Journal of Science and Technology in Civil Engineering, HUCE, 2025, 19 (2): 92–106

# ENHANCEMENT OF POLYVINYL ALCOHOL ADSORBENT VIA CROSSLINK WITH CITRIC ACID AND L-LYSINE FOR BIOCHEMICAL RECOVERY FROM FOOD PROCESSING WASTE STREAMS

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***Article history:***
*Received 06/5/2025, Revised 08/6/2025, Accepted 16/6/2025*

## Abstract

Industrial food wastewater typically contains rich organic matters and their discharge flows into water sources can cause severe environmental pollution. This study explored a novel generation of biodegradable adsorbent to extract carboxylates generated from fermented broth from the downstream wastewater in the food industry. A successful synthesis of Polyvinyl Alcohol (PVA) crosslinked Citric Acid (CA), foamed using Polyethylene Glycol (PEG), PVA−c-CA/PEG with CA 66% of total PVA−PEG (1:1 in weight) showed the maximum gel fraction and lowest swelling degree, the most effective crosslink materials. The incorporation with crosslinker L-lysine (Lys) into the polymer network of PVA−c-CA materials attained a considerable improvement in the material's surface morphology and adsorption capacity. Lab-scale series of adsorption experiments with a model volatile fatty acid (VFA) as acetic acid in solution achieved a maximum adsorption capacity ($Q_e$) of 74 mg/g and 86 mg/g after 60 min and 120 min, respectively at approximately 1 g/L acetic acid solution. The carboxylates in the effluent were recovered by this innovative green adsorption film, can be used as a biochemical platform for number purposes such as productions of detergents, polymers and biofuels. The new direction of VFA extraction is an eco-friendly opportunity which is in line with national and international targets such as using resources wisely, making products last longer, and causing as little damage to the environment as possible.

*Keywords:* volatile fatty acids; acetic acid; polyvinyl alcohol; citric acid; L-lysine; adsorption; crosslink reactions.

https://doi.org/10.31814/stce.huce2025-19(2)-07

## 1. Introduction

The accumulation of significant organic amounts in industrial food wastewater is a top concern in most countries [1]. Conventional activated sludge systems are often costly in treating these kinds of waste streams. Anaerobic digestion can be alternatives for high-strength wastewater and organic waste, especially the organic waste streams from food-processing/agro-industrial activities [2, 3]. In this process, these organic compounds can be converted to methane or intermediates such as volatile fatty acids (VFA), alcohol, hydrogen, as chemical blocks for biofuels and chemicals which are bio-based economy and circular economy [4, 5]. There poses a need for finding a cost-effective extraction of VFA out of downstream which is still challenging areas of research and not yet state of art technologies [6, 7].

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Polyvinyl alcohol (PVA), is a synthetic polymer known for its outstanding properties, including water solubility, non-toxicity, and biodegradability. In terms of biodegradability, enzymes secreted by microorganisms such as oxidases and hydrolases, can degrade the polymer chains into smaller molecules like acetic acid, ethanol, $CO_2$, and $H_2O$. Thus, PVA finds applications in the fabrication of biodegradable materials, agricultural coatings, construction materials such as paints and mortars, and wastewater treatment systems owing to its ability to form complexes with heavy metal ions [8]. With its superior properties, PVA continues to be a versatile and sustainable material, attracting ongoing research and development efforts aimed at eco-friendly and future-oriented applications.

Polyvinyl Alcohol (PVA) is capable of absorbing carboxylate but easily dissolved in water. This problem can be solved by crosslinking the PVA chain with Citric acid (CA) and L-lysine (Lys) [9–13]. Chemically, citric acid's structure enables it to act as a strong chelating agent. Thanks to its chelating capacity and mild acidity, it is used in cleaning agents, bio-based detergents, water softeners, and metal treatment processes [9].

Similarly, L-lysine has attracted increasing interest in the field of environmentally friendly materials, especially for wastewater treatment. Due to its strong affinity for metal ions and reactive functional groups, L-lysine has been utilized to modify various adsorbent materials such as graphene oxide (GO), montmorillonite, and magnetic nanoparticles. For example, Yan et al. successfully grafted L-lysine onto graphene oxide, resulting in an efficient adsorbent for methylene blue dye and $Cu^{2+}$ ions [13]. Similarly, Jiang et al. (2020) developed a lignosulfonate–lysine hydrogel capable of adsorbing heavy metal ions like $Co^{2+}$ and $Cu^{2+}$ from wastewater [14]. Moreover, coating L-lysine onto $CoFe_2O_4/\gamma\text{-}Fe_2O_3$ magnetic nanoparticles has been shown to significantly enhance the adsorption of pharmaceutical contaminants such as acetylsalicylic acid from aqueous environments [12].

Polyethylene Glycol (PEG) is a foaming agent that increases the surface area of PVA membranes and reduces crystallinity, thereby increasing the free volume in the membrane's structure [15]. These porous materials demonstrate enhanced adsorption capacities for pollutants such as heavy metals, dyes, and toxic organic compounds in wastewater [16]. This application highlights PEG 6000's potential in the development of green, reusable materials for sustainable environmental remediation.

This research focused on improvement of the weakness and the adsorption capacity of the PVA via crosslinking with CA and Lys and creating foam with PEG at different CA/PEG and L-lysine compositions. A novel synthesis of PVA−c-CA(−Lys)/PEG adsorbent material through chemical modification with citric acid and lysin, foaming with PEG was developed. The aim of this study was to develop an advanced green version of PVA as PVA−c-CA(−Lys)/PEG to expand its absorbent capacity for VFA extraction in the fermented broth. Characteristics of the new generation adsorbent material were examined via Gel Fraction Measurement, Scanning Electron Microscopy and Fourier Transform Infrared spectroscopy. The research assessed the carboxylic, i.e. acetic acid adsorption capacity of the fabricated PVA-c-CA/PEG adsorbent material.

## 2. Material and Methods

### *2.1. Materials for synthesis of PVA−c-CA−Lys/PEG adsorbent*

The synthesis of new green adsorbent used four biodegradable chemicals: (i) Polyvinyl alcohol, CAS: 9002-89-5 (PVA), with the chemical formula $[CH_2CH(OH)]_n$; (ii) Citric Acid, CAS: 5949-29-1 (CA), a weak organic tricarboxylic acid containing three carboxyl (−COOH) groups and one hydroxyl (−OH) group; (iii) L-Lysine, CAS: 56-87-1 (Lys), molecular formula $C_6H_{14}N_2O_2$ and consists of a primary amino group ($-NH_2$), a carboxyl group (−COOH), and a distinctive $\varepsilon$-amino group in its side chain; and (iv) Polyethylene Glycol 6000, CAS: 25322-68-3 (PEG), a synthetic polyether with the general formula $H-(O-CH_2-CH_2)_n-OH$, synthesized via the polymerization of ethylene oxide.

### 2.2. *Fabrication of the new generation adsorbent PVA – c-CA – Lys/PEG*

A total weight (wt) of 3 g of PVA was dissolved in 70 mL of distilled water at 150 °C under continuous stirring for 30 min. The solution was then allowed to cool to room temperature and cast into a mold. The resulting film was dried at 50 °C using an oven (Memmert GmbH + Co.KG) for 24 h to obtain the pure PVA film.

Following a similar procedure, PVA – c-CA/PEG and PVA – c-CA – Lys/PEG composite films were prepared. Specifically, 70 mL of the previously prepared PVA solution was mixed with 50 mL of a secondary solution containing $x$ wt% (20–100% PEG/PVA, wt/wt) of PEG 6000, $y$ wt% citric acid, and $z$ wt% L-lysine ($x$, $y$ from 5 to 100%). Then 5 mL of $H_2SO_4$ (0.1 M) was added in the mixture. The mixture was stirred for 2 h to ensure homogeneous blending. After mixing, the PVA – c-CA/PEG and PVA – c-CA – Lys/PEG solutions were cast into molds and dried at 50 °C for 24 h. Subsequently, the dried films were subjected to a thermal crosslinking process at 100 °C for 1 h to promote esterification reactions among the functional groups of PVA, citric acid, and L-lysine.

The crosslinking of the polymeric network in the composite films involves several esterification reactions between functional groups of PVA, citric acid (CA), and L-lysine (Lys). These reactions enhance the mechanical strength, water resistance, and structural stability of the resulting materials.

### 2.3. *Crosslinking Reactions*

#### a. Esterification between PVA and CA

Citric acid, a tri-carboxylic acid, can form ester bonds with the hydroxyl groups of PVA upon thermal treatment. At 100 °C, the carboxyl groups of citric acid reacted with hydroxyl groups of PVA in acidic condition ($H_2SO_4$), leading to covalent crosslinking through ester bridges [17]. This reaction was reported as the primary crosslinking mechanism in many PVA – c-CA based networks [18].

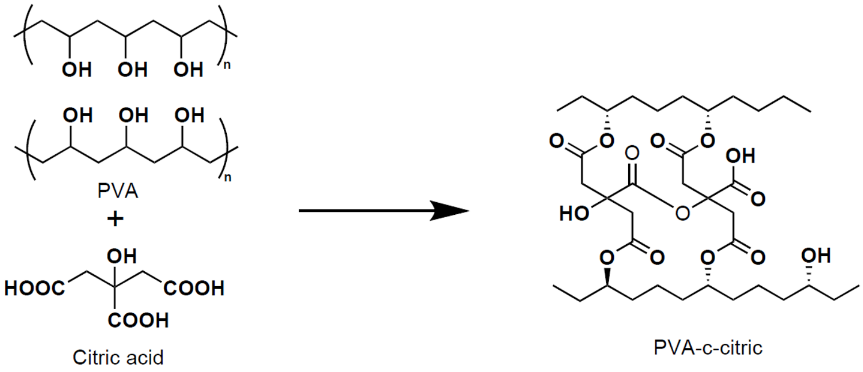


Figure 1. Esterification between PVA and CA

#### b. Esterification between PVA and L-lysine

L-lysine contains both amine and carboxyl groups, with the $\varepsilon$-amine group offering additional sites for reaction. In the presence of hydroxyl-rich PVA, esterification may occur between the carboxyl groups of L-lysine and the hydroxyl groups of PVA, forming PVA – c-lys ester linkages. Although less commonly reported than PVA – c-CA systems, this crosslinking pathway contributes to enhanced network density and potential bioactivity [10].

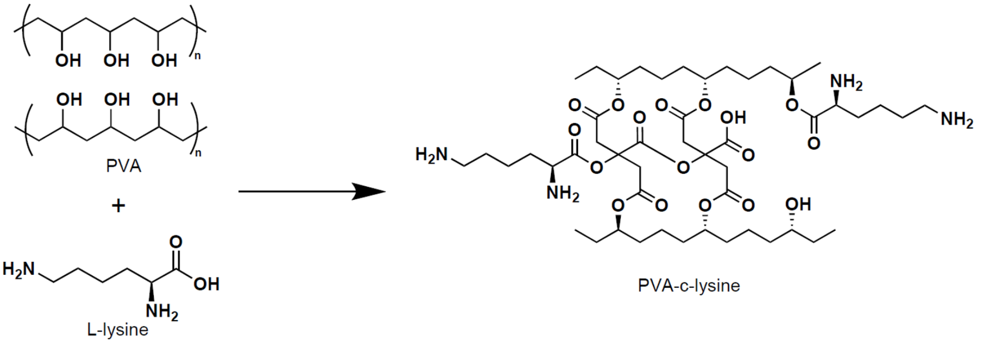


Figure 2. Esterification between PVA and L-lysine

c. Synergistic crosslinking among PVA, citric acid, and L-lysine

When all three components are combined, a complex crosslinked network may form. Citric acid can act as a bridging agent, linking both PVA and Lys through multiple ester bonds, while Lys provides additional sites for crosslinking through both its amine and carboxyl functionalities. The resulting three-dimensional network is expected to exhibit improved physicochemical stability and functional performance in various applications.

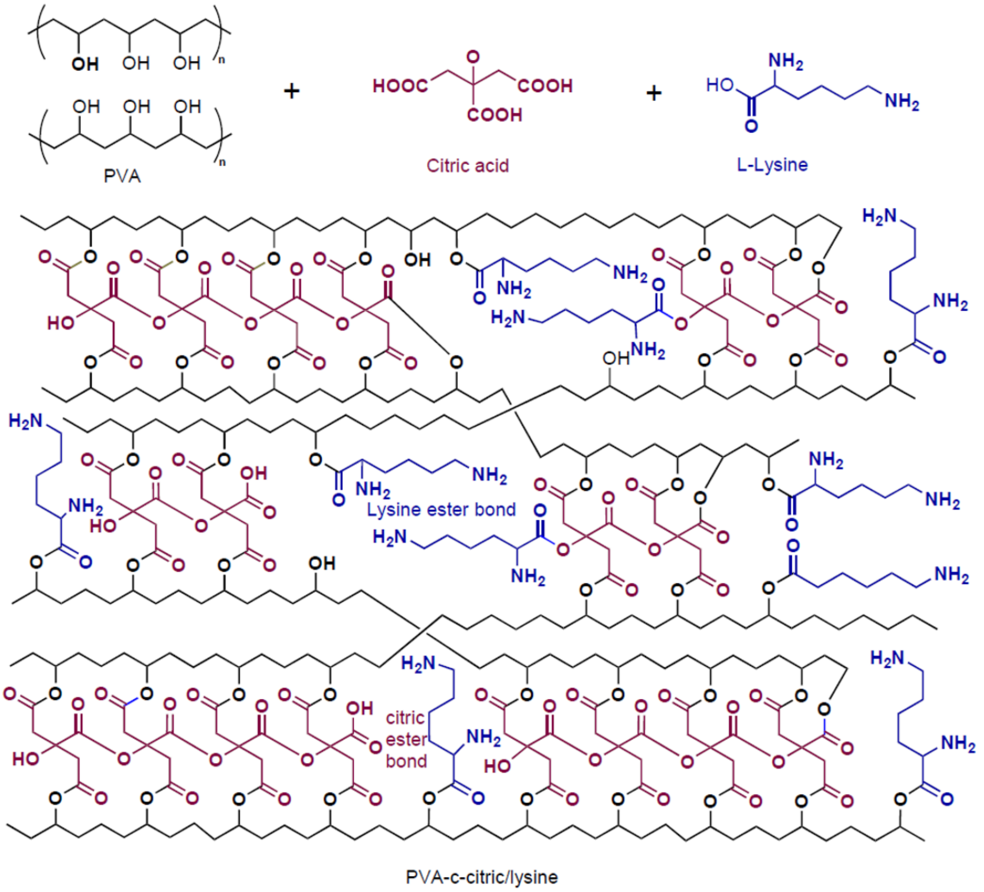


Figure 3. Esterification crosslinking among PVA, citric acid, and L-lysine

### *2.4. Characterization of the fabricated adsorbent PVA – c-CA – Lys/PEG*

a. Determination of crosslink density via gel fraction measurement

The gel fraction is a critical parameter that reflects the crosslink density within the polymer network of the film. A higher gel content indicates a higher degree of crosslinking, which contributes to improved structural stability and reduced solubility.

To determine the gel content, square film samples with dimensions of 2 cm × 2 cm and a thickness of approximately 20 µm to 30 µm were prepared. Each sample was immersed in 50 mL of distilled water at a controlled temperature of approximately 25 °C. The system was stirred and gently heated for 3 h to 5 h to facilitate the extraction of soluble (non-crosslinked) components.

After the extraction period, the films were carefully removed, rinsed thoroughly with distilled water to eliminate residual soluble, and dried to a constant weight. The dried samples were then weighed, and the gel fraction was calculated using the following equation:

$$C = \frac{(K_d - K_w) \times 100}{K_d} \quad (\%) \tag{1}$$

where $C$ is gel fraction (crosslink density, %), $K_w$ is initial dry weight of the film before extraction (g), and $K_d$ is initial dry weight of the film after extraction and drying (g).

All measurements were conducted in duplicate. This method allows for a quantitative assessment of the extent of crosslinking in the composite films and provides insight into the influence of chemical composition and reaction conditions on the network formation.

b. Fourier Transform Infrared (FTIR)

In this study, FTIR spectra were recorded using a Bruker TENSOR 27 spectrometer, operating in the range of $400\,\mathrm{cm^{-1}}$ to $4000\,\mathrm{cm^{-1}}$. This spectral window includes the vibrational frequencies of common functional groups such as hydroxyl ($-$OH), carboxylic ($-$COOH), amine ($-NH_2$), and ester (C$=$O) groups. This analysis provides detailed insights into the molecular interactions within the PVA-based films, particularly the formation of ester or amide linkages due to crosslinking agents, which are detectable by shifts or appearance of specific bands in the IR spectra.

c. Scanning Electron Microscopy (SEM)

In this study, the surface morphology of PVA films was observed using the JEOL NeoScope JCM-7000 benchtop SEM (JEOL, 2024). Its analytical method supports low-vacuum operation, which allows direct imaging of non-conductive samples without metal coating, preserving their native morphology. Thus, it was suited for polymeric materials such as PVA films, providing detailed insights into film surface structure and homogeneity under various formulations.

### *2.5. Determination of adsorption capacity of the adsorbent material*

The adsorption capacity of the material for acetic acid ($CH_3COOH$) was evaluated by measuring the concentration of $CH_3COOH$ in the solution before and after the adsorption process. The concentration of $CH_3COOH$ was quantified using a total organic carbon (TOC) analyzer (TOC-Control L, Shimadzu). The TOC-Control L had its limit of detection at 0 mg/L to 1000 mg/L and its error margins of 2%, the calibration curve was set up, ranging from 5 mg/L to 150 mg/L. All the analytical measures were conducted in triplicate.

The adsorption capacity, $Q_e$, is calculated using the following equation:

$$Q_e = \frac{(C_i - C_f)}{W} \times V \tag{2}$$

where $Q_e$ is the adsorption capacity (mg/g); $C_i$ is the initial concentration of $CH_3COOH$ in the solution (mg/L); $C_f$ is the concentration of $CH_3COOH$ in the solution after adsorption (mg/L); $W$ is the mass of the adsorbent material used (g); $V$ is the volume of the adsorbate solution (L).

This method provides a quantitative measure of the material's ability to adsorb acetic acid, based on the change in concentration before and after the adsorption process. In this study, the adsorption capacity of the PVA – c-CA – Lys/PEG adsorbent for acetic acid solution (adsorbate) was investigated by varying the concentration of acetic acid from 50 mg/L to approximately 1000 mg/L. The experimental temperature was maintained at room temperature, and the mass of the adsorbent film used in each experiment was 0.05 g. The PVA – c-CA – Lys/PEG membrane was immersed in acetic acid solution at different concentrations for 2 h until equilibrium was reached. After the adsorption process was completed, the concentration of acetic acid in the solution was measured by TOC analyzer, and the adsorption capacity was calculated as Eq. (2).

To investigate the effect of adsorption time on the material's adsorption capacity, PVA – c-CA/PEG and PVA – c-CA – Lys/PEG films were immersed in acetic acid solutions at a concentration of 1042 mg/L for different time intervals (20 min to 120 min). Each sample had a mass of 0.05 g and was immersed in 25 mL of acetic acid solution at room temperature. The adsorption process was conducted until equilibrium was reached, and the acetic acid concentration in the solution was then measured to calculate the adsorption capacity of the membrane. All the measures were conducted in duplicate.

The conventional adsorption models, Langmuir and Freundlich isotherm, were applied to investigate the adsorption kinetics of the PVA – c-CA/PEG and PVA – c-CA – Lys/PEG and determine the adsorption constants. The isotherm models are expressed mathematically as follows:

Langmuir isotherm (assumes monolayer adsorption on a homogeneous surface) [19]:

$$\frac{C_e}{Q_e} = \frac{1}{K_L \times q_m} + \frac{1}{q_m} \times C_e \tag{3}$$

where $C_e$ is the equilibrium concentration (mg/L), $Q_e$ is the amount adsorbed per unit mass of adsorbent (mg/g), $q_m$ is the maximum adsorption capacity (mg/g), and $K_L$ is the Langmuir constant (L/mg).

Freundlich isotherm (describes adsorption on a heterogeneous surface) [20]:

$$\log Q_e = \log K_F + \frac{1}{n} \times \log C_e \tag{4}$$

where $K_F$ is the Freundlich constant indicating adsorption capacity, and $1/n$ is the intensity factor.

These measurements and analysis, and adsorption experiments provided a better understanding of how factors such as solution concentration, adsorption time and kinetics, and the chemical composition of the material affect the adsorption capacity of the PVA – c-CA/PEG and PVA – c-CA – Lys/PEG, leading to the identification of optimal conditions for acetic acid adsorption.

## 3. Results and Discussions

### *3.1. Identification of Crosslinked PVA with citric acid and L-lysine*

Fig. 4 shows the FTIR spectrum of the PVA, PVA – c-CA (CA of 13%, 66% and 106% wt of PVA) and PVA – c-CA – Lys (CA of 66% wt, Lys of 11% and 33% wt of PVA) films. The FTIR spectrum of PVA displayed characteristic features of polyvinyl alcohol (PVA), notably a broad absorption band in the 3500 $cm^{-1}$ to 3200 $cm^{-1}$ range corresponding to the stretching vibrations of hydroxyl (–OH) groups. A distinct absorption band observed at 1720 $cm^{-1}$ was attributed to the carbonyl (C=O) stretching of ester groups formed during the crosslinking reaction between PVA and CA. This band confirmed the successful formation of ester linkages, contributing to the enhanced structural integrity of the polymer network. The persistence of the −OH band also indicated the presence of hydrogen bonding interactions within the crosslinked matrix, which could influence the swelling behavior and adsorption characteristics of the film.

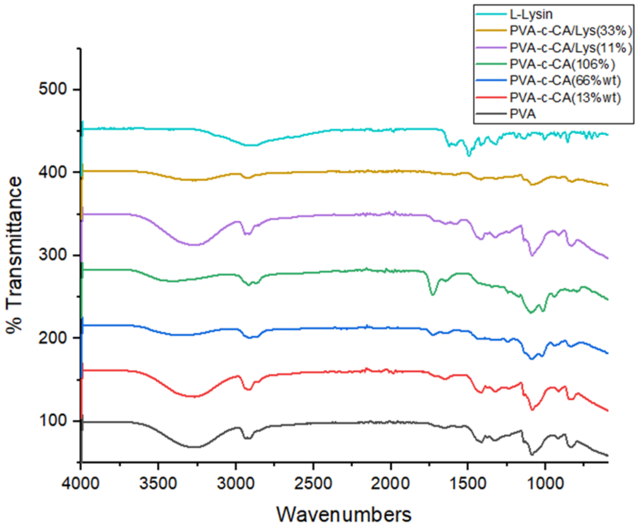


Figure 4. FT-IR spectra of various PVA-based films modified with citric acid (CA, 13%, 66% and 106% wt of PVA and PEG) and lysine (Lys, 11% and 33% wt of PVA and PEG)

Upon incorporation of L-lysine into the PVA−c-CA network, significant spectral changes were observed. Notably, a sharper band appears at 3300 cm$^{-1}$ to 3400 cm$^{-1}$, corresponding to the stretching vibrations of amine ($NH_2$) groups. This suggests that lysine not only participated in crosslinking but also introduces additional functional groups, amine and carboxyl groups, into the polymer matrix. These groups could enhance the film's potential for interactions with various adsorbates, particularly organic acids, due to the increased number of active binding sites.

At Lys concentration of 11% wt, a clearer shift in the amine-associated bands than Lys 33%, might indicate a higher degree of crosslinking and the development of a more complex polymer network. This structural enhancement likely improves adsorption efficiency by increasing the number of accessible interaction sites, as supported by experimental data.

### 3.2. *Effect of citric acid concentration on the swelling degree and gel fraction of PVA−c-CA*

The gel fraction is a critical parameter that reflects the crosslink density within the polymer network of the film. A higher gel content indicates a higher degree of crosslinking, which contributes to improved structural stability and reduced solubility. Fig. 5 showed the influence of citric acid crosslinker content (wt% relative to the total weight of PVA and PEG) on the swelling behavior and crosslinking density of the absorbent PVA−c-CA films. As the citric acid content increased, the crosslinking density expressed in gel fraction of the film improved steadily, reaching a maximum value of 91% at a citric acid content of 66%. This enhancement in crosslinking density was accompanied by a marked reduction in the film's swelling capacity, with the swelling ratio decreasing from 212% to 117% as the crosslinking density increased from 51% to 91%.

This inverse relationship can be attributed to the consumption of hydroxyl (−OH) groups on the PVA chains during the crosslinking reaction. Citric acid, which contains carboxyl (−COOH) groups, reacts with the –OH groups in PVA to form ester bonds, thereby reducing the number of hydrophilic sites available for water absorption. In addition, the formation of a dense crosslinked network restricts the mobility and orientation of polymer chains, leading to a more compact structure with reduced free volume. This structural constraint limits water molecule penetration, ultimately suppressing the swelling ability of the membrane. Thus, the higher the crosslinking density, the lower the membrane's capacity to swell. These results indicated that at 66% wt CA of total weight of PVA–PEG the highest gel fraction the lowest swelling degree indicated the most effective crosslink achieved, thus was used for fabricating the PVA–c-CA/PEG in the following experiments of this research.

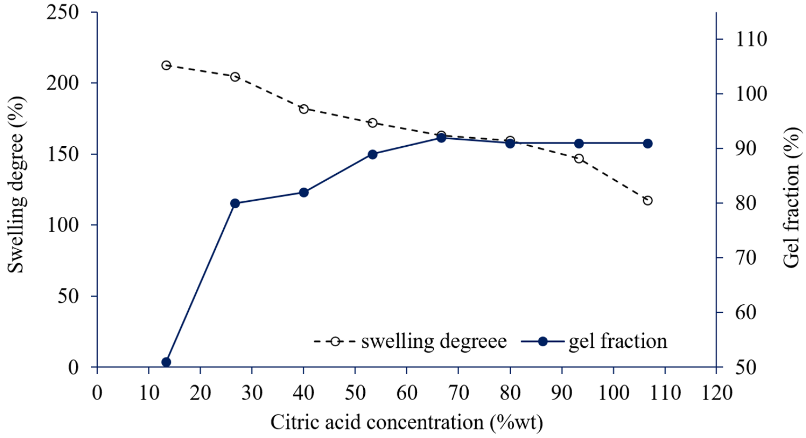


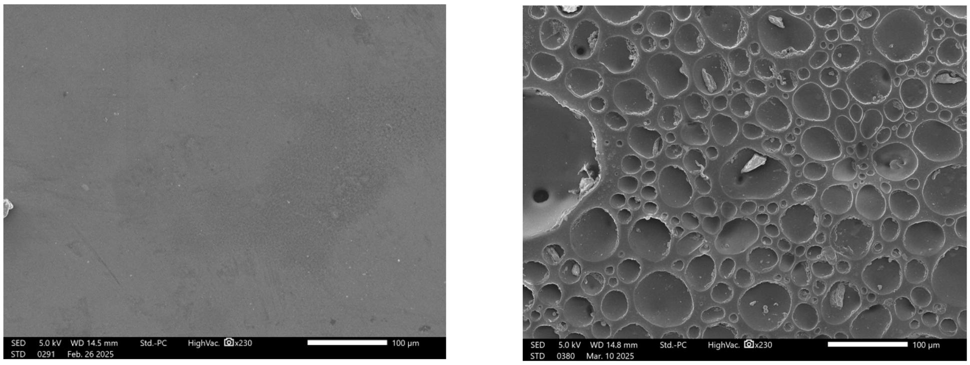
Figure 5. Effect of citric acid concentration on the swelling degree and gel fraction of PVA–c-CA (data expressed the average of measurements)

### 3.3. *Evaluation of the surface morphology of PVA films at different PEG proportions*

The SEM images of the PVA–c-CA(–Lys)/PEG films with increasing PEG wt ratios (20%, 50%, and 100% of PVA's wt); PVA–c-CA and PVA revealed distinct morphological features that influence their adsorption properties, as demonstrated in Fig. 6. The PVA–c-CA–Lys membrane without PEG showed a relatively smooth surface, lacking the porous structure needed for efficient adsorption (Fig. 6(a)). The fewer surface sites available for adsorbate interaction are likely consistent with its limited adsorption capacity.

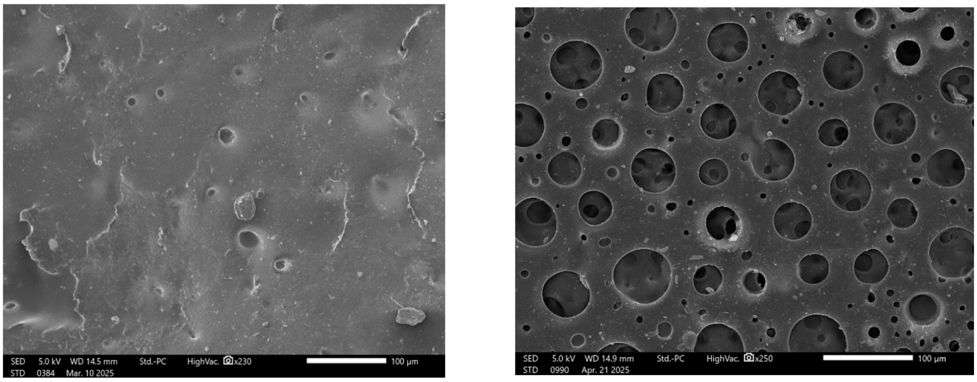
Figs. 6(b)–(d) compares between the PVA–c-CA/PEG and PVA–c-CA–Lys/PEG, at PEG 50% wt of PVA. In the SEM image of the PVA–c-CA/PEG membrane (Fig. 6(b)), the surface morphology exhibited a dense structure with shallow and unevenly distributed pores. The crosslinking reaction between polyvinyl alcohol (PVA) and citric acid (CA) played a dominant role in this structure. Due to the presence of three carboxyl groups (–COOH) in each citric acid molecule, extensive esterification with the hydroxyl groups (–OH) of PVA occurs, resulting in a highly crosslinked and compact polymer network. This dense crosslinked network significantly restricts the phase separation and pore formation by PEG, leading to the observed shallow pore morphology. Consequently, the membrane's porosity and accessible surface area was substantially reduced, which might negatively impact its adsorption performance toward acetic acid molecules.

The film with 20% PEG (Fig. 6(c)) exhibited the formation of small pores, but these pores were not uniformly distributed. The PVA–c-CA–Lys/PEG (50%) membrane (Fig. 6(d)) demonstrated a significant improvement in porosity, with well-defined and evenly distributed pores. The film containing 50% PEG, exhibited a uniform and optimized pore structure, which could enhance the adsorption capacity by increasing the surface area and promoting better interaction between the membrane and adsorbates. This moderate PEG content provides the best balance between high surface area, uniform pore size, and mechanical stability, making it the most effective membrane for adsorption applications among the samples tested. However, the PVA – c-CA – Lys/PEG (100%) membrane (Fig. 6(e)), exhibited the largest pore sizes, suffering from irregular pore distribution. The excessive PEG content led to larger pores, which reduces the surface area available for adsorption, potentially compromising the membrane's performance. The increased porosity also impacts the mechanical stability of the membrane, making it less suitable for applications that require long-term durability.



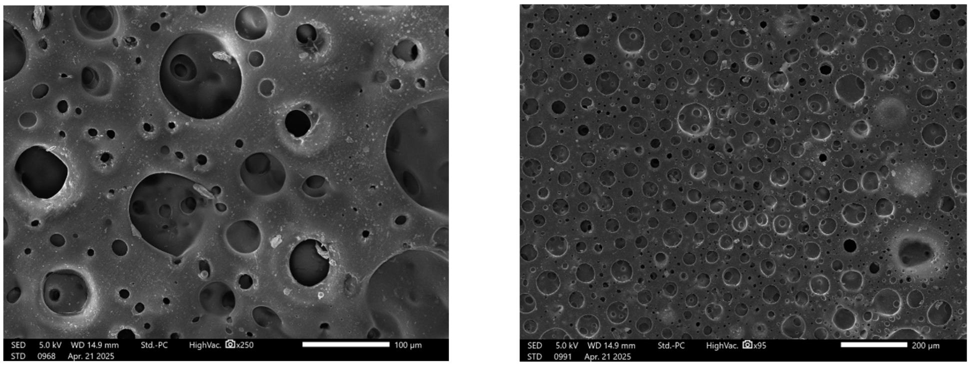
(a) PVA

(b) PVA – c-CA/PEG 50%



(c) PVA – c-CA – Lys/PEG 20%

(d) PVA – c-CA – Lys/PEG 50%



(e) PVA – c-CA – Lys/PEG 100%

(f) PVA – c-CA/Lys/PEG 50% (× 200 scale)

Figure 6. SEM Images of PVA – c-CA(– Lys)/PEG with varying PEG content (% wt PEG/PVA)

In the SEM image of the PVA – c-CA – Lys/PEG (50%) membrane (Figs. 6(d)–(f)), a well-developed porous structure with uniformly distributed and interconnected pores is observed. This indicated that the introduction of L-lysine (Lys) into the crosslinking system effectively modulated the crosslinking density between PVA and citric acid. L-lysine, possessing both amino and carboxyl functional groups, acted as a spacer within the polymer network by forming selective crosslinks with hydroxyl groups from PVA and carboxyl groups from citric acid. This moderated crosslinking prevents excessive network densification, thereby facilitating phase separation during PEG incorporation and promoting the formation of deeper and more interconnected pores.

In conclusion, the PVA – c-CA – Lys/PEG (50%) membrane achieved the most uniform and optimal porous structure, which could offer the highest adsorption capacity and the best mechanical stability. Therefore, the introduction of 50% PEG mass was used to fabricate the new adsorbent films and investigation of its adsorption capacity in this study.

### *3.4. Adsorption capacity of the new adsorbent PVA – c-CA( – Lys)/PEG*

Fig. 7 showed the adsorption capacity ($Q_e$) of the PVA – c-CA (66% wt)/PEG with and without Lys (11% wt), dependent on the concentration of adsorbate acetic acid. Both attained a significant increase in $Q_e$ as the acetic acid concentration increased from 300 mg/L to 1091 mg/L. Specifically, for PVA – c-CA – Lys/PEG the $Q_e$ value increased from 11.8 mg/g to 84.3 mg/g over a 120 min period as the concentration went up from 352 mg/L to 1042 mg/L, then decreased to 77 mg/g when the concentration reached 1091 mg/L. The PVA – c-CA/PEG had a similar trend except for a lower $Q_e$ maximum value of 67.1 mg/g. These trends were consistent with previous studies, where higher concentrations of acetic acid led to an increased adsorption capacity due to the larger number of molecules available to interact with the adsorbent surface. For instance, Pervez et al. observed a similar trend, where $Q_e$ increased as the concentration of the target pollutant (organic acid) in the solution increased [21].

The simultaneous incorporation of citric acid and L-lysine into the PVA membrane structure significantly enhances the adsorption efficiency of acetic acid due to the presence of additional functional groups and specific molecular interaction mechanisms. Citric acid primarily introduces carboxyl ($-$COOH) groups, which can form hydrogen bonds with the $-$OH and $-$COOH groups of acetic acid, thereby contributing to physical adsorption mechanisms. Furthermore, Lysine, an amino acid containing both amine and carboxyl groups, allows the formation of hydrogen bonds and ionic interactions with adsorbate molecules such as organic acids or metal ions. Crosslinking with L-lysine introduces primary amine ($-NH_2$) groups into the polymer network. These amine groups can form stronger hydrogen bonds and engage in weak acid–base interactions with the carboxyl groups of volatile fatty acids (VFAs), including acetic acid, thus enhancing both affinity and selectivity, as previously observed by Elhami et al. [22]. This aligns with the study by Wu et al., where lysine was used to functionalize the surface of biomaterials to enhance affinity for metal ions [23]. Additionally, Lan et al., indicated that the presence of porous structures and polar functional groups facilitates the diffusion and retention of adsorbate molecules within the polymer network [24]. This is consistent with our results, where membranes containing lysine show prolonged adsorption delays and higher retention capacity. Moreover, the inclusion of amino acids or multifunctional molecules like L-lysine can reduce the crystallinity of PVA by disrupting the orderly arrangement of polymer chains. This phenomenon, similarly, observed in PVA-dopamine-citric acid membranes, leads to an increase in the effective surface area and the availability of active adsorption sites.

Tonucci et al. synthesized hybrid imprinted polymer-based adsorbent for recovering acetic acid from fermented food waste, obtained the maximum VFAs adsorption capacity of $Q_e$ approximately

50 mg/g [25]. Our results attained the maximum value of $Q_e$ for PVA−c-CA(−Lys)/PEG was 1.7 times greater than that observed in previous studies, demonstrating better adsorption performance at higher acetic acid concentrations [25, 26].

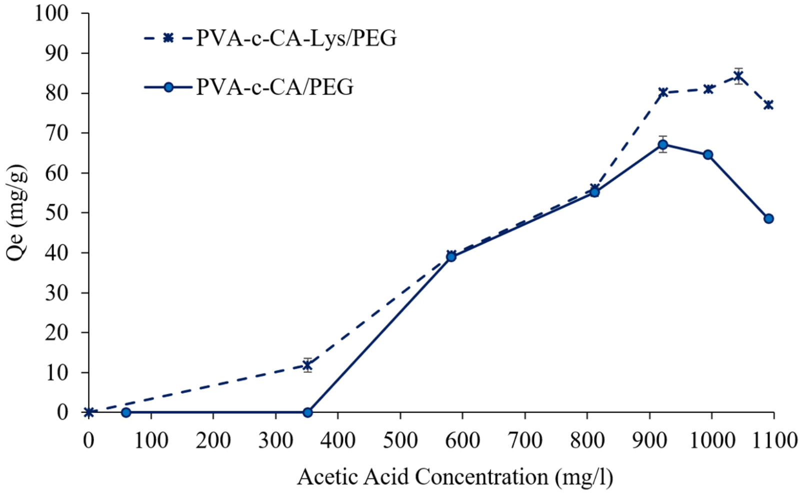


Figure 7. Effect of concentration of adsorption capacity of PVA−c-CA/PEG and PVA−c-CA−Lys/PEG (data expressed the median and the standard deviation as error bars)

The adsorption behavior of the material was analyzed using both Langmuir and Freundlich isotherm models. The adsorption isotherm constant and the correlation coefficients for the adsorption of $CH_3COOH$ according to the Langmuir Isotherm and Freundlich Isotherm at room temperature. As shown in Table 1, the Freundlich model for PVA−c-CA−Lys/PEG provided a more accurate fit to the experimental results, with a correlation coefficient ($R^2$) of 0.974, compared to 0.757 obtained from the Langmuir model. The PVA−c-CA/PEG could only be expressed by the Freundlich Isotherm. The $K_F$ value of PVA−c-CA−Lys/PEG (0.002) suggests a favorable adsorption affinity for $CH_3COOH$ than PVA−c-CA/PEG (0.067). Furthermore, the adsorption intensity factor $1/n$ of both PVA−c-CA−Lys/PEG (1.535) and PVA−c-CA/PEG (1.001), indicates a heterogeneous surface with varying adsorption site energies, as also supported by Fig. 6. This implies that functional groups on the material's surface are not uniformly distributed, resulting in non-uniform adsorption capacities across the surface. These results demonstrate that the material exhibits multilayer adsorption behavior on an energetically diverse surface, which is more accurately modeled by the Freundlich equation.

Table 1. The adsorption isotherm constant and the correlation coefficients for the adsorption of $CH_3COOH$ according to the Langmuir Isotherm and Freundlich Isotherm at room temperature

| Models | Langmuir Isotherm | | | Freundlich Isotherm | | |
|---|---|---|---|---|---|---|
| | $b$ (L/mg) | $Q_{\max}$ (mg/g) | $R^2$ | $K_F$ (mg/g) | $1/n$ | $R^2$ |
| PVA−c-CA/PEG | – | 67.15 | – | 0.067 | 1.001 | 0.968 |
| PVA−c-CA−Lys/PEG | 0.0004 | 84.26 | 0.757 | 0.002 | 1.535 | 0.974 |

### *3.5. Effect of adsorption time on adsorption capacity of PVA−c-CA(−Lys)/PEG*

The adsorption capacity of the synthesized PVA−c-CA−Lys/PEG adsorbent was dependent on the adsorption time, presented in Fig. 8. All materials tend to reach equilibrium within 60 min to

80 min, but the 11% lysine sample continues to show a significant increase up to 120 min, indicating its potential application in extended adsorption systems or those requiring sustained performance over time. This is a considerable advantage in wastewater treatment contexts, where pollutants need to be retained in a stable and continuous manner.

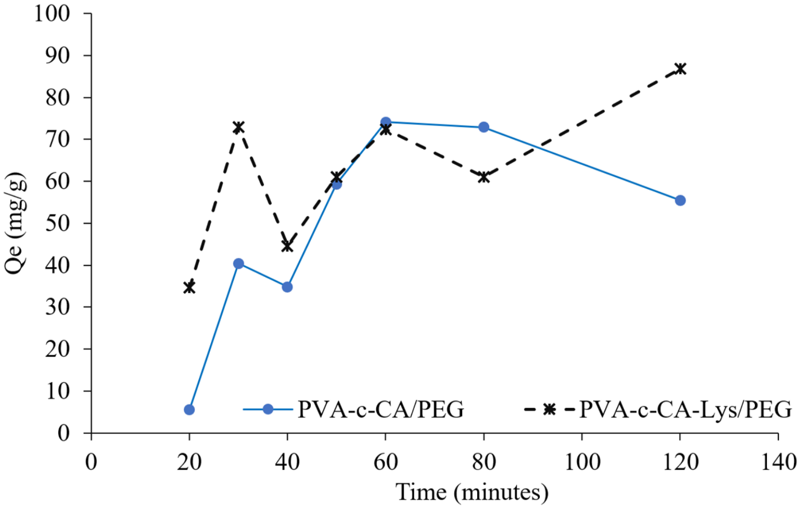


Figure 8. Effect of adsorption time on adsorption capacity of PVA−c-CA/PEG and PVA−c-CA−Lys/PEG (data expressed the average of measurements)

Experimental results show that the original PVA−c-CA membrane only reaches a maximum $Q_e$ value of about 74.12 mg/g at 60 min, while membranes containing lysine exhibit significantly higher values under the same conditions. Specifically, the PVA−c-CA−Lys/PEG membrane reaches 86.79 mg/g at 120 min. These results suggest that lysine not only increases the number of interacting functional groups but also affects the kinetics and mechanism of adsorption. The addition of lysine into the polymer network of PVA−c-CA membranes has demonstrated a considerable improvement in the material's adsorption capacity.

### 3.6. *Potential use of the new generation green adsorbent for recovery of biochemicals from waste streams*

Our results aligned with the general trends observed in literature suggest that the PVA−c-CA(−Lys)/PEG composite could provide superior adsorption performance of PVA. The results are a considerable advantage of the PVA−c-CA(−Lys)/PEG in resource recovery from wastewater treatment contexts, where pollutants need to be converted and recovered in a stable and continuous manner. This opens opportunities for further research on the saturation dynamics and practical applications of this material in larger-scale adsorption processes.

The addition of lysine into the polymer network of PVA−c-CA has demonstrated a significant improvement in the material's adsorption capacity, prolonged adsorption delays and higher retention capacity. Results of SEM showed the fabricated PVA−c-CA (66% wt)-Lys (11%)/PEG film a significantly more open and porous morphology, which is expected to enhance its adsorption capacity for acetic acid.

In a sustainable approach, waste streams must be used as a resource. Anaerobic treatment of wastewater and wastes can combine pollution control with energy recovery such as methane gas or recovery of valuable metabolites such as volatile fatty acids (VFAs). Developing and improving the biodegradable polymer PVA helps sustainable management of resources while reducing environmental impact as it can replace petroleum-based plastics, helping to reduce plastic waste. In addition, all materials used for synthesis of the new generation green adsorbent PVA – c-CA – Lys/PEG are all safe and environmentally friendly polymer and natural compounds that help reduce the possibility of environmental pollution after decomposition.

Adsorption relies on physicochemical interactions between volatile fatty acids (VFAs) and porous adsorbents. Electrostatic attraction occurs between carboxylate anions and positively charged functional groups (e.g., amine groups). The process involves three stages: (i) diffusion to adsorbent surfaces, (ii) binding to active sites, and (iii) desorption via solvent/thermal regeneration. In this study, the desorption phase, i.e via increasing the temperature to break these interactions, releasing VFAs into the nitrogen gas stream has not yet been examined. The VFA vapors can then be cooled and condensed into a concentrated solution [7, 27]. Further studies may explore the desorption processes and reusability of the membrane, its performance with mixed VFAs, and long-term operational stability. Overall, this research contributes a significant step forward in green materials science for sustainable wastewater valorization.

## 4. Conclusions

This study successfully developed and characterized a novel biodegradable adsorbent film based on polyvinyl alcohol (PVA), citric acid (CA), polyethylene glycol (PEG), and L-lysine (Lys) for the efficient recovery of carboxylates, particularly acetic acid from fermented industrial food wastewater. The optimized formulation, incorporating 66% CA, 11% Lys (of PVA and PEG) and 50% PEG (of PVA) in weight, exhibited superior gel fraction and mechanical stability, while the addition of Lys significantly enhanced pore uniformity and surface morphology. Lysine could function as a molecular spacer, effectively modulating the crosslinking density and enabling the formation of well-distributed, interconnected pores, which improved adsorption performance. FT-IR spectra of various PVA-based films modified with citric acid and lysine confirmed the formation of ester linkages, contributing to the enhanced structural integrity of the polymer network. Adsorption experiments demonstrated that the PVA – c-CA – Lys/PEG membrane achieved the highest adsorption capacity ($Q_e$ of 86 mg/g) at elevated acetic acid concentrations, outperforming control membranes and previously reported materials. These results highlight the membrane's potential for recovering valuable carboxylates as platform chemicals for downstream applications, such as in the production of biofuels, biodegradable polymers, and green detergents. Importantly, the proposed method represents a sustainable and environmentally friendly approach to industrial wastewater treatment, aligning with circular economic principles and global environmental objectives.

## Acknowledgements

Financial support from Vietnam Ministry of Education and Training, research project No. B2024. XDA.04 entitled "Research on improved anaerobic process for production of biochemical materials from food processing wastewater treatment" at Hanoi University of Civil Engineering is greatly acknowledged. We would like to thank Dr. Tran Thi Thuy for her insightful and valuable ideas and contributions, and Nguyen Minh Duc for his great support in this study.

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