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Adsorption research of lycopene from waste tomato using zein covered ionic liquid-based silica

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Abstract

Three kinds of ion liquid materials modified by silica gel and a new material composed of corn zein were prepared. Zein@PIM-Si-IL、Zein@HIM-Si-IL and Zein@Si-IL-37, which were used to separate lycopene from waste tomato. The adsorption capacity of three new materials to lycopene standard solution was studied by single factor method. At 20℃ and 0.001-0.005 mg/mL, the Zein@Si-IL-37 obtained the highest adsorption amount in 2.0 h, the adsorption efficiency is above 80%. Then the sorbent was applied in practical sample, the recoveries and RSD were in the range of 93.0-101.0% and 3.0-5.0% highlighting the accuracy of Zein@Si-IL-37.

Keywords: Zein, lycoypene, ionic liquid, composite material

Introduction

With the vigorous development of the biomedical field and the increasing pursuit of healthy living, biomedical scientific research has received unprecedented attention. Among this, lycopene has become a focal point for both the scientific community and the public, owing to its exceptional strong antioxidant properties and outstanding free radical scavenging capabilities. As a natural carotenoid food pigment, lycopene not only enriches the color of food but also exhibits highly efficient antioxidant activity due to its unique molecular structure, which is rich in conjugated double bonds [1]. The application areas of lycopene are extremely broad. In the food industry, it is widely used as a nutritional fortifier and natural pigment in products such as bread baking, tomato juice processing, and lycopene soft capsules. It not only enhances the visual appeal of the products but also offers multiple health benefits, including cancer prevention and anti-aging effects [2]. In the pharmaceutical field, lycopene has shown immense potential as a metabolic regulator. It can effectively delay the aging process, resist mutation and radiation damage, regulate cholesterol levels, and significantly reduce the risk of cancer, offering new strategies for modern medicine. In the cosmetics sector, lycopene is utilized as a natural, safe, and effective skincare ingredient in a variety of forms. It can provide moisturizing benefits while exerting antioxidant, whitening, and spot-fading effects, along with more potent repairing and anti-aging functions [3].

Lycopene is generally extracted from tomatoes using different technologies including the solvent extraction method, supercritical CO_2 extraction, ultrasonic extraction, and vegetable oil solvent extraction, *et al* [4]. The solvent extraction method involves crushing tomatoes, adding alkali, heating and stirring, and removing peels, seeds, and fiber residues to obtain the original juice for further extraction [5]. Supercritical CO_2 extraction utilizes the high solubility of carbon dioxide in a supercritical state to efficiently separate lycopene, making it suitable for protecting heat-sensitive substances [6]. Ultrasonic extraction enhances mass transfer rates through cavitation effects, avoiding the degradation of active components at high temperatures, and has been widely applied in the food industry in recent years [7]. Additionally, extraction methods using vegetable oils such as coconut oil and olive oil as solvents have gained attention for their environmental friendliness, particularly for extracting lycopene from tomato paste [8]. Each technique has its advantages, and the appropriate method can be selected based on the desired purity, activity, and cost requirements of the target product.

However, a significant portion of fresh tomatoes is discarded due to damage and spoilage resulting from improper methods during transportation, storage, and processing. Consequently, the valuable lycopene contained in waste tomato is not effectively recovered and utilized. Furthermore, traditional extraction methods prove to be unsuitable for reclaiming lycopene from waste tomato. For isolation and purification, adsorption-based methods utilizing materials are regarded as the most efficient due to their high selectivity and capacity.

Zein is the main protein in corn, which has high proportion of non-polar amino acids, strong hydrophobicity and unique self-assembly ability. These properties have led to its widespread application in the encapsulation, protection, and delivery of drugs and bioactive molecules [9]. Furthermore, the hydrophobic core structure of zein can significantly enhance its interaction with lycopene, making it a particularly promising carrier for this compound [10]. Ionic liquids (ILs) were well-known as green reaction medias with excellent chemical properties. Their hydrophobicity, miscibility with several inorganic/organic solvents, and interactions between functional groups allowed ILs to be applied widely as solvents or modified sorbents [11].

Hence, in this research, we selected a zein covered ionic liquid-based silica as sorbent to isolate lycopene from waste tomato.

Materials and Methods

Synthesis of Zein@PIM-Si-IL、Zein@HIM-Si-IL

The specific steps for synthesis are as follows

1. **Synthesis of silica-modified imidazolium ionic liquid**

First of all, add 10% dilute hydrochloric acid to 400.0 mL of water. Use this mixture to activate silica gel for 24.0 h. Then wash the material with water until pH=7.0 is reached, then dry at 70℃ for 10.0 h to obtain activated silica (SO_2), denoted as Sil. Secondly, add 5.0 g SiO_2, 5.0 mL 3-chloropropyltrimethoxysilane and 80.0 mL xylene to a

250.0 mL round-bottom flask. Mix uniformly and stir at 100°C for 8.0 h. After cooling, wash with absolute ethanol until no xylene odor remains, then dry at 60°C for 10.0 h to obtain chloro-functionalized silica gel (denoted as Sil-Cl). Subsequently, add Sil-Cl, 4.0 mL triethylamine, 4.0 g imidazole and 80.0 mL xylene to a 250.0 mL round-bottom flask. Heat to 100°C and stir for 8.0 h. After cooling, wash with absolute ethanol until odor-free, then subject to drying at 60°C for 10.0 h to yield imidazolium-modified silica gel (denoted as Sil-Imidazole).

2. Synthesis of PIM-Si-IL、HIM-Si-IL

Accurately weigh 5.0 g Sil-Imidazole and combine with 4.0 mL 1-chlorohexane and 80.0 mL xylene in a 250.0 mL round-bottom flask. Mix the components uniformly, then heat to 80°C with continuous stirring for 8.0 h. After cooling to room temperature, wash the product repeatedly with absolute ethanol until completely xylene-free, then dry at 60°C for 10.0 h to obtain pentylimidazolium-modified silica ionic liquid (PIM-Si-IL). Following an identical procedure but replacing 1-chlorohexane with 4.0 mL 1-chloropentane yields hexylimidazolium-modified silica ionic liquid (HIM-Si-IL).

3. Synthesis of Zein@PIM-Si-IL、Zein@HIM-Si-IL、Zein@Si-IL-37

Prepare 75% (v/v) aqueous ethanol in small conical flasks. Add 0.375 g citric acid and 1.0 g zein to each flask, then simultaneously add 0.1 mL glutaraldehyde and 0.1 mL glycerol dropwise. Incorporate 0.5 g PIM-Si-IL, seal with parafilm, stir until homogeneous, and sonicate at 300.0 W for 5.0 min. Transfer the mixture to PTFE dishes and dry at 60°C for 12.0 h to obtain Zein@PIM-Si-IL composite. Following the same protocol, replace PIM-Si-IL sequentially with: (a) 0.5 g HIM-Si-IL to prepare Zein@HIM-Si-IL; (b) 0.5 g hybrid filler (PIM-Si-IL: HIM-Si-IL=3:7 w/w) to prepare Zein@Si-IL-37 composite.

Material characterization

Fourier transform infrared spectroscopy (FTIR) spectroscopy utilizes the absorption characteristics of substances at different infrared wavelengths for molecular and chemical structure detection. This experiment employed a Nicolet 6700 spectrometer (Thermo Fisher, Waltham, USA), using the KBr pellet method with a scanning range of 400-4000 cm^{-1} at a rate of 20 scans per minute.

The scanning electron microscope (SEM) is MIRA3 (TESCAN, Brno, Czech Republic).

The thermal gravimetric analyzer (TGA) is Labsys evo (setaram, calurie, France), with a heating rate of 10°C/min. Nitrogen is introduced and 8mg sample is weighed in an alumina crucible and heated to about 800°C.

Static adsorption experiment

Lycopene standard solution preparation: Accurately weigh 20.0 mg lycopene standard (to the nearest 0.01 mg) and dissolve completely in 20.0 mL dichloromethane to obtain 1000 μg/mL stock solution. Store in light-sensitive containers at -20°C. Prior to adsorption experiments, dilute the stock solution with dichloromethane to prepare 0.005 mg/mL working solution, designated as LYC-1 (Lycopene), and store under identical conditions.

The high-performance liquid chromatography system was LC3000 (CXTH, Beijing, China). The detection of lycopene was performed on the TC-C18 column (4.60×250.00 mm, 3.80 μm, Agilent, USA).

Adsorption experiment: Weigh 0.5 g of Zein@PIM-Si-IL, Zein@HIM-Si-IL, and Zein@Si-IL-37 materials into three separate 10.0 mL glass vials. Add 5.0 mL of LYC-1 solution (0.005 mg/mL) to each vial. Shake at 150 rpm in a thermostatic water bath at 25°C for 24.0 h. After standing for 30.0 min, filter the supernatant through 0.22 μm nylon membranes. Quantify lycopene concentrations before and after adsorption by HPLC. Calculate adsorption capacity using equation (1).

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Analysis of actual samples

Tomato sample preparation: Weigh 110.0 g fresh tomato (homogenized) and immerse in 50.0 mL dichloromethane in a light-proof sealed beaker. After 4.0 h extraction, filter through PTFE membrane and store extract at -20°C. For adsorption test: Pipette 4.0 mL extract into a glass vial, spike with 1.0 mL LYC-1 standard solution (0.005 mg/mL), add 0.5 g Zein@Si-IL-37 adsorbent, and shake at 25°C for 24.0 h. Filter through 0.22 μm PTFE membrane, inject 10.0 μL filtrate to HPLC for lycopene quantification.

Results and Discussion

Characterization

The results of material characterization are analyzed as follows

1. Infrared spectroscopic analysis

As shown in Fig. 1, the fourier infrared spectroscopy analysis of Zein@Si-IL-37 reveals prominent vibration peaks at 1160 cm^{-1}, 1640 cm^{-1}, and 1700 cm^{-1} from C-C, C=C, and C=O bonds in zein. The 3315 cm^{-1} peak in Fig. 1 indicates N-H vibrations associated with imidazole-based ionic liquids. A distinct vibration peak at 2350 cm^{-1} demonstrates optimized proportions of ionic liquid in Zein@Si-IL-37 compared to Zein@HIM-IL. Vibrational peaks at 845 cm^{-1} and 960 cm^{-1} suggest the presence of O-Si-O structures, confirming the successful synthesis of Zein@Si-IL-37.

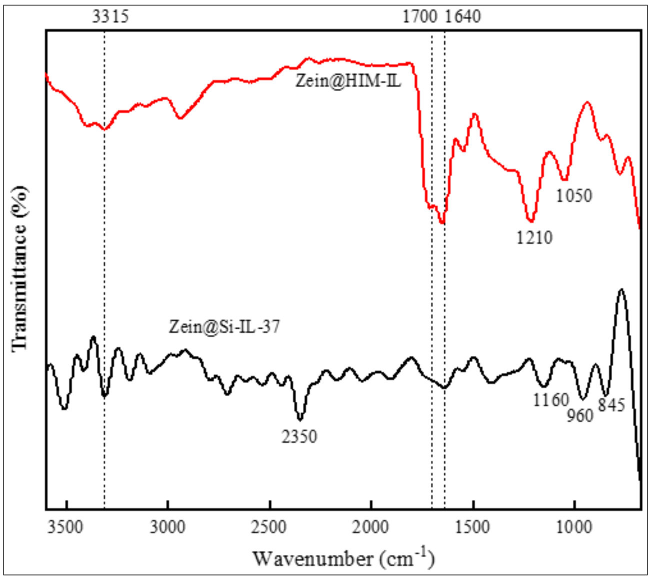

Fig 1: FT-IR of Zein@Si-IL-37 and Zein@HIM-IL

2. SEM

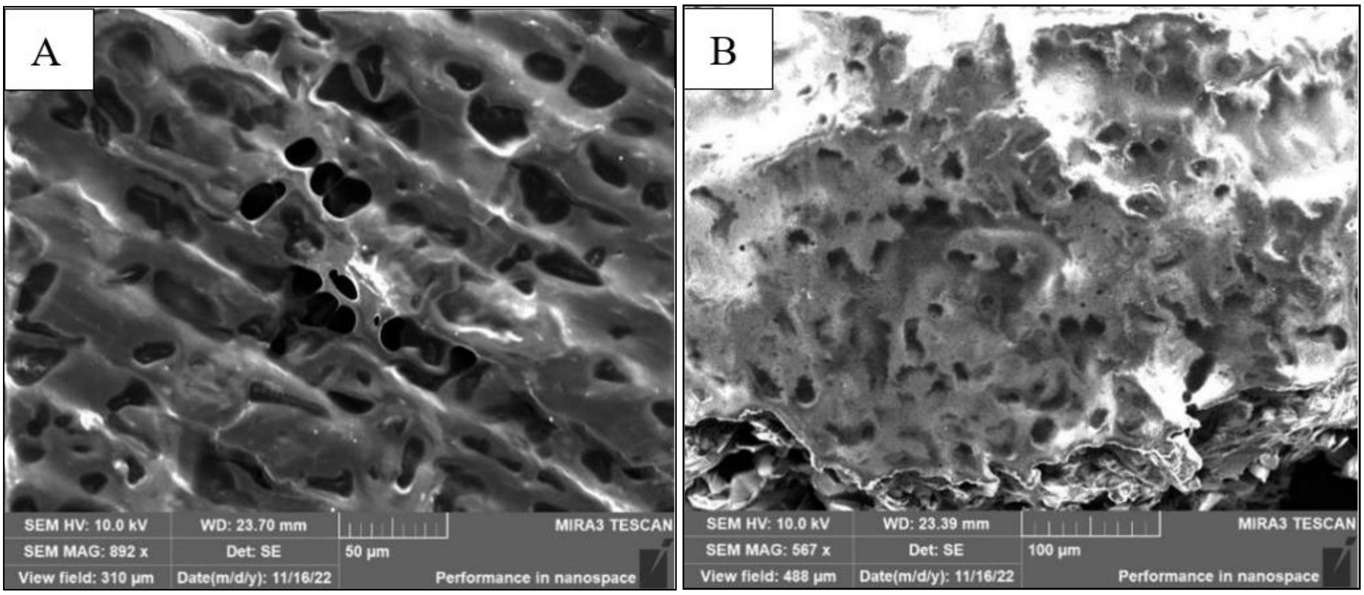

Fig 2: The SEM picture of A: Zein@HIM-Si-IL and B: Zein@PIM-Si-IL

As shown in Fig. 2, the modified materials Zein@HIM-Si-IL and Zein@PIM-Si-IL are labeled as A and B respectively. Although Fig. A displays a less favorable external morphology, these materials exhibit larger pores and better water permeability, demonstrating relatively strong adsorption performance for lycopene. Fig. B shows smaller pores compared to Fig. A, but it demonstrates advantages in external morphology with uniform distribution of pores and nearly consistent pore sizes. Compared to the base materials and the ionic liquid-modified materials, both materials show significant improvements in pore structure and superior external morphology, resulting in relatively stronger adsorption capacity for lycopene. By combining the advantages of Zein@HIM-Si-IL and Zein@PIM-Si-IL, the modified material Zein@Si-IL-37 was formed through different ratios, as shown in Fig. 3. As illustrated in Fig 3, the surface morphology of the modified Zein@Si-IL-37 becomes more complex. The rough surface increases friction during contact with lycopene, thereby enhancing adsorption efficiency. Additionally, the material exhibits nearly uniform pore sizes and distribution, ensuring optimal adsorption at all positions. Overall, this material successfully integrates the strengths of both Zein@HIM-Si-IL and Zein@PIM-Si-IL, making it a highly successful modification.

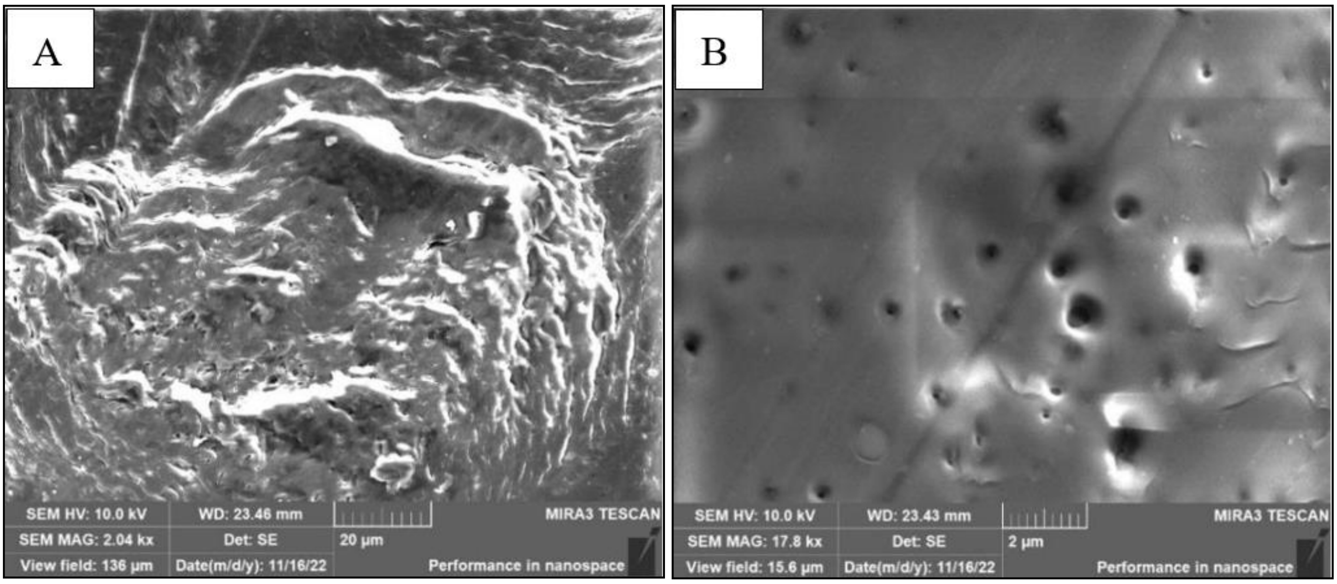

Fig 3: The SEM picture of Zein@Si-IL-37

3. Thermogravimetric analysis

As shown in Fig. 4 below, the optimized material Zein@Si-IL-37 exhibits two distinct weight loss phases compared to the base material: a 10% weight loss phase caused by zein and a 37% weight loss phase attributed to the silicone-modified ionic liquid. This demonstrates that the modified material exhibits superior thermal stability relative to the original formulation.

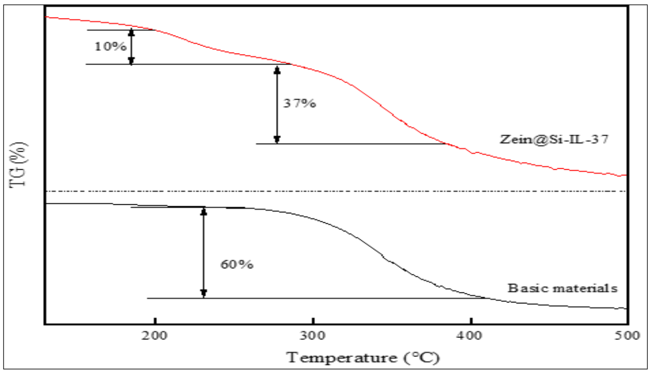

Fig 4: Basic materials and Zein@Si-IL-37 material thermogravimetric curve

Adsorption research

To further investigate the adsorption behavior of lycopene by adsorbent materials and examine how time affects adsorption efficiency, the graph clearly shows that adsorption capacity initially increases rapidly. As time progresses, adsorption gradually reaches saturation with a slowing rate, peaking at 120.0 min. This occurs because during the initial stage, the adsorbent surface contains abundant active sites enabling efficient adsorption. However, as adsorption continues, these sites become occupied, leading to adsorption saturation and subsequent deceleration. The adsorption kinetics curve was analyzed using the Langmuir model, with results presented in Fig. 5.

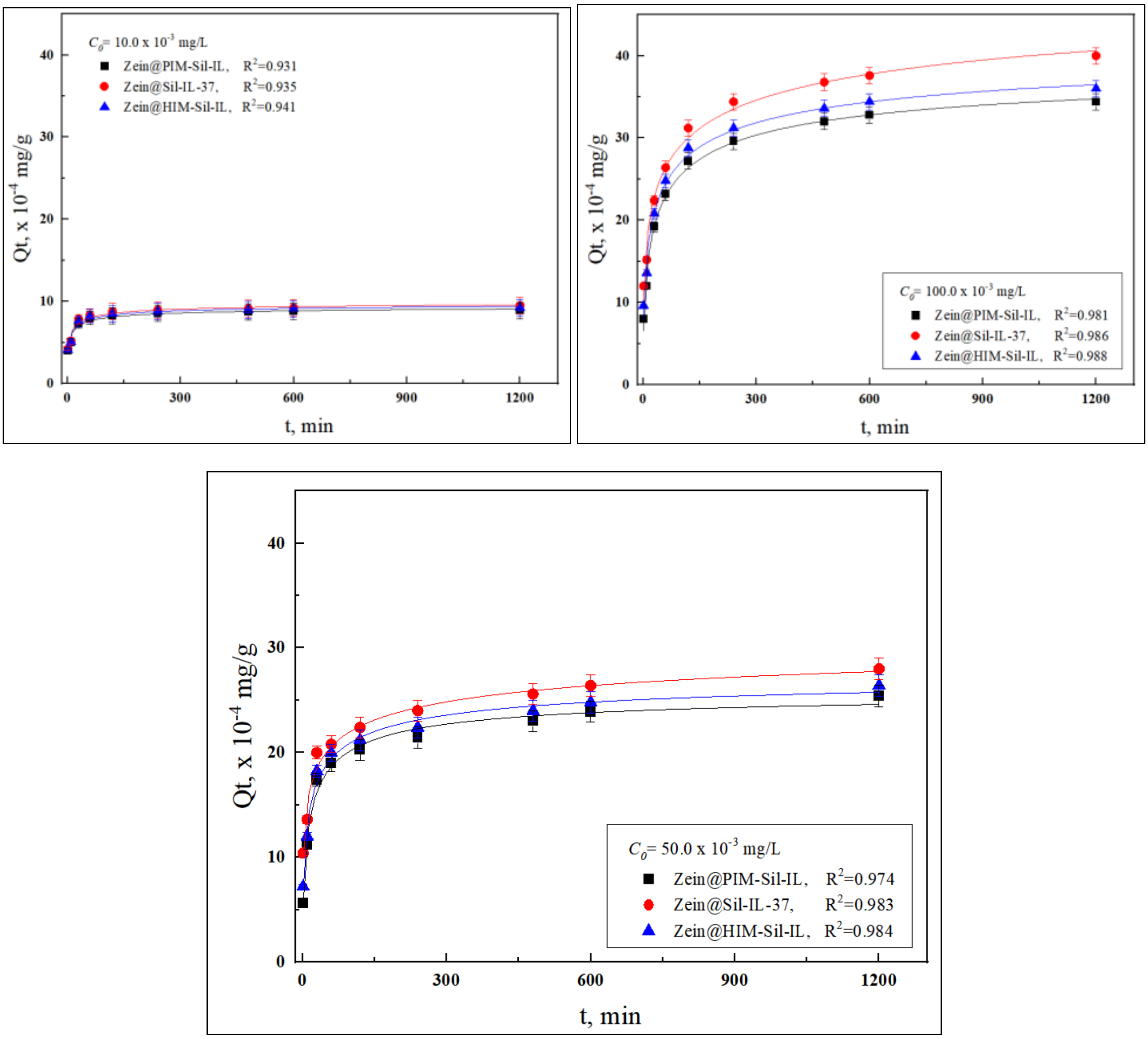

Fig 5: Maximum adsorption capacity of three materials at different times

As shown in Fig. 5, adsorption at high concentrations achieves higher saturation capacity but faster kinetics. Comparing the 0.005 mg/mL and 0.01 mg/mL concentrations, the difference in maximum adsorption efficiency between these two levels is minimal. This indicates that at high concentrations, pore blockage becomes more severe during adsorption, leading to quicker saturation and reduced material utilization efficiency.

Similarly, at the low concentration of 0.001 mg/mL, although saturation is achieved over time, the resulting capacity remains too low, resulting in poor adsorption efficiency. Therefore, this experiment focuses on analyzing adsorption at approximately 0.005 mg/mL for 2.0 hours, ensuring more complete material adsorption and better adsorption effects, thereby obtaining data with greater analytical value.

Condition optimization

The single-factor method was employed to investigate the effects of ionic liquid dosage, reaction time, and concentration on the adsorption of lycopene:

1. The effect of lycopene solvent on adsorption

Under identical experimental conditions, we adjusted the solvent for lycopene extraction while maintaining another adsorption parameters constant, as demonstrated in Fig. 6. Comparative experiments revealed that despite using the same adsorbent material, HPLC analysis showed varying detection levels of lycopene mass. Dichloromethane exhibited the fastest dissolution rate and complete absorption, yielding the highest detection values. Ethyl acetate and petroleum ether followed with relatively good performance, while acetone and acetonitrile demonstrated slower dissolution rates but still measurable amounts. Ethanol and methanol, whether used individually or in combination, showed negligible lycopene detection due to minimal structural disruption caused by their solvents, resulting in significant analytical loss. Given the need to avoid highly toxic materials, dichloromethane and ethyl acetate were ultimately selected as the preferred solvents for lycopene extraction in subsequent experiments.

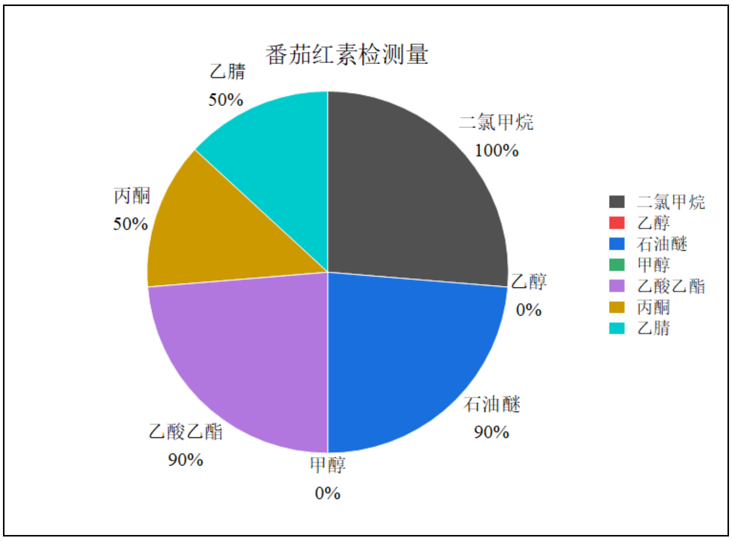

Fig 6: Lycopene dissolution solvent detection effect

2. The effect of different adsorption materials

The maximum adsorption capacity of lycopene was investigated under the same experimental conditions when Zein@PIM-IL, Zein@HIM-IL, Zein@PIM-Si-IL, Zein@HIM-Si-IL and Zein@Si-IL-37 were at high concentration.

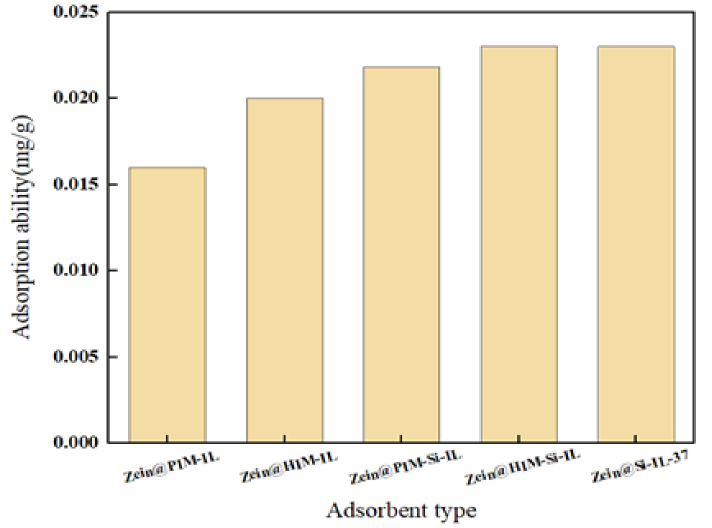

Fig 7: Effect of adsorbent type on adsorption of LYC-1

As shown in Fig. 7, the adsorption performance of materials progressively improves through continuous modification. Zein@PIM-IL and Zein@HIM-IL are ionic liquid-modified materials that essentially represent physical modification, specifically the attachment of ionic liquids to the surface of base materials. The elongation of C chains enhances hydrophobicity, enabling stronger affinity between the molecules adsorbed on these materials and lycopene macromolecules in liquid environments. Under van der Waals forces, these molecules attract each other, causing liquid-bound lycopene macromolecules to adhere to the adsorbent surfaces. Notably, under certain conditions, these adsorbed macromolecules can revert to liquid state without altering their original properties. Experimental data indicates Zein@HIM-IL demonstrates superior adsorption efficiency compared to Zein@PIM-IL.

Zein@PIM-Si-IL, Zein@HIM-Si-IL, and Zein@Si-IL-37 demonstrate enhanced chemical modification approaches. By incorporating silica-modified ionic liquids into the materials, their affinity properties are significantly improved. When these materials interact with lycopene in liquid environments, chemical bonds between them undergo hydrogen bonding interactions. This process generates forces substantially stronger than van der Waals forces, resulting in superior adsorption efficiency. Although the slight increase in carbon chain length causes minimal difference in adsorption performance, SEM characterization reveals that silica-modified materials exhibit better surface morphology and more complex topographies. These characteristics collectively make them more valuable for research applications.

3. The effect of concentration on adsorption

In Fig. 8, A, B and C correspond to the adsorption of Zein@PIM-Si-IL, Zein@HIM-Si-IL and Zein@Si-IL-37 at different concentrations.

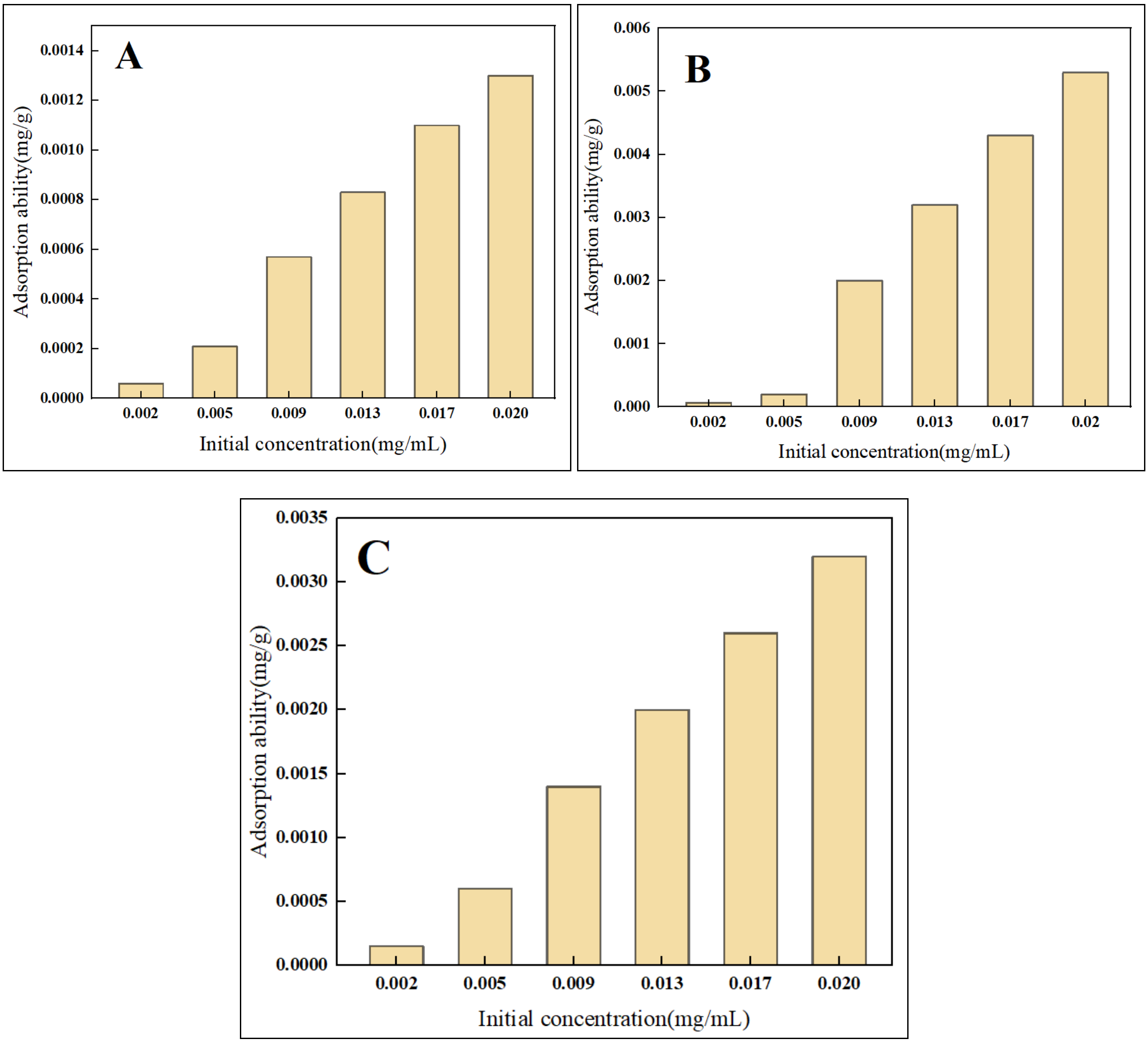

Fig 8: Effect of concentration on adsorption of LYC-1

As shown in the figure, all three modified materials exhibited increased adsorption capacity with higher solution concentrations under identical experimental conditions. This phenomenon stems from the silica-modified ionic liquid generating additional affinity sites on the adsorbent material. The structural similarity between the silica-modified ionic liquid and lycopene facilitates both π–π bond interactions and hydrogen bonding, thereby enhancing the adsorption capacity of Zein@PIM-Si-IL, Zein@HIM-Si-IL, and Zein@Si-IL-37 for lycopene.

As the difference in C atoms between the materials is relatively small, there is no significant variation in adsorption efficiency, as shown in Fig. 8. At low concentrations, Zein@Si-IL-37 exhibits relatively better adsorption performance compared to Zein@PIM-Si-IL and Zein@HIM-Si-IL. The long chain length enhances hydrophobicity, allowing the silica-modified ionic liquid to bind more stably with zein as the primary component. Tomato red pigment, being inherently hydrophobic, shows enhanced adsorption by longer C chains under hydrophobic effects. This trend becomes evident at high concentrations.

SEM characterization demonstrates Zein@Si-IL-37 exhibits superior surface characteristics compared to the other two materials. Based on the adsorption conditions shown in Fig. 9, Zein@Si-IL-37 demonstrates better adsorption performance at low concentrations, while its adsorption efficiency between high concentrations falls between Zein@PIM-Si-IL and Zein@HIM-Si-IL. Given that the actual samples contain extremely low levels of lycopene, Zein@Si-IL-37 proves more suitable for adsorption with superior overall performance. Therefore, this material will be adopted for subsequent practical applications.

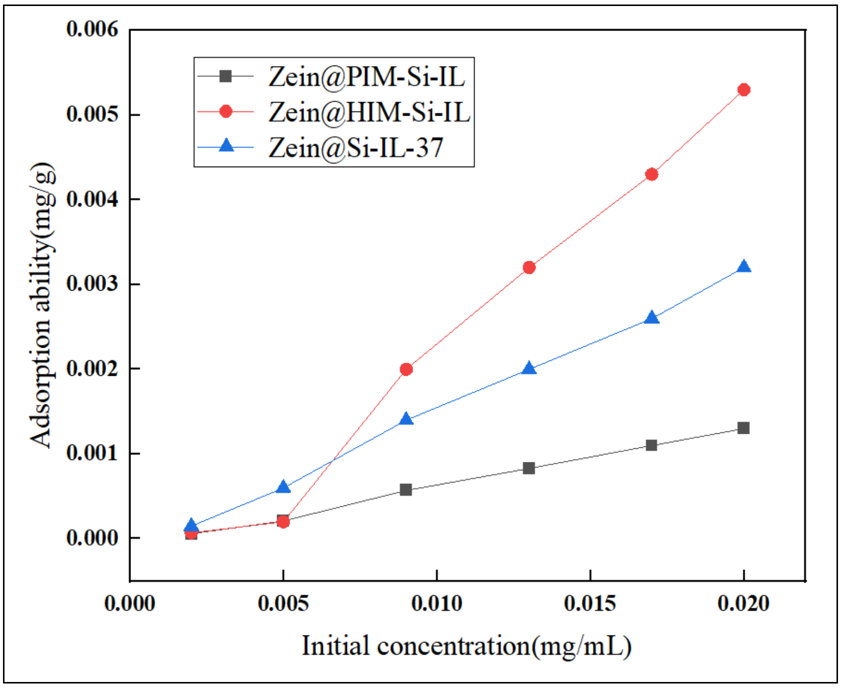

Fig 9: Effect of material and concentration on adsorption of LYC-1

Repeated experiments

We aliquoted 2.0 mL of lycopene solution into centrifuge tubes and added 0.5 g Zein@Si-IL-37 material, which was then vibrated adsorbed under optimized conditions. The solution was filtered through a 0.22 μm membrane before being injected into a high-performance liquid chromatograph (HPLC) for concentration analysis. The used Zein@Si-IL-37 material was desorbed using dichloromethane as the eluent for 3-5 minutes via ultrasonic treatment, followed by drying and reuse. This procedure was repeated 4-5 times. As shown in Fig.10, the adsorption efficiency remained above 80% after five reuses, with minimal mass difference observed between pre-use and post-desorption drying conditions. These results demonstrate that Zein@Si-IL-37 material exhibits suitable performance for lycopene adsorption and separation from waste tomatoes.

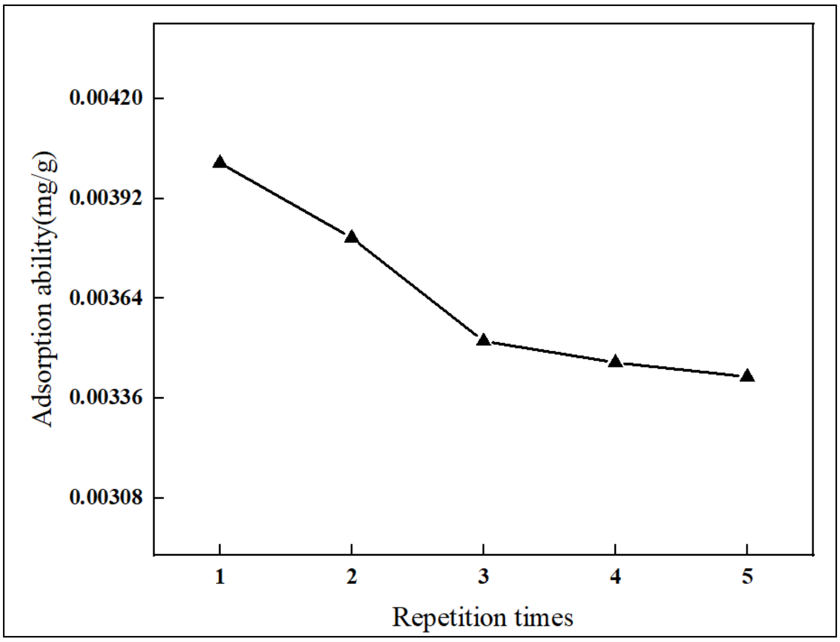

Fig 10: Repetitive experiments

Practical sample application and analysis

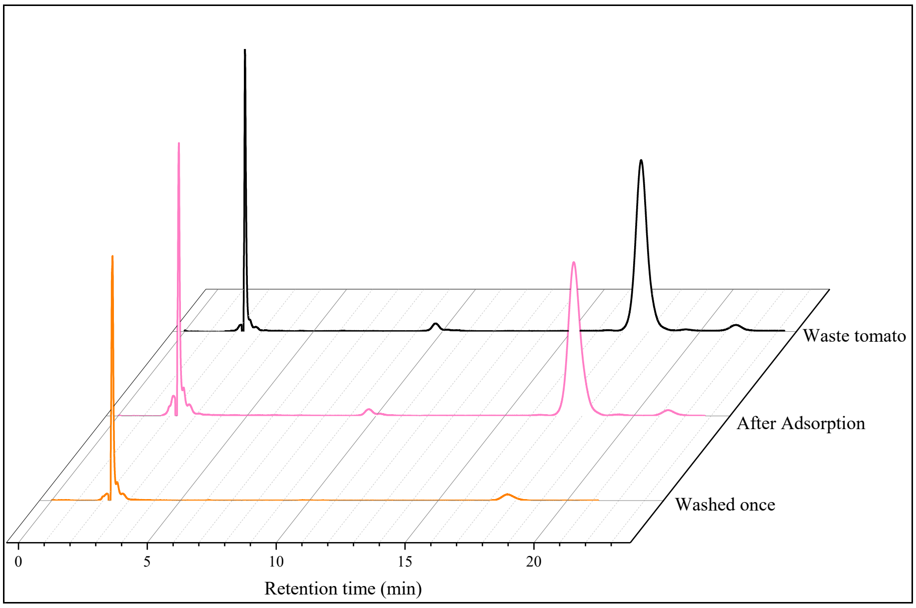

Fig 11: The chromatogram of the waste tomato sample shows the lycopene extract from the waste tomato from top to bottom, 0.1 g Zein@Si-IL-37 material is adsorbed under optimized conditions, and 1.00mL dichloromethane is eluted once

As shown in Fig. 11, the peak area of lycopene detected in discarded tomatoes was larger than that observed after adsorption by Zein@Si-IL-37 material. This indicates that the material achieved effective adsorption performance when applied to actual samples, demonstrating successful modification of the silica-modified base material. The improved surface affinity, increased functional groups, and expanded pore structure of the adsorbent enhanced its interaction with lycopene macromolecules, resulting in superior adsorption efficiency. The subsequent elution with dichloromethane revealed that this solvent effectively separated lycopene without significant material loss, though further optimization of elution efficiency remains necessary. The samples after the addition of standard were analyzed, and the results are shown in Table 1. The recovery rate of the added standard was between 93.0% and 101.0%, and the RSD was between 3.0% and 5.0%. It showed that the method and materials could obtain high accuracy when applied to waste tomato samples.

Table 1: Method recovery(n=3) and relative standard deviation (RSD)

Lycopene concentration (mg/g)	**Additive amouny (mg/g)**	**Recent days**		**Day time**	
		Recovery (%)	**RSD (%)**	**Recovery (%)**	**RSD (%)**
0.111	0.0888	93.19	3.32	96.34	3.26
	0.1110	98.05	3.58	101.20	3.35
	0.1332	96.55	4.01	97.54	4.73

Conclusion

This study successfully synthesized a novel silica-modified ionic liquid adsorbent, which significantly enhanced the affinity between the adsorption material and lycopene, resulting in superior adsorption performance. Simultaneously, material synthesis success was demonstrated through SEM, FTIR, and TGA characterization techniques. Combined with HPLC analytical technology, a detection method for lycopene was established. Single-factor experiments were employed to investigate the effects of different adsorbents, concentrations, and lycopene-dissolving reagents. The final material Zein@Si-IL-37 demonstrated optimal adsorption performance for lycopene under conditions of 0.001-0.005 mg/mL concentration at 20°C and 2-hour adsorption duration. Simultaneous kinetic model simulations corroborate this conclusion, revealing that the silica-modified ionic liquid complexing zein significantly enhances adsorption capacity. This modification achieves remarkable efficacy in extracting lycopene from discarded tomato samples during practical applications.

References

1. Nandeshwar KA, Kodape SM, Rathod AP, Zodape SP. Coupling solvent extraction with pervaporation for efficient separation of lycopene from tomato waste using chitosan/polyvinylpyrrolidone (CS/PVP) pervaporative membranes and its optimization study. Biomass Conversion and Biorefinery,2024:14:31183–31202.
2. Liu Y, Liu J, Chen X, Liu Y, Di D. Preparative separation and purification of lycopene from tomato skins extracts by macroporous adsorption resins. Food Chemistry,2010:123(4):1027–1034.
3. Ciurlia L, Bleve M, Rescio L. Supercritical carbon dioxide co-extraction of tomatoes (*Lycopersicum esculentum* L.) and hazelnuts (*Corylus avellana* L.): A new procedure in obtaining a source of natural

lycopene. The Journal of Supercritical Fluids,2009:49(3):338–344.

4. Seifi M, Seifi P, Hadizadeh F, Mohajeri SA. Extraction of lycopene from tomato paste by ursodeoxycholic acid using the selective inclusion complex method. Journal of Food Science,2013:78(11):1680–1685.
5. Choudhari SM, Ananthanarayan L, Singhal RS. Purification of lycopene by reverse phase chromatography. Food Bioprocess Technology,2009:2(4):391–399.
6. Honda M, Watanabe Y, Murakami K, Takemura R, Fukaya T, Wahyudino, *et al*. Thermal isomerization pre-treatment to improve lycopene extraction from tomato pulp. LWT-Food Science and Technology,2017:86:69–75.
7. Rosario M, Samantha M, Yvelse F. A rapid and cheap method for extracting and quantifying lycopene content in tomato sauces: Effects of lycopene micellar delivery on human osteoblast-like cells. Nutrients,2022:14(3):717–723.
8. Kehili M, Sayadi S, Frikha F, Zammel A, Allouche N. Optimization of lycopene extraction from tomato peels industrial by-product using maceration in refined olive oil. Food and Bioproducts Processing,2019:117:321–328.
9. Yan X, Li M, Xu X, Liu X, Liu F. Zein-based nano-delivery systems for encapsulation and protection of hydrophobic bioactives: A review. Frontiers in Nutrition,2022:9:999373.
10. Sun X, Pan C, Ying Z, Yu D, Duan X, Huang F, *et al*. Stabilization of zein nanoparticles with k-carrageenan and tween 80 for encapsulation of curcumin. International Journal of Biological Macromolecules,2020:146:549–559.
11. Fang L, Tian M, Yan X, Xiao W, Kyung Ho Row. Dual ionic liquid-immobilized silicas for multi-phase extraction of aristolochic acid from plants and herbal medicines. Journal of Chromatography A,2019:1592:31–37.