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Garlic Peel Waste as an Eco-Friendly Biosorbent for Used Cooking Oil Regeneration: Adsorption Efficiency and Mechanistic Evaluation

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Abstract

This study explores the valorization of garlic peel waste as a sustainable biosorbent for the purification of used cooking oil through removal of free fatty acids (FFA) and other oxidation-related undesirable byproducts. Garlic peel adsorbent was prepared in both unactivated and chemically activated forms using hydrochloric acid (HCl) to enhance its adsorption performance. The effects of adsorbent mass and contact time on the adsorption process was systematically evaluated, while adsorption behavior and mechanisms were analyzed using isotherm, kinetic, and surface morphology approaches. The activated garlic peel exhibited superior adsorption performance, achieving a 76.74% reduction in FFA content under optimum conditions, using 24 g adsorbent/100 mL sample within 45 min. Adsorption equilibrium was best represented by the Langmuir isotherm model, suggesting monolayer adsorption on homogeneous active sites, whereas pseudo-second-order kinetics indicates that chemisorption dominates the adsorption process. Scanning Electron Microscopy (SEM) analysis confirmed that chemical activation enhances surface roughness, pore formation, and the availability of active adsorption sites, thereby improving adsorption efficiency. In addition to reducing FFA levels, the adsorbent contributes to lowering peroxide value and acid number, indicating a broader improvement in oil quality. These findings demonstrate that garlic peel waste possesses strong potential as a low-cost, environmentally benign, and renewable biosorbent for cooking oil regeneration. The study provides an alternative strategy for agricultural waste valorization while supporting sustainable and household-scale oil purification technologies.

Keywords: adsorption; garlic peel waste; mechanism; natural adsorbent; purifying

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INTRODUCTION

In Indonesia, cooking oil that has been repeatedly used for frying is commonly known as minyak jelantah, or used cooking oil. In fact, oil quality declines in proportion and chemical composition to the number of heating and reuse cycles it undergoes. Repeated heating raises both free fatty acid (FFA) content and peroxide value, while also darkening the oil and producing unpleasant odor. Beyond reducing palatability, this degradation possesses serious health risks when frying oil is consumed over an extended period. Oxidation and thermal breakdown during repeated frying generate toxic compounds that potentially harm human health (Zhang & Chen, 2020).

It is necessary to find a comprehensive and sustainable solution to this issue by employing natural adsorbents derived from agricultural or industrial residues. According to Patel and Mondal (2019), plant materials, such as coconut shells, banana peels, sugarcane bagasse, and turmeric residues can be utilized to effectively purify wasted cooking oil by removing the generated undesirable particles through adsorption process. Recently, this approach has been very popular due to its economics, operability, availability, and sustainability. Despite the fact garlic peel contains a variety of substances, including cellulose, lignin, and phenolic compounds, it remains underutilized. Both physical and chemical adsorption may be utilized to bind contaminants in used oil, and the cellulose found in garlic skin has the potential to serve as an active site for this purpose (Chen et al., 2018). Gupta and Jain (2018) proposed a method to utilize garlic peel in used-cooking purification and environmental management.

Earlier research has shown that various natural adsorbents can improve the quality of used cooking oil. For example, activated carbon derived from coconut shells or banana peels has been shown to effectively lower FFA and peroxide values. The effectiveness of the adsorption process depends on several factors, including the quantity and fineness of the adsorbent, the contact time with the oil, and the treatment method applied, whether soaking, stirring, or heating (Suryani et al., 2021). Although these alternative natural adsorbents show encouraging results, the application of garlic skin waste for used cooking-oil purification remains largely unexplored, and its adsorption performance and underlying mechanism have not been established. The novelty of this study lies in its integrated evaluation of garlic skin as a single-source biosorbent for used cooking oil purification: unlike previous reports that examined natural adsorbents individually against one oil-quality parameter, this work simultaneously (i) compares unactivated and HCl-activated garlic skin, (ii) tracks three complementary quality indicators (FFA, acid value, and peroxide value), and (iii) couples isotherm and kinetic modeling with SEM-based surface characterization to establish the adsorption mechanism. This combined approach has not previously been reported for garlic skin waste and provides a more complete basis for assessing its potential as a used-cooking-oil biosorbent than single-parameter studies of other agricultural by-products.

The results of this study are anticipated to facilitate the advancement of purification techniques that are more cost-effective, environmentally friendly, and user-friendly, particularly for small-scale users. It also offers a practical way to valorize garlic skin waste that would otherwise be discarded. In a broader sense, making useful adsorbent products out of agricultural waste supports the idea of a circular economy, in which waste is turned into materials that add value. In addition to the use of Freundlich and Langmuir isotherm models, kinetic models like the pseudo-first-order and pseudo-second-order equations (Azizian et al., 2018) were employed. This study aims to: assess the effectiveness of garlic skin as an adsorbent in reducing free fatty acid (FFA), acid value, and peroxide value in used cooking oil; assess the effectiveness of garlic skin in removing contaminants from oil; and analyze the adsorption behavior, mechanism, and rate of adsorption. The research is relevant for improving the safety and quality of recycled cooking oil while reducing the environmental effects of agricultural waste.

MATERIALS AND METHOD

Materials

The materials utilized in this study include garlic **(*Allium sativum* L.)** peel waste (GPW) as the raw material for adsorbent preparation and used cooking oil as the object for purification. The solvents and other chemical reagents used throughout this research were distilled water, 1% starch solution, 0.1 N hydrochloric acid solution, 0.1 N sodium hydroxide solution, 0.1 N sodium thiosulfate, analytical grade (≥ 96% purity) phenolphthalein indicator, chloroform, glacial acetic acid, potassium iodide, and ethanol.

Equipment

The equipment used in this research comprised an electric blender, 100-mesh sieve, and analytical balance. Additionally, laboratory glassware such as burettes, stands, Erlenmeyer flasks, beakers, volumetric flasks, graduated cylinders, and dropper pipettes were employed in material measurement and chemical analysis. Thermometers, spray bottles, and filter paper were utilized during the sample preparation and separation stages. Meanwhile, a hot plate and magnetic stirrer were used for the heating and mixing processes.

Preparation of Used Cooking Oil

The used cooking oil utilized in this study was sourced from a home industry located in the vicinity of Arun residential complex in Lhokseumawe. Firstly, the oil was carefully filtered using a filter cloth to remove solid contaminants, such as food remnants and burnt particles. Afterward, the oil was left to stand for 24 hours at room temperature to allow the gravity-

based separation of finer particles. Then, the oil was further filtered using a filter paper to ensure the removal of any residual contaminants. Finally, the oil obtained was ready for the further experimental stage (Kannan & Wankhade, 2017).

Preparation of Adsorbent

First, the garlic peel, which had been thoroughly washed, was prepared as the raw material for the adsorbent. The peel was then sun-dried until dry. Then, the garlic peel was finely ground using an electric blender until to obtain fine powder. The resulting powder was shifted through a 100-mesh sieve to obtain uniform-sized particles, which were then ready for use as an adsorbent in the used cooking oil purification process (Shukla & Sharma, 2016).

Chemical Activation of Garlic Peel Powder

The fine garlic peel was chemically activated using a 0.1 N HCl solution. A total of 20 grams of garlic peel powder was mixed with 200 mL of 0.1 N HCl solution in an Erlenmeyer flask. The mixture was stirred continuously for approximately 30 minutes to ensure uniform exposure of the adsorbent surface to the acid solution. Subsequently, the mixture was left to stand for 24 hours at room temperature to allow complete activation. Afterward, the garlic peel powder was filtered and thoroughly washed with distilled water until the pH of the filtrate was neutral (pH ±7). The clean adsorbent was dried in an oven at 60–80°C for approximately 4 hours (Saha & Bhattacharyya, 2016). The activated adsorbent was then stored in a sealed container and was ready for use in the oil adsorption process.

Adsorption Process

One hundred milliliters of used cooking oil was introduced into an Erlenmeyer flask, and garlic peel-based adsorbent was added in varying amounts of 18 g, 20 g, 22 g, and 24 g. Then, the mixture was heated to 70°C using a controllable hot plate heater. The mixture was then stirred with a magnetic stirrer for different durations of 15, 30, and 45 minutes. Upon the completion of the mixing process, the mixture was allowed to stand at room temperature (approximately 25–30°C) for 15 minutes to allow separation of the adsorbent from the oil (Zhang & Chen, 2020). Finally, the oil was further filtered using a filter paper to completely separate the remaining adsorbent from the oil.

Determination of FFA, Acid Value and Peroxide Value

The process of testing the quality of used cooking oil involves three primary tests utilizing titration methods (Choi & Rhee, 2018; Ferrante & Rinaldi, 2019; Zeng & Lin, 2021). The Free Fatty Acid (FFA) content of the oil was quantified using the titration method employing titration with NaOH solution. Accordingly, the acid value test was also performed utilizing titration method by adding a solvent mixture of ethanol and ether with a few drops of phenolphthalein indicator, followed by titration with NaOH solution. Finally, the peroxide value was carried out by titration with 0.1 N sodium thiosulfate solution after adding a mixture of glacial acetic acid and chloroform.

Calculation of Adsorption Capacity and Data Analysis

The adsorption capacity at equilibrium (Q_e, mg/g) was calculated using the standard mass-balance equation:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad \text{.....eq. 1}$$

where

C_0 = initial FFA concentration (mg/L)
C_e = equilibrium FFA concentration (mg/L)
V = volume of oil treated (L)
m = mass of adsorbent (g).

C_0 and C_e were derived from the titration-based FFA percentage using the oil density and the molar mass of oleic acid, consistent with the FFA/acid-value determination described above. Based on the plateau observed in the FFA-versus-time profile (Figure 1), the adsorption equilibrium was assumed to be achieved at 45 min of the adsorption process, and the oil volume was assumed to be constant throughout the adsorption experiment. All adsorption experiments (FFA, acid value, and peroxide value measurements) were performed in triplicate (n = 3) under each combination of adsorbent mass and contact time, and the values were the mean of the three replicates, with the standard deviation (SD) reported as error bars in Figures 1 and 2.

Adsorption Isotherm

Adsorption isotherms evaluation was conducted to obtain insights into the mechanism of garlic peel adsorbent in the purification of used cooking oil. For the isotherm analysis, variations in adsorbent mass (18, 20, 22, and 24 g) were tested at a fixed contact time of 45 min, followed by determination of the free fatty acid (FFA) content in the adsorbed oi. The experimental data are then analyzed using the Langmuir and Freundlich adsorption isotherm models to evaluate the efficiency and capacity of the garlic peel adsorbent (Azizian et al., 2018).

Langmuir Model:

$$\frac{1}{q_e} = \frac{1}{q_{max}}\left(\frac{1}{K_L C_e} + \frac{1}{q_{max}}\right) \quad \text{.....eq. 2}$$

where:

C_e = concentration of adsorbate (mg/L)
q_e = amount of adsorbate (mg/g)
q_{max} = maximum adsorption capacity (mg/g)
KL = Langmuir constant (L/mg)

Freundlich Model:

$$\ln qe = \ln KF + \frac{1}{n}\ln Ce \quad \text{.....eq. 3}$$

where:

KF = Freundlich constant
$1/n$ = adsorption intensity
C_e = equilibrium concentration of adsorbate (mg/L)

Kinetic Model

The adsorption kinetics model of used cooking oil describes how the adsorption process of used cooking oil by the garlic peel adsorbent occurs over time. Generally, adsorption kinetics can be analyzed using various models that characterize the rate and mechanism of the adsorption process, including the first-order and second-order models (Brandani, 2021; Zhang et al., 2019).

Pseudo-First Order Kinetic Model:

$$\ln(q_e - q_t) = \ln q_e - k_1.t \quad \text{.....eq. 4}$$

Pseudo-Second Order Kinetic Model:

$$\frac{t}{q_t} = \frac{1}{k_2.{q_e}^2} + \frac{t}{q_e} \quad \text{.....eq. 5}$$

where:

q_t = amount of adsorbate adsorbed at time (mg/g)
q_e = amount of adsorbate at equilibrium (mg/g)
k_1 = pfo adsorption rate constant (1/min)
k_2 = pso adsorption rate constant (g/mg·min)

SEM (Scanning Electron Microscope)

Surface morphology analysis of the adsorbent was conducted using a Scanning Electron Microscope (SEM) at the Testing Laboratory of the Department of Chemical Engineering, Politeknik Negeri Lhokseumawe. This analysis aimed to observe the surface structure, porosity, and morphological changes of the garlic peel adsorbent (GPA) before and after the adsorption process. The microscopic observations were expected to provide visual insights into pore's density and surface area, which are crucial factors in the adsorption efficiency of used cooking oil. A comparison of the SEM images of both types of adsorbents will help determine which adsorbent exhibits superior physical characteristics that enhance adsorption performance (Dinesh & Nithyanand, 2017).

RESULTS AND DISCUSSION

Effectiveness of Activated and Unactivated Garlic Skin-based Adsorbents in Purifying Used Cooking Oil

Performance of garlic-skin adsorbents both chemically activated and unactivated showed a remarkable decrease in free fatty acid (FFA) percentage with the increasing adsorption time. As seen in Figure 1, used cooking oil, with an initial FFA of 1.367±0.021%, indicated substantial oxidative deterioration. After 45 minutes adsorption, the unactivated adsorbent reduced FFA to 0.370±0.027%, whereas the chemically activated adsorbent achieved a lower final FFA of 0.318±0.030%. The fastest FFA content decline occurred within the first 15 minutes, after which the FFA content reduction rate slowed and approached adsorption equilibrium after 45 minutes.

These findings indicate that chemical activation enhances adsorbent's effectiveness in reducing FFA. By the end of the observation period, the activated adsorbent reduced FFA by 76.74% from its initial value, while the unactivated adsorbent achieved a 72.93% reduction. This improvement is attributable to the activation induced refinement of surface structure, increased specific surface area, greater pore development, and the formation of additional surface functional groups that together improve adsorption capacity (Foo & Hameed, 2010; Liew et al., 2018). Activation can also partially disrupt cellulose, hemicellulose, and lignin matrices in garlic skins, increasing porosity and, consequently, adsorption capacity and kinetics. As a low-cost, environmentally friendly agricultural by-product, garlic skin is a promising natural adsorbent for purifying used cooking oil. The substantial reduction of FFA to below 0.5% within 45 minutes using the activated adsorbent suggests strong potential for practical applications in used-oil regeneration.

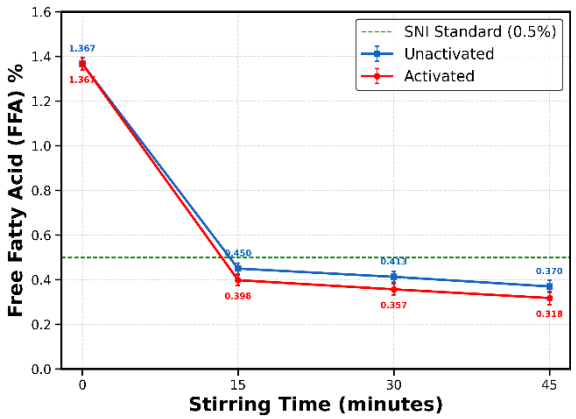

Figure 1. Comparison of unactivated vs. HCl-activated garlic skin-based adsorbents efficiency for FFA reduction

The Effect of Adsorbent Mass and Stirring Time on FFA (%) Content

As depicted in Figure 2, garlic skin-based adsorbent showed high efficiency in reducing free fatty acids (FFA) in used cooking oil. A consistent decline in FFA was observed across all adsorbent-mass variations, with 24 g yielding the most optimal result: FFA decreased to 0.370±0.027% for the unactivated adsorbent and to 0.318±0.030% for the chemically activated adsorbent within 45 minutes. This pattern accords with the adsorption principle that increasing adsorbent mass generally provides more active sites for binding FFA molecules (Foo & Hameed, 2010). The sharpest reduction occurred during the first 15 minutes, followed by a slower decline until minute 45, indicating that the system was approaching adsorption equilibrium (Thines et al., 2017). The standard deviations for all FFA measurements ranged from 0.021% to 0.030%, indicating good reproducibility of the triplicate experiments.

Chemical activation markedly enhanced the adsorption capacity of garlic skin. For every mass tested, activated adsorbents achieved greater FFA

reductions than unactivated ones; at 24 g, the efficiency gain was approximately 3.8 %. Activation of lignocellulosic biomass increases surface area, develops porosity, and introduces surface functional groups features that strengthen affinity for fatty acids (Liew et al., 2018; Ukanwa et al., 2019). Referring to the Indonesian National Standard *SNI 7709:2019* on palm cooking oil quality, all activated-adsorbent masses reduced FFA below the Quality II limit (≤ 0.5 %), and the 24 g condition approached the Quality I limit (≤ 0.3 %). These results support garlic skin as a low-cost, sustainable, and environmentally friendly adsorbent aligned with green-processing principles for used-oil regeneration.

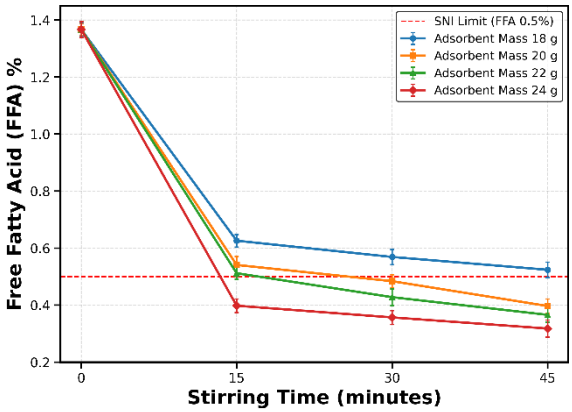

Figure 2. Effect of garlic skin-based adsorbent mass and contact time on FFA content of used cooking oil

The Effect of Adsorbent Mass and Stirring Time on Peroxide Value

Based on Figure 3, a consistent decline in peroxide value was observed across all adsorbent-mass variations, indicating that increasing adsorbent dosage improved peroxide removal efficiency. However, unlike the trend observed for FFA reduction, the activated adsorbent exhibited a higher peroxide value than the unactivated adsorbent under the same operating conditions. At the optimal condition of 24 g adsorbent and 45 minutes of contact time, the peroxide value decreased to 6.660 m_{eq} O_2/kg after activation and 4.440 m_{eq} O_2/kg before activation. This suggests that although chemical activation enhanced surface properties and adsorption sites, it may also have reduced the natural antioxidant compounds present in garlic peel, such as phenolics and organosulfur compounds, which are known to inhibit lipid oxidation. Nevertheless, increasing adsorbent mass and sufficient contact time consistently improved peroxide removal performance across all treatments (Devianti et al., 2023; Rahmayanti et al., 2021; Susilowati et al., 2021). The most pronounced decrease occurred during the first 15 minutes of stirring; thereafter, the decline slowed until minute 45, a pattern typical of adsorption kinetics in which rapid initial uptake driven by a steep concentration gradient and abundant free sites is followed by a slower approach to equilibrium (Azizian, 2004).

One key finding from this study was the effect of chemical activation on peroxide-value reduction. Contrary to the trend seen for free-fatty-acid decrease, the unactivated adsorbent was more effective at lowering the peroxide value than the chemically activated one: at 24 g, the unactivated adsorbent reduced the peroxide value to 4.440 meq O_2/kg, whereas the activated adsorbent reached 6.660 meq O_2/kg within 45 minutes. This divergence can be explained by differences between peroxide species and FFAs as adsorbates and by surface-chemistry changes caused by activation. Chemical activation is known to reorganize pore structure and alter surface functional groups, which can modify adsorption selectivity (Chew et al., 2023). In parallel, garlic peels naturally contain antioxidant compounds (e.g., allicin and phenolics) capable of quenching peroxides or retarding lipid oxidation (Shang et al., 2019; Subroto et al., 2021; Wang et al., 2023). Harsh thermal/chemical treatments can diminish such labile functionalities and active groups (Elgarahy et al., 2021; Ukanwa et al., 2019).

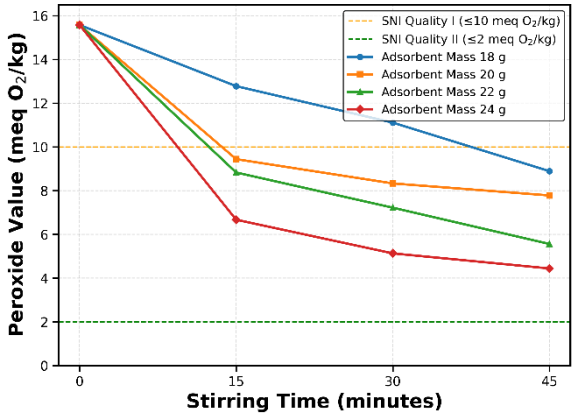

Figure 3. Effect of garlic skin-based adsorbent mass and contact time on peroxide value of used cooking oil

Referring to SNI 7709:2019 for palm cooking oil quality, the maximum peroxide value permitted for marketable oil under the Quality II category is ≤ 10 meq O_2/kg; the values observed here therefore remained within that limit, with the best outcome obtained for the 24 g unactivated condition (4.440 meq O_2/kg). Overall, these results are consistent with an interpretation that unactivated garlic-peel adsorbent retained more native antioxidant activity while providing sufficient porosity for physical adsorption, whereas chemical activation improved textural properties but likely reduced antioxidant-mediated peroxide quenching.

The Effect of Adsorbent Mass and Stirring Time on Acid Value

Based on the data obtained, a consistent decline in acid value was observed across all adsorbent-mass

variations. The 24-gram adsorbent mass showed the best performance, lowering the acid value to 0.578 mg NaOH/g (before activation) and 0.560 mg NaOH/g (after activation) within 45 minutes (Figure. 4). These results indicated that increasing adsorbent mass significantly improved the reduction in acid value, consistent with reports that higher biosorbent dosages decrease the acid number of used cooking oil (Devianti et al., 2023; Rahmayanti et al., 2021). The first 15 minutes of stirring produced the largest decrease for all masses, after which the decline proceeded more slowly until the 45th minute, a kinetic pattern typical of adsorption where rapid initial uptake driven by a steep concentration gradient is followed by a slower approach to equilibrium (Azizian, 2004; Brandani, 2021). Chemical activation further improved the effectiveness of acid-value reduction across mass variations; at 24 g, activation reduced the acid value from 0.578 to 0.560 mg NaOH/g, aligning with findings that surface modification and increased porosity can enhance adsorption performance when sufficient active sites are available (Brandani, 2021).

This efficiency improvement was explained by chemical and physical modifications introduced during activation. Chemical activation of lignocellulosic biomass (including garlic skin) develops porosity and alters surface functional groups, especially generating (and exposing) basic sites that can neutralize acidic species thereby enhancing uptake pathways beyond simple physisorption (Alcañiz-Monge et al., 2022; Oickle, 2010; Schönherr, 2018). Based on the conversion results, the oil treated with garlic-skin adsorbents satisfied the Indonesian SNI 7709:2019 Quality I threshold for free fatty acids (≤ 0.3%), indicating effective reduction of acidity to meet edible-oil standards (Zuliyama et al., 2023). Mechanistically, the acid-value decrease involved both adsorption and acid-base neutralization: garlic skin provides a porous carbonaceous matrix for physical adsorption and contains bioactive/ash constituents (e.g., organosulfur and phenolic compounds, minerals) that can participate in peroxide/acid quenching or neutralization reactions (Utama, 2024; Velciov, 2024).

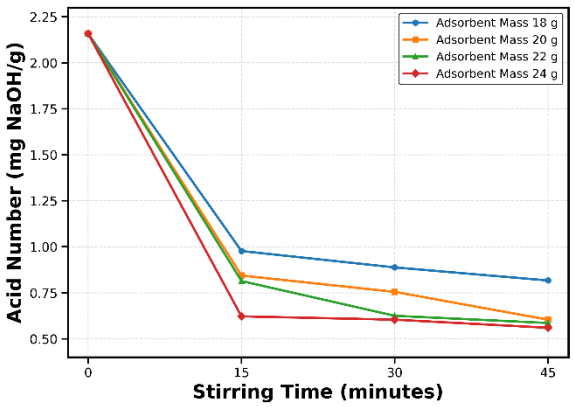

Figure 4. Effect of garlic peel adsorbent mass and contact time on acid value of used cooking oil using garlic skin-based adsorbent

Taken together, the findings supported garlic-skin adsorbents as effective materials for lowering acid value in used cooking oil, with chemical activation further improving performance by tuning surface chemistry and accessible area.

Adsorption Efficiency of Garlic Skin Adsorbent on Used Cooking Oil

Based on the data analysis, the adsorption efficiency of the garlic skin-based adsorbent increased significantly with both adsorbent mass and contact time (Figure 5). Under the optimal conditions of 24 g adsorbent and 45 minutes of contact, the efficiency reached 72.93% for the unactivated adsorbent and 76.74% for the chemically activated adsorbent. This pattern was consistent with adsorption fundamentals: increasing adsorbent dosage (and thus accessible surface area) supplies more active sites for solute uptake. Chemical activation further enhanced performance, yielding an average efficiency gain of 2.85% across mass variations, which aligns with evidence that activation of lignocellulosic precursors increases surface area, develops pore networks, and introduces additional surface functional groups that strengthen affinity for target molecules (Liew et al., 2018; Ukanwa et al., 2019).

Kinetic analysis of adsorption shows that the early phase of the process (the first 15 minutes) contributes the most to the adsorption efficiency, reaching 60–70% of the total adsorption capacity. This phenomenon is consistent with the second-order adsorption kinetic model, which indicates that the highest adsorption rate occurs in the initial phase due to the high concentration gradient between the liquid phase and the adsorbent surface. From an application perspective, these findings provide valuable insights for the development of sustainable used cooking oil purification technology. The adsorption efficiency of over 75% achieved by the garlic skin adsorbent demonstrates competitive potential for both household and small-scale industrial applications.

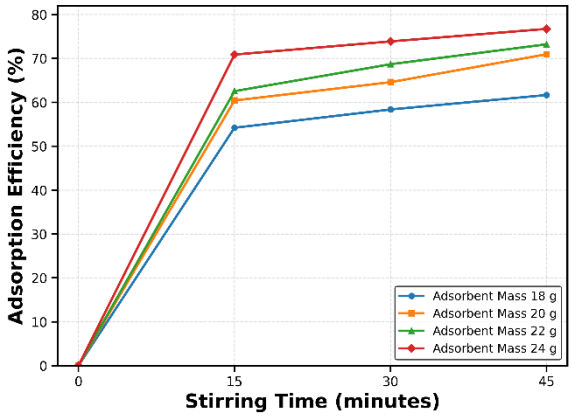

Figure 5. Adsorption efficiency (%) of garlic skin-based adsorbent for used cooking oil purification at varying adsorbent masses and contact times

However, a limitation of this study is that it evaluated only single-use adsorption performance; the regeneration and reusability of the garlic-skin adsorbent across repeated adsorption-desorption cycles were not assessed. Because reusability directly affects both the operating cost and the environmental footprint of a biosorbent-based purification process, this should be considered a limitation of the present work rather than an established strength. Adsorbent regeneration would likely require solvent washing, mild acid/base treatment, or thermal reactivation to desorb bound FFA and restore active sites, and each of these routes carries its own cost, energy, and potential capacity-loss trade-offs that have not yet been quantified for garlic skin. Future studies should therefore evaluate adsorption-desorption cycling (e.g., across three to five reuse cycles), track the accompanying loss in adsorption capacity and selectivity, and pair this with a basic technical-economic analysis before garlic-skin adsorbent can be recommended for practical, large-scale used-cooking-oil regeneration.

Adsorption Capacity of Garlic Skin Adsorbent on Used Cooking Oil

Figure 6 presents the analysis of adsorption capacity (Q_e), revealing an interesting phenomenon where an increase in adsorbent mass beyond a certain optimal point led to a decrease in adsorption capacity per unit mass. The adsorbent mass of 20 grams demonstrated the highest performance with an adsorption capacity of 43.650 mg/g, whereas the 24-gram mass achieved only 39.338 mg/g. This pattern can be attributed to several fundamental mechanisms. Firstly, particle agglomeration at a higher adsorbent mass reduces the effective surface area available for the adsorption process (Chen et al., 2018). Secondly, diffusion barriers occur, as a thicker adsorbent layer hinders the mass transfer of target molecules to the active sites (Wang et al., 2023). Thirdly, a non-optimal adsorbent-to-oil ratio at excessive mass leads to inefficient utilization of active sites (Zhang & Chen, 2020).

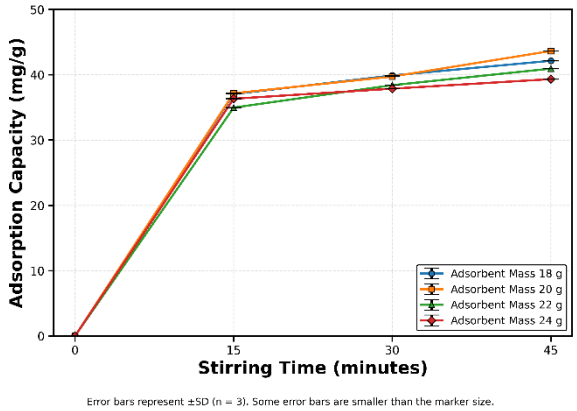

Figure 6. Adsorption capacity of garlic skin-based adsorbent on used cooking oil

The crowding effect also contributes, where excessive adsorbent density causes competition between active sites, thereby reducing the efficiency of each individual site (Devianti et al., 2023). This finding aligns with the fundamental principle of adsorption, which posits that an optimal adsorbent-adsorbate ratio is essential for maximum efficiency.

Additionally, factors such as adsorbent particle size and pore-size distribution also affected adsorption capacity. Increasing the adsorbent mass without properly adjusting particle size reduced effectiveness, because larger particles typically exhibit lower external-film and intraparticle diffusion rates, which in turn limited the adsorbent's ability to capture target compounds over short contact times (Zhang et al., 2019). Theoretically, when the adsorbent mass became too large, particle crowding and site overlap could occur, so that some active sites were screened or became inaccessible to solutes in used cooking oil, leading to a net decrease in capacity per unit mass; this behavior is consistent with dosage effects and pore/transport constraints reported in adsorption systems (Li et al., 2023; Reza, 2020).

Adsorption Isotherms of Garlic Skin Adsorbent

The experimental results (Table 1) demonstrated the effect of activation on adsorption efficiency by comparing two adsorbent conditions unactivated and activated at several adsorbent masses (18, 20, 22, and 24 g). The data comprised three primary parameters: the residual adsorbate concentration in solution (Ce), the adsorption capacity (Qe, mg/g), and the Ce/Qe ratio. In both conditions, Qe increased as adsorbent mass increased, indicating that adding more adsorbent enhanced the uptake of the adsorbate.

Table 1. Isotherm parameters of garlic skin adsorbent

Parameter	Unactivated	With Activation	Explanation
Langmuir Isotherm			
Q_{max} (mg/g)	52.32	51.51	Maximum Adsorption Capacity
KL (L/mg)	77.711	113.460	Langmuir Constant
R^2	0.9026	0.9738	Coefficient of Determination
Freundlich Isotherm			
KF ((mg/g)(L/mg)$^{1/n}$)	48.50	46.83	Relative Adsorption Capacity
1/n	0.2241	0.1301	Adsorption Intensity Factor
N	4.46	7.69	-
R^2	0.4578	0.3850	Coefficient of Determination

Based on the isotherm parameters in Table 1, the adsorption process for both conditions fit the Langmuir model more strongly than the Freundlich model, as indicated by higher coefficients of determination (R^2): 0.9026 for the unactivated adsorbent and 0.9738 for the activated adsorbent, versus 0.4578 and 0.3850 for the Freundlich model. The Langmuir R^2 values approaching 1, especially after activation, support monolayer adsorption on a relatively homogeneous surface, consistent with the Langmuir assumptions (Wang et al., 2023; Zhang & Chen, 2020). Further analysis of the maximum adsorption capacity (Qmax) showed that activation did not markedly change the number of available sites (Qmax decreased only slightly from 52.32 to 51.51 mg/g). This suggests that activation primarily modified surface properties rather than creating new active sites. By contrast, the marked increase in the Langmuir constant (KL) from 77.711 to 113.460 L/mg indicates stronger surface affinity for the adsorbate and more robust adsorbent–adsorbate interactions (Elgarahy et al., 2021; Zhang et al., 2020).

Although the Freundlich model is less suitable for this system, its parameters still offer useful insight. The Freundlich exponent n is well above 4.46 unactivated adsorbent and 7.69 with activation indicates favorable adsorption. The post-activation rise in n suggests greater adsorption intensity and some surface heterogeneity, aligning with the higher Langmuir constant KL that reflects increased affinity between the adsorbent and adsorbate (Al-Ghouti & Da'ana, 2020). Overall, these results indicate that activation improves adsorption quality rather than maximum capacity: it increases binding affinity, leads to more favorable adsorption, and yields better linearity with the Langmuir model, thus strengthening the adsorbent's effectiveness for removing target molecules in water treatment applications (Murphy et al., 2023).

The role of HCl activation in driving these changes merits closer examination. Dilute-acid treatment of lignocellulosic biomass such as garlic skin is understood to act through at least three concurrent mechanisms: (i) protonation and partial hydrolysis of hemicellulose and pectic substances, which loosens the cell-wall matrix and opens previously inaccessible micro- and mesopores; (ii) dissolution and removal of soluble ash, mineral salts, and low-molecular-weight extractives that otherwise block pore mouths, thereby increasing the accessible surface area confirmed by the SEM images in Figure 7; and (iii) generation of new oxygen-containing surface functional groups (e.g., additional hydroxyl and carboxyl moieties) through partial oxidation and exposure of previously buried cellulose microfibrils, which supply fresh binding sites for FFA molecules (Alcañiz-Monge et al., 2022; Saha & Bhattacharyya, 2016).

These combined effects explain why activation left Qmax nearly unchanged while sharply increasing KL (Table 1): pore opening and surface cleaning primarily improve the affinity and accessibility of existing sites rather than creating a proportionally larger number of new ones. The same mechanism is consistent with the reduced peroxide-removal performance after activation (Figure 3): acid treatment likely leached or degraded part of the native phenolic and organosulfur antioxidants in garlic skin, so the gain in FFA-binding affinity came at the cost of reduced radical-scavenging capacity. Because this study did not include direct surface characterization of functional groups before and after activation (e.g., FTIR or Boehm titration), this mechanistic interpretation should be confirmed in future work; nonetheless, it is consistent with both the isotherm/kinetic trends and the SEM morphology reported here.

Adsorption Kinetics of Garlic Skin Adsorbent

Adsorption kinetics were analyzed to elucidate the mechanism and rate of free-fatty-acid (FFA) removal using a garlic-skin adsorbent (Table 2). The pseudo-second-order (PSO) kinetic model fit the experimental data exceptionally well (R^2=1.0000), outperforming the pseudo-first-order (PFO) model, which despite an excellent fit (R^2=0.9970), was statistically less accurate for this system. A notable discrepancy emerged in the predicted equilibrium capacity (q_e) between models: the PFO model yielded qe = 9.7444 mg/g, which was physically implausible given that the measured capacity at 15 minutes had already reached qt = 34.200 mg/g. By contrast, the PSO model predicted qe = 39.2157 mg/g, closely matching the experimental equilibrium. This mismatch suggested that uptake was not governed solely by diffusional constraints but was more strongly limited by the availability and chemistry of active sites on the adsorbent surface.

Table 2. Kinetic Parameters of Garlic Skin Adsorbent

Parameter	PFO Kinetics	PSO Kinetics
Before activation		
Rate constant	0.060867/min	0.011211 g/(mg·min)
Equilibrium adsorption capacity (q_e)	9.7444	39.2157
Coefficient of determination (R^2)	0.9970	1.0000
After activation		
Rate constant	0.039451/min	0.024781 g/(mg·min)
Equilibrium adsorption capacity (q_e)	4.4352	38.6598
Coefficient of determination (R^2)	0.8790	0.9999

PSO kinetics are commonly associated with chemisorption on biomass-based adsorbents bearing heterogeneous or chemically active sites (Brandani, 2021; Zhang et al., 2019).

In this context, FFA reduction likely involves electron exchange or partial covalent interactions between polar surface groups of garlic skin (e.g., hydroxyl and carbonyl moieties from cellulose, pectin, and polyphenols) and the carboxyl (COOH) groups of FFA molecules. The second-order rate constant, k_2 = 0.011211 g/(mg·min), quantified the rate of this surface-reaction process. These observations align with recent studies on natural adsorbents linking PSO behavior to specific active-site interactions and chemisorption (Azizian, 2004), underscoring that performance gains arise less from surface area or adsorbent mass alone and more from targeted surface chemistry.

Morphological Analysis of Garlic Skin Adsorbent

Surface morphological analysis using scanning electron microscopy (SEM) was performed to visualize how activation altered the garlic-skin adsorbent and to relate those changes to adsorption performance Figure 7. Comparing the unactivated and activated samples, there are clear structural changes that were consistent with the isotherm and kinetic results.

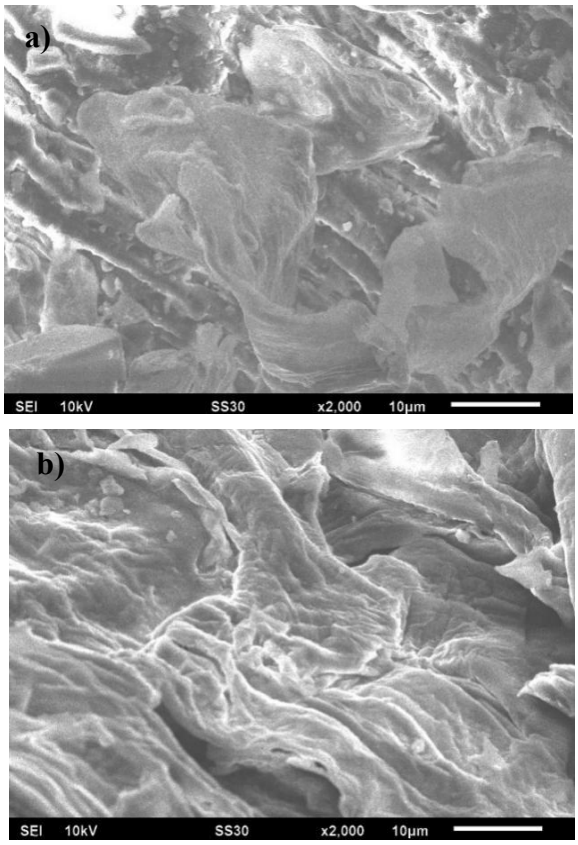

Figure 7. Morphological analysis of garlic skin-based adsorbent: (a) before activation, and (b) after HCl activation.

Figure 7a exhibits the appearance of the relatively compact and smooth surface on the garlic skin-based adsorbent with limited porosity, suggesting that natural pores were still partly blocked by volatiles, lipids, or amorphous lignocellulosic domains; such morphologies typically yield lower accessible surface area and pore volume, which in turn limit the number of available active sites and depress the Langmuir capacity (Qmax) (Gupta & Jain, 2018). By contrast, Figure 7b shows a markedly rougher and more heterogeneous surface after activation with well-developed pore structures. This transformation is expected: activation (thermal/chemical) removes occluding organics and opens the cellulose–lignin matrix, increasing surface area and generating new pore networks, thereby raising site availability and strengthening affinity often reflected by higher Langmuir (Al-Ghouti & Da'ana, 2020). The morphological shift also aligned with kinetic evidence for chemisorption under the pseudo-second-order model: activation exposes more polar functionalities (e.g., –OH, –COOH) on lignocellulosic surfaces that can form strong interactions with FFA carboxyl groups, while increased pore complexity can introduce longer diffusion paths and intraparticle-diffusion resistances that modulate apparent rate constants. Taken together, the SEM observations corroborated the isotherm/kinetic analyses: activation transformed a relatively smooth, less porous surface into a highly porous, heterogeneous adsorbent with more chemically active sites, thereby improving affinity and equilibrium performance consistent with a chemisorption-dominated mechanism.

CONCLUSION

Based on the research conducted to evaluate the effectiveness of garlic skin as an adsorbent in used cooking oil purification, several key conclusions were drawn. The HCl-activated adsorbent proved to be the most effective, reducing free fatty acids (FFA) by 76.74% and lowering the acid value, thereby meeting the SNI Quality I category. However, the unactivated adsorbent was more effective at reducing peroxide value, likely due to the preservation of natural antioxidants. Chemical activation was found to enhance adsorption efficiency, and the highest adsorption capacity was observed at an adsorbent mass of 20 g, suggesting that excessive mass led to inefficiency due to a crowding effect. The adsorption process followed the Langmuir model and pseudo-second-order kinetics, indicating a chemisorption mechanism; activation strengthened the bonds between the adsorbent's functional groups and free fatty acid molecules, as reflected in the increased Langmuir constant. SEM analysis further showed that activation resulted in a rougher, more porous surface, which explained the improved adsorption performance. These findings underscored the potential of garlic skin as a sustainable and effective adsorbent for used cooking oil purification, with chemical activation playing a crucial role in enhancing its

performance. A limitation of this study is that adsorbent regeneration and reusability were not evaluated; future work should examine adsorption-desorption cycling and conduct a technical-economic assessment before recommending garlic-skin adsorbent for large-scale application.

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