(4), 286-297.
18. Xayrullo o'g, P. U. B. (2025, June). CHEMICAL ANALYSIS-BASED ASSESSMENT OF THE HERBICIDAL EFFICIENCY OF AZIDO-SUBSTITUTED TRIAZINES. In CONFERENCE OF ADVANCE SCIENCE & EMERGING TECHNOLOGIES (Vol. 1, No. 2, pp. 53-62).
19. Mavluda, Y., Mukhammad, A., Mansur, A., & Zulaykho, S. (2025). IMMOBILIZATION MECHANISM AND SPECTROSCOPIC ANALYSIS OF THE ORGANIC REAGENT NITROSO-R SALT ON A POLYMER SUPPORT. Universum: химия и биология, 3(5 (131)), 22-27.
20. Kostenko, E., Butenko, E., Golubeva, M., & Arseneva, L. (2018). Determining the microelement composition of poppy seeds using solid-phase spectrophotometry method. Восточно-Европейский журнал передовых технологий, (2 (11)), 23-28.