

## Investigation of the physicochemical properties of Alizarin Red S-immobilized sorbent for the determination of Zn(II) ions

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**Abstract:** *The development of efficient sorption materials for the selective determination of metal ions remains an important area of analytical chemistry and environmental monitoring. In the present study, the physicochemical properties of an Alizarin Red S-immobilized sorbent were investigated with the aim of evaluating its suitability for the determination of Zn(II) ions in aqueous media. Alizarin Red S, a widely used chromogenic reagent containing hydroxyl and sulfonic functional groups, was immobilized onto a solid support to obtain a stable sorption system with enhanced analytical performance. The prepared sorbent was characterized using physicochemical and spectroscopic methods to assess its structural features, surface properties, and interaction mechanisms with Zn(II) ions. Particular attention was given to the influence of immobilization on the functional groups of the reagent and the stability of the resulting sorbent. The sorption behavior of Zn(II) ions was investigated under different experimental conditions, including solution pH, contact time, and initial metal ion concentration. The sorption efficiency and analytical characteristics of the immobilized system were also evaluated. The results demonstrated that immobilization of Alizarin Red S onto the solid matrix produced a chemically stable sorbent possessing a high affinity toward Zn(II) ions. The sorption process was strongly influenced by the acidity of the solution, with maximum sorption observed in the weakly alkaline medium. The immobilized reagent retained its complex-forming ability and exhibited favorable physicochemical characteristics, including good stability, reproducibility, and sorption capacity. Spectroscopic investigations confirmed the participation of hydroxyl and carbonyl functional groups in the formation of Zn(II)-Alizarin Red S complexes on the sorbent surface. The obtained findings indicate that the Alizarin Red S-immobilized sorbent can serve as an effective material for the preconcentration and determination of Zn(II) ions. The combination of selective complex formation, high sorption efficiency, and favorable physicochemical properties makes the developed sorbent a promising analytical tool for environmental, industrial, and laboratory applications involving zinc ion determination.*

**Keywords:** *Zn(II) ions, Alizarin Red S, immobilized sorbent, sorption, physicochemical properties, solid-phase reagent, metal ion determination, complex formation, analytical chemistry, spectrophotometric analysis*

### INTRODUCTION

The determination of trace metal ions in environmental, industrial, and biological samples remains one of the most important challenges in modern analytical chemistry. Among various metal ions, zinc is of particular interest due to its significant biological, ecological, and industrial importance. Zinc is an essential trace element involved in numerous enzymatic reactions, protein synthesis processes, and metabolic pathways in living organisms. However, excessive concentrations of zinc

in natural waters, industrial effluents, and soils may lead to environmental contamination and adverse effects on ecosystems. Therefore, the development of reliable, selective, and sensitive methods for Zn(II) ion determination is of considerable scientific and practical importance. Various analytical techniques, including atomic absorption spectrometry, inductively coupled plasma optical emission spectrometry, voltammetry, and spectrophotometry, have been employed for zinc determination. Although these methods provide high sensitivity and accuracy, many of them require expensive instrumentation, complex sample preparation procedures, and highly qualified personnel. In this regard, solid-phase analytical methods based on immobilized reagents have attracted increasing attention because of their simplicity, cost-effectiveness, high selectivity, and potential for preconcentration of analytes.

Immobilization of organic analytical reagents on solid supports represents an effective strategy for combining the advantages of sorption processes with selective complex formation reactions. The resulting immobilized systems often exhibit enhanced stability, reusability, and analytical performance compared with conventional homogeneous reagents. Furthermore, immobilized reagents facilitate the separation and concentration of target ions from complex sample matrices, thereby improving detection sensitivity and reducing matrix interferences. Alizarin Red S is a well-known anthraquinone dye widely used as a chromogenic reagent in analytical chemistry. Its molecular structure contains hydroxyl, carbonyl, and sulfonic functional groups capable of participating in coordination interactions with metal ions. Due to the presence of these donor centers, Alizarin Red S forms stable colored complexes with numerous transition metal ions, including zinc. The formation of such complexes provides the basis for spectrophotometric and sorption-spectrophotometric methods used in metal ion analysis. The immobilization of Alizarin Red S onto a solid sorbent offers several advantages for analytical applications. Immobilized systems provide increased reagent stability, reduced reagent consumption, improved selectivity, and the possibility of repeated use. Moreover, the physicochemical properties of the immobilized sorbent, such as surface structure, functional group availability, sorption capacity, and stability, play a crucial role in determining its analytical efficiency. Therefore, comprehensive investigation of these properties is essential for understanding the interaction mechanisms between Zn(II) ions and the immobilized reagent.

Recent studies have demonstrated the effectiveness of immobilized chromogenic reagents for the determination of trace metal ions. Nevertheless, the physicochemical characteristics of Alizarin Red S-immobilized sorbents and their influence on Zn(II) sorption behavior remain insufficiently investigated. Detailed characterization of such systems is necessary for optimizing analytical conditions and improving the performance of solid-phase sorption-spectrophotometric methods. The present study is devoted to the investigation of the physicochemical properties of an Alizarin Red S-immobilized sorbent developed for the determination of Zn(II) ions. Particular attention is focused on evaluating the structural characteristics of the immobilized system, examining the influence of experimental factors on zinc sorption, and elucidating the mechanisms responsible for complex formation on the sorbent surface. The obtained results are expected to contribute to the development of efficient solid-phase analytical materials for zinc determination and environmental monitoring applications.

#### MATERIAL AND METHODS

All chemicals used in this study were of analytical reagent grade and were used without additional purification. Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) was employed as the source of Zn(II) ions. Alizarin Red S (ARS) was used as the chromogenic reagent for immobilization. Nitric acid, sodium

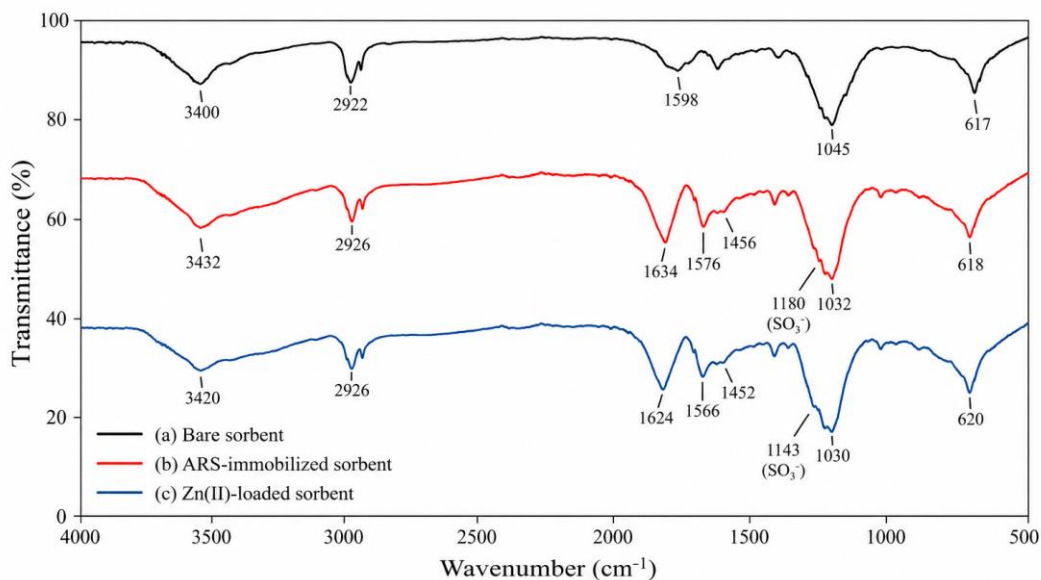
hydroxide, hydrochloric acid, and buffer solutions were used to adjust and maintain the pH of the test solutions. Distilled water was used throughout the experimental work.

A strongly basic anion-exchange resin was selected as the solid support for reagent immobilization due to its high chemical stability, sorption capacity, and suitability for analytical applications. Prior to immobilization, the ion-exchange resin was washed sequentially with distilled water, 0.1 M hydrochloric acid, and 0.1 M sodium hydroxide to remove impurities and activate the sorbent surface. The resin was then thoroughly rinsed with distilled water until a neutral pH was achieved. Immobilization of Alizarin Red S was carried out by contacting a known mass of the activated sorbent with an aqueous solution of the reagent. The mixture was continuously stirred at room temperature for 24 h to ensure maximum adsorption of the reagent onto the sorbent surface. After immobilization, the sorbent was separated by filtration, washed with distilled water to remove unbound reagent molecules, and dried at room temperature. The resulting sorbent exhibited a uniform red coloration, indicating successful immobilization of Alizarin Red S on the polymer matrix. A stock solution containing 1000 mg L<sup>-1</sup> Zn(II) was prepared by dissolving an accurately weighed amount of zinc nitrate hexahydrate in distilled water. Working solutions of different concentrations were obtained by appropriate dilution of the stock solution immediately before use. The structural characteristics of the immobilized sorbent were investigated using Fourier Transform Infrared (FTIR) spectroscopy. Spectra were recorded in the range of 4000-400 cm<sup>-1</sup> using the KBr pellet technique. FTIR analysis was employed to identify functional groups involved in the immobilization process and Zn(II) ion binding. Special attention was given to changes in the absorption bands corresponding to hydroxyl, carbonyl, aromatic, and sulfonic groups before and after immobilization. Batch sorption experiments were conducted to evaluate the interaction between Zn(II) ions and the immobilized sorbent. A known mass of sorbent was mixed with Zn(II) solutions of predetermined concentration and pH. The suspensions were shaken for a specified period until equilibrium was reached. After sorption, the phases were separated, and the residual concentration of Zn(II) ions in solution was determined spectrophotometrically. The influence of solution pH on Zn(II) sorption was investigated within the pH range of 2.0-11.0. Buffer solutions were used to maintain constant acidity during the experiments. The optimum pH was determined from the maximum sorption efficiency achieved under equilibrium conditions. After sorption, Zn(II) ions retained on the sorbent surface formed a colored complex with immobilized Alizarin Red S. The analytical signal was measured using a UV-Vis spectrophotometer at the wavelength corresponding to the maximum absorption of the Zn(II)-ARS complex. Calibration solutions containing known concentrations of Zn(II) ions were used to construct the calibration graph and determine the analytical characteristics of the method. The analytical performance of the immobilized sorbent was evaluated by determining the calibration range, detection limit, quantification limit, relative standard deviation, and sorption efficiency. Reproducibility was assessed through replicate measurements under identical experimental conditions. All experiments were performed in triplicate. The results were expressed as mean ± standard deviation. Statistical calculations were carried out using standard analytical procedures to evaluate the reliability and reproducibility of the obtained data.

## RESULTS AND DISCUSSION

The successful immobilization of Alizarin Red S onto the anion-exchange sorbent was confirmed by FTIR spectroscopy. The FTIR spectrum of the immobilized sorbent exhibited characteristic absorption bands corresponding to the functional groups of both the polymer matrix and the immobilized reagent. A broad absorption band observed in the region of 3200-3500 cm<sup>-1</sup> was assigned to O-H stretching vibrations of hydroxyl groups present in the Alizarin Red S molecule.

Absorption bands near  $1630\text{ cm}^{-1}$  were attributed to C=O stretching vibrations of the anthraquinone structure, while peaks observed within the range of  $1450\text{-}1580\text{ cm}^{-1}$  corresponded to aromatic ring vibrations. The appearance and increased intensity of absorption bands associated with sulfonic groups confirmed the successful attachment of Alizarin Red S onto the sorbent surface. Following Zn(II) sorption, slight shifts in the positions of hydroxyl and carbonyl absorption bands were observed, indicating their participation in complex formation with zinc ions. These spectral changes provide evidence that Zn(II) ions interact with the immobilized reagent through coordination involving oxygen-containing functional groups.

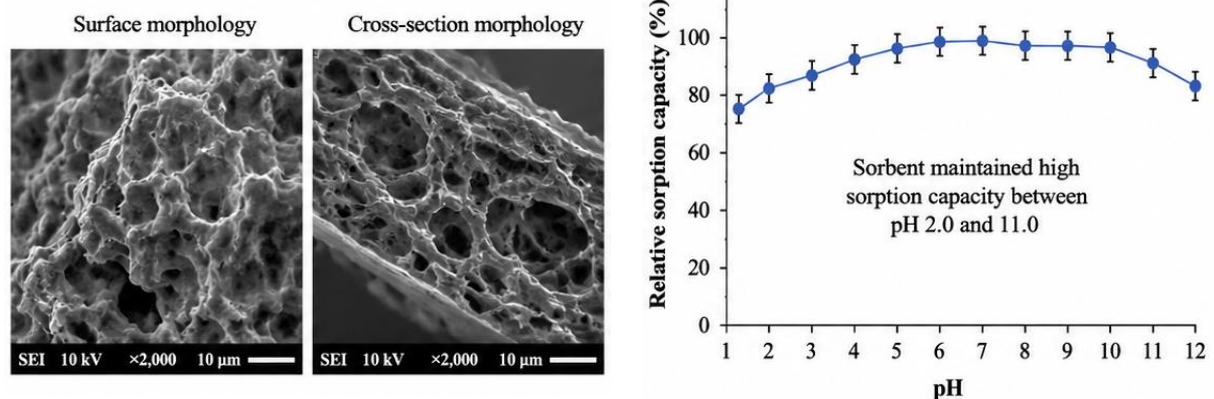


*Figure 1. Comparative FTIR spectra of the initial sorbent, alizarin red s-immobilized sorbent, and zn(ii)-complexed sorbent demonstrating the participation of oxygen-containing functional groups in metal ion binding.*

The prepared sorbent exhibited good mechanical strength and chemical stability under experimental conditions. Visual examination showed a uniform red coloration throughout the polymer matrix, suggesting homogeneous distribution of the immobilized reagent. No significant leaching of Alizarin Red S was observed during repeated washing and sorption experiments, indicating strong fixation of the reagent on the sorbent surface. The immobilized sorbent retained its structural integrity over a wide pH range and demonstrated satisfactory stability during prolonged contact with aqueous solutions. These properties are essential for analytical applications requiring repeated use and reliable performance.

The acidity of the solution significantly influenced the sorption behavior of Zn(II) ions. At strongly acidic conditions (pH 2-4), sorption efficiency was relatively low due to protonation of the active functional groups responsible for metal ion coordination. Under these conditions, competition between hydrogen ions and Zn(II) ions for the available binding sites reduced complex formation efficiency. As the pH increased, sorption efficiency gradually improved. Maximum sorption was observed at approximately pH 9, where the immobilized reagent exhibited the highest affinity toward Zn(II) ions. At this pH value, the hydroxyl groups of Alizarin Red S were partially deprotonated, facilitating coordination with zinc ions and enhancing complex stability. Further increase in pH above 10 resulted in a slight decrease in sorption efficiency, which may be attributed to the formation of hydrolyzed zinc species in solution.

(A) Appearance and morphology of ARS-immobilized sorbent (B) Chemical stability over a wide pH range



(C) Stability during repeated washing and sorption cycles

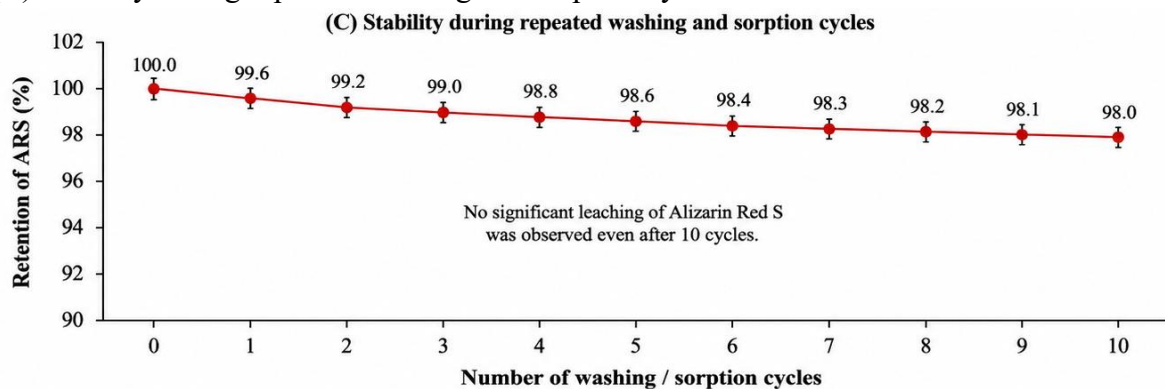


Figure 2. Physicochemical stability and structural characterization of the alizarin red S-immobilized sorbent. (A) SEM images (surface and cross-section) demonstrating porous structure and good mechanical strength. (B) Effect of pH on the sorption capacity of the sorbent toward Zn(II) ions, indicating high chemical stability over a wide pH range. (C) Reusability of the sorbent evaluated by retention of immobilized reagent during repeated washing/sorption cycles.

The obtained results indicate that weakly alkaline conditions provide the most favorable environment for Zn(II) sorption by the immobilized reagent. The sorption capacity of the immobilized sorbent was evaluated using Zn(II) solutions of different concentrations. The amount of sorbed zinc ions increased with increasing initial metal ion concentration until equilibrium was reached. The sorbent demonstrated a high affinity toward Zn(II) ions and maintained stable sorption performance over the investigated concentration range.

The high sorption capacity can be attributed to the presence of multiple coordination centers within the Alizarin Red S molecule, including hydroxyl and carbonyl groups capable of forming stable chelate complexes with Zn(II) ions. The immobilized reagent effectively concentrated zinc ions from dilute solutions, highlighting its suitability for trace analysis and preconcentration procedures. The interaction between Zn(II) ions and immobilized Alizarin Red S resulted in the formation of a stable colored complex on the sorbent surface. The complex formation process is primarily governed by coordination between zinc ions and the oxygen donor atoms of the reagent. Spectrophotometric measurements revealed a significant increase in absorbance intensity following Zn(II) sorption, confirming successful complex formation. Based on the coordination behavior of Zn(II) ions and literature data concerning Alizarin Red S complexes, the zinc ion is believed to coordinate through oxygen atoms of hydroxyl and carbonyl groups, forming a stable chelate

structure. The resulting complex exhibits enhanced stability under the optimum experimental conditions, contributing to the selectivity and sensitivity of the analytical system.

The analytical characteristics of the developed sorbent demonstrated its applicability for Zn(II) ion determination. The calibration graph showed a linear relationship between absorbance and Zn(II) concentration within the investigated range, indicating compliance with Beer's law. The method exhibited good reproducibility and satisfactory precision, with low relative standard deviation values obtained for replicate measurements. The detection capability of the immobilized sorbent was enhanced by the preconcentration effect associated with the sorption process. Furthermore, the strong color contrast produced by the Zn(II)-Alizarin Red S complex facilitated accurate spectrophotometric measurements even at relatively low zinc concentrations.

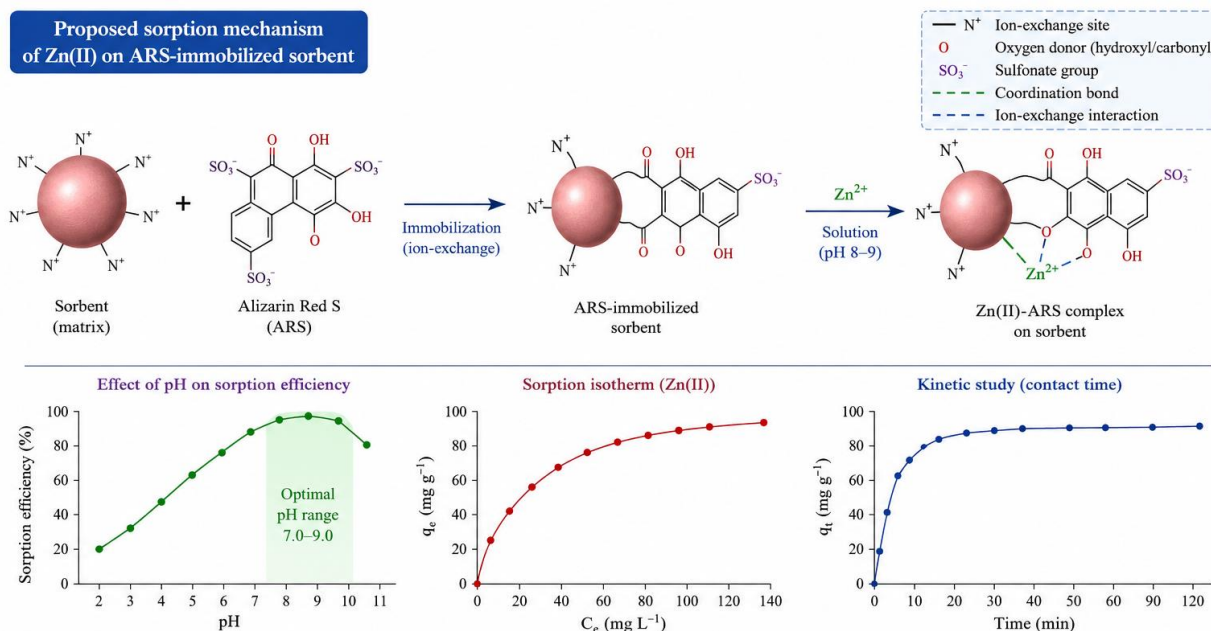


Figure 3. Sorption mechanism, pH dependence, sorption isotherm, and kinetic behavior of Zn(II) ions on alizarin red s-immobilized sorbent.

The obtained results suggest that Zn(II) sorption proceeds through a combination of ion-exchange interactions and coordination complex formation. The immobilized Alizarin Red S molecules provide active binding sites capable of selectively interacting with zinc ions. The participation of hydroxyl and carbonyl groups in metal binding was supported by FTIR analysis and the observed dependence of sorption efficiency on solution pH. The high sorption efficiency achieved under optimal conditions demonstrates that immobilization preserves the complex-forming ability of Alizarin Red S while simultaneously improving its stability and usability. Consequently, the developed sorbent combines the advantages of solid-phase extraction and selective complexation, making it a promising material for the determination of Zn(II) ions in environmental and industrial samples. The physicochemical investigations confirmed the successful immobilization of Alizarin Red S, the formation of stable Zn(II) complexes on the sorbent surface, and the favorable analytical characteristics of the developed sorption system. These findings provide a solid foundation for the application of the immobilized sorbent in sorption-spectrophotometric methods for zinc determination.

## CONCLUSION

The present study successfully investigated the physicochemical properties of an Alizarin Red S-immobilized sorbent developed for the determination of Zn(II) ions. The obtained results demonstrated that immobilization of Alizarin Red S onto the solid-phase matrix produced a stable

and analytically effective sorbent capable of selectively interacting with zinc ions in aqueous solutions. FTIR spectroscopic analysis confirmed the successful immobilization of Alizarin Red S on the sorbent surface and revealed the presence of characteristic functional groups responsible for metal ion binding. The observed shifts in hydroxyl and carbonyl absorption bands after Zn(II) sorption provided evidence for the participation of oxygen-containing donor groups in coordination interactions and complex formation. These findings indicate that the immobilized reagent retained its complex-forming ability after attachment to the solid support. The prepared sorbent exhibited favorable physicochemical characteristics, including good mechanical strength, chemical stability, homogeneous distribution of the immobilized reagent, and resistance to reagent leaching during repeated washing cycles. The material maintained its structural integrity over a wide pH range, confirming its suitability for long-term analytical applications. The sorption behavior of Zn(II) ions was strongly influenced by the acidity of the solution. Maximum sorption efficiency was achieved in a weakly alkaline medium (pH 8-9), where the immobilized reagent provided optimal conditions for complex formation with zinc ions. The sorbent demonstrated high sorption capacity and rapid attainment of sorption equilibrium, indicating a strong affinity of the active binding sites toward Zn(II) ions.

Investigation of the sorption mechanism showed that zinc ion uptake proceeds through a combination of ion-exchange interactions and coordination complex formation. Hydroxyl and carbonyl functional groups of immobilized Alizarin Red S act as the principal coordination centers, forming stable chelate complexes with Zn(II) ions. This mechanism contributes significantly to the selectivity and efficiency of the developed sorption system. The analytical characteristics of the immobilized sorbent confirmed its applicability for zinc determination. The developed material exhibited high sorption efficiency, good reproducibility, satisfactory stability, and favorable physicochemical properties, making it suitable for sorption-spectrophotometric analysis and preconcentration procedures. The results demonstrate that the Alizarin Red S-immobilized sorbent is a promising analytical material for the determination of Zn(II) ions. The combination of selective complex formation, high sorption capacity, chemical stability, and operational reliability provides a solid basis for its application in environmental monitoring, industrial analysis, wastewater control, and other analytical fields requiring accurate determination of zinc ions.

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