

## RESEARCH ARTICLE

## EMPLOYMENT OF NON-CONVENTIONAL MATERIAL IN PURIFICATION OF CONTAMINATED AQUEOUS SOLUTIONS

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### ABSTRACT

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In this study, the ability of pistachio shells, as an unconventional adsorbent, to recover thallium cations from contaminated aqueous solutions was investigated. To achieve the objective of the study, practical experiments were conducted using a batch-mode adsorption unit under various operating conditions. The results obtained showed that the pistachio shells have the ability to remove thallium cations with a high efficiency exceeding 86% at room temperature. The results indicated that the maximum treatment efficiency was achieved at values of 7, 350 rpm, 86 ppm, 5 g, 150 min of pH, agitation speed, initial concentration of thallium, dosage of pistachio shell used, and contact time, respectively. Morphological results confirmed that the adsorbed pistachio shells suffered significant changes compared to the virgin shells, as SEM examination showed that the accumulation of thallium cations in their pores led to the formation of a heterogeneous layer of metal particles. On the other hand, adsorption resulted in the consumption of functional groups, according to FT-IR analysis, while the remaining surface area after adsorption was less than 5% of the original surface area.

### KEYWORDS

Adsorption, aqueous solution, batch unit, pistachio shells, and thallium

### 1. INTRODUCTION

Every sentient creature is connected to its encompassing habitat in a concurrent interaction of life, since no other location in the cosmos offers a means of survival besides this azure world, at least for this moment (Al-Hermizy et al., 2022). From prehistoric times, the surroundings have passed through phases of severe alterations periodically, and straightforward changes at other periods, which resulted in evident impacts on the existence of biological creatures, encompassing mankind (Hashem et al., 2021). People's grasp of the essentials of cultivation resulted in the rise of urban centers and residence in close to waterways, which fostered the advancement of populations and the creation of societies (Ali et al., 2024a). Yet this advancement was attended by unfavorable impacts on the nature equal to the headway gained by humankind, since agrarian progress resulted in the buildup of farming refuse, which was not at first an observable issue (Alhamd et al., 2024b). Given the expansion in farmed regions and the growth of the populace, this refuse has become a genuine weight on the surroundings, for which answers ought to be sought (Hajam et al., 2023). Small concepts have arisen to utilize from these wastes, like transforming them into fuel to furnish power or employing some categories of them as livestock nourishment and others (Alminshid et al. 2025). Since human uninterrupted to progress technologically, he became more reliant on manufacturing to simplify the needs of existence, particularly following the Industrial Revolution. During the passage of time, immense plants and colossal manufacturing establishments, which helped immensely to supplying diverse requirements, financial well-being, and employment openings. Technological advancement was likewise joined by numerous detrimental consequences like disasters, depletion of natural resources,

and most significantly, ecological contamination (Abbas and Ibrahim, 2020). Environmental contamination is commonly described as the addition of materials or energy into one or more components of the biological surroundings (water, atmosphere, land, and space), whether these materials or energies are of original or synthetic source, in a manner that produces an adverse alteration in the equilibrium of the ecosystem and results in detrimental consequences on living creatures, human well-being, and the condition of environmental assets (Gadooda et al., 2025). From the above clarification, it is evident that humanity is currently confronts two significant categories of contamination: farming pollution and manufacturing contamination (Dong et al., 2023). Considering the present populace, that has surpassed 8 billion inhabitants, they require massive amounts of sustenance and varied provisions, to which farming supplies a significant proportion. Consequently, the types of agricultural and industrial residues discharged into the surroundings are huge in amount and nature (Abdulkareem et al., 2023). Heavy metals are recognized to be the basic of manufacturing, as they are utilized in the production of batteries, electronics, chemicals, coatings, pharmaceuticals, glass, ceramics, manures, military hardware, and a host of other things (Abbas and Alalwan, 2019). Given their extreme toxicity and harmfulness, they should be discharged into nature within worldwide or regional boundaries. Hence, handling the consequent contamination is a vital concern for any field in which these harmful elements are applied (Rajaa et al., 2023). Heavy metals are categorized as the elements possessing a substantial atomic mass and a density measured at five times that the density of water or greater. They are not categorized in a particular group of the periodic table and include antimony (Sb), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), mercury (Hg), nickel (Ni), platinum (Pt), silver (Ag), thallium (Tl), tin (Sn),

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titanium (Ti), vanadium (V), zinc (Zn), and others (Khaleel et al., 2022). Presently, there are numerous approaches and techniques are employed to address water contamination by heavy metals, including biofiltration, bioremediation, chelation, chemical precipitation, coagulation and flocculation, electrochemical treatment, electrocoagulation, electrodeposition, evaporation, incineration, ion exchange, nanofiltration, permeable reactive barriers (PRB), photocatalysis, physical precipitation, phytoremediation, redox reactions, reverse osmosis, thermal stabilization, and so on (Abbas et al., 2020). Even though every one of the aforementioned techniques has possess adequate effectiveness in handling heavy metals, they encounter constraints and disadvantages that impact their application as a remediation process. These involving considerable cost, substantial power usage, the necessity for sizable areas, pre-treatment needs, or the inability of specialized apparatus, or their incapacity to incapacity with severe concentrations and other impediments (Abbas and Abbas, 2013a). Nevertheless, the adsorption technique has appeared as a powerful rival against other process owing to its merits. It is a straightforward method that does not needs prior preparations, and it can handle all contaminants at high concentrations. It does not demand big areas, special equipment, or substantial expenses, alongside its reasonable power consumption, which has attracted the attention of researchers as an encouraging approach for water purification (Ali et al., 2023). Adsorption method has proven its efficiency in treating various types of pollutants such as dyes organic materials, acids, inorganic toxins, pharmaceutical industry waste, pesticides, drugs, eutrophication elements, water hardness, as well as various heavy metals, not only from polluted water, but also from contaminated soil, and crude oil (Ali et al., 2021; Alwan et al., 2021; Alalwan et al., 2021; Abbas and Abbas, 2014; Alalwan et al., 2020; Ibrahim et al., 2020a; Abd ali et al., 2018; Abd Ali et al., 2024; Abbas, 2015; Ibrahim et al., 2021; Abbas et al., 2019a; Alalwan et al., 2018). Notwithstanding these merits and great purification effectiveness, costly adsorption materials have been a significant barrier to this process. Activated carbon, alumina, zeolite, and other well-known adsorption media require great effort and high cost to produce (Abed et al., 2025; Shadhan et al., 2024; Khudair et al., 2024). This drives experts to seek for affordable and productive options, and they discovered what they were sought in agricultural and industrial waste, which offered a renewable and low-cost source of adsorption media or raw material for making other adsorption materials (Maddodi et al., 2020). Algae, almond peels, aluminum foil, banana peels, eggshells, lemon, mandarin peels, mango peels, orange peels, pineapple peels, pomegranate peels, rice husks, spent tea leaves, sunflower husks, tree leaves, water hyacinth and watermelon rinds, have shown to be remarkably effective in purifying polluted media at minimal expense relative to other adsorption materials (Abbas et al., 2019b; Hameed et al., 2025; Ghulam et al., 2020; Ali et al., 2020a; peels (Alsarayreh et al., 2024; Alhamd et al., 2024a; Abed et al., 2025a; Hasan et al., 2021; Ibrahim et al., 2025a; Ali et al., 2024b; Abbas and Abbas, 2013c; Al-Ali et al., 2023; Abdulkareem et al., 2023; Hameed and Abbas, 2024; Ali and Abbas, 2020; Abbas and Nussrat, 2020). Due to the quantities produced, it is considered an available and non-valuable resource. On the other hand, this method is considered one of the economic methods for disposing of this waste (Abbas and Abbas, 2013b). Although the accumulation of these wastes is a significant problem, which are often loaded with toxic substances, the concept of zero residue level has opened up wide horizons for benefiting from these residues as raw materials in the preparation of useful chemicals such as acetone and promoted bioethanol, or as a catalyst, as additives to reinforce concrete mixtures, or as pesticides for rodents such as rats and rabbits, or by converting them into nanomaterials (Alminshid et al., 2021; Abbas et al., 2022b; Hamdi et al., 2024; Abbas et al., 2021; Abbas et al., 2022a; Ibrahim et al., 2020b; Al-Latif et al., 2023). Notwithstanding its poisonous nature, studies on addressing thallium- polluted water via adsorption are remaining constrained. To tackle this clear shortcoming, the current research intends to use pistachio shells as an inexpensive adsorbent to remove thallium cations from polluted simulated wastewater, and to ascertain the optimum parameters that establish the highest percentage removal, in addition to ascertaining the morphological influence of pistachio shells as a result of exposure to solutions polluted with thallium cations.

## 2. METHODOLOGY

### 2.1 Adsorbent medium (Pistachio shell)

Pistachio shells, were collected from home consumption and were sourced from a nut shop in Baghdad. Scientifically, the collected pistachio shells were documented as Iranian pistachio shells according to the taxonomy of the Biological the Department's herbarium, College of Education for Pure Sciences, University of Diyala. The collected agricultural waste was separated by size, and the pistachio shells meeting the 28/30 standard were used for adsorption experiments. After

scientific taxonomy and sorted, the shells were cleaned to ensure they were ready for adsorption of thallium cation. They were washed with excess tap water after their inner coatings, which are usually found attached to the inside of the shells, were removed, then they were washed twice by double-distilled water. The first stage of the drying process began with the completion of the cleaning process. The clean shells were spread out on a round stainless steel serving tray ( $\phi=55$  cm,  $h=3.6$  cm), and exposed to sunlight in Baghdad for 10 continuous hours in a clean area at a temperature of 35-38 °C. The final step of drying process was achieved by exposing the shells to a temperature of 55°C using a drying oven (TR 450, Nabertherm, Germany) until the weight was constant, not exceeding 45 minutes. The complete dried shells were collected in 100 ml amber jars with double plastic lids and stored in a dry place away from light to avoid moisture.

### 2.2 Stock Solution

The preparation of the stock solution is an essential step, as it provides a base solution that can later be diluted to obtain different concentrations of thallium ions for use in adsorption experiments. By preparing this solution, a constant source of the chemical compound is established that can be used to precisely adjust concentrations in various experiments (Alhamd et al., 2025). In addition, stock solutions provide a reliable basis for adjusting ion concentrations throughout the experiment, helping to reduce experimental errors that result from using real contaminated water. To prepare the stock solution of thallium ions at a concentration of 1000 ppm, 2.175 g of thallium nitrate ( $Tl(NO_3)_3 \cdot 3H_2O$ ) was used, which was accurately weighed using a sensitive balance (NBD1000-3 NANBI INSTRUMENT LIMITED, China). This quantity was dissolved in a suitable quantity of distilled water in a 1-liter glass beaker. To ensure complete dissolution of the thallium nitrate, a magnetic stirrer (Fisher Scientific, IKA™ C-MAG MS 7) was used, which helps distribute the heat and maintain a homogeneous mixture. Stirring was carried out at room temperature for approximately 30 minutes to ensure complete dissolution of the compound. After ensuring complete dissolution, more distilled water was added until the final volume of the solution reached 1 liter. After the preparation is complete, the stock solution is stored in a tightly sealed volumetric bottle of suitable capacity, in a cool, and dark place, to maintain the stability of the ions and prevent them from being affected by environmental factors such as heat or light, before using it in preparing the solutions used in the experiments (Ibrahim et al., 2025b).

### 2.3 Calibration curve

The concentration of thallium ions was measured using atomic absorption spectroscopy (AAS) at a wavelength of 258 nm as in (Ali et al., 2020b). The absorbance of each standard solution was measured and the results were carefully recorded. After obtaining the experimental absorbance values for each of the standard solutions, a correction curve was drawn as shown in Figure 1. This curve represents a mathematical relation used to convert absorbance to a readable concentration of thallium ions in unknown solutions. The validity of the calibration curve is so high, which very close to one.

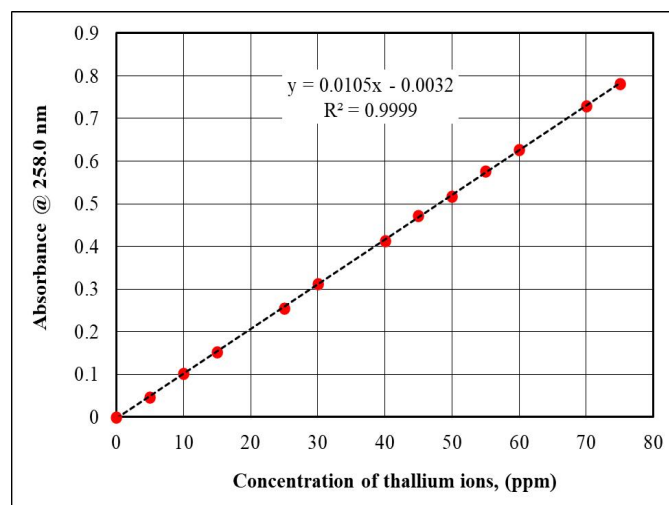


Figure 1: AAS Calibration curve of thallium (III)

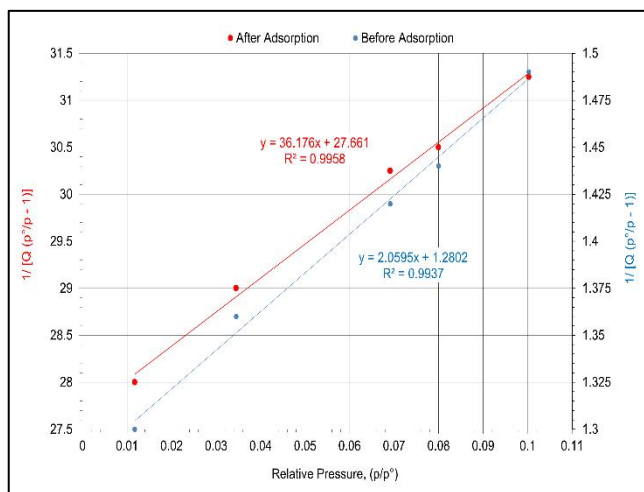
### 2.4 Adsorption Unit

The adsorption unit used in the current study to carry out the adsorption experiments was of a batch mode, which represents an integrated laboratory unit used to evaluate the ability of pistachio shells to remove thallium cations from aqueous solutions under pre-determined

conditions. This type of laboratory units is characterized by its efficiency, accurate results, and low cost compared to continuous units or pilot plants, which enables the study of the adsorption phenomenon as a closed system without the influence of continuous flows or interferences. The batch adsorption unit mainly consists of a shaking water bath (SHKA7000-1CE 4304, Thermo Fisher Scientific), in which experimental flasks, commonly known as Erlenmeyer flasks, of 250 ml capacity are placed. After adjusting the acidity of the solution, the initial concentration of the contaminant, and the dosage of the adsorbent, the test flasks containing 100 ml of the contaminated solution are charged into the water bath shaker and set in a suitable manner, so that no spillage of the solution occurs during the experiment. The shaking water bath contributes to providing effective and continuous contact between the surface of the adsorbent and the target component in the solution, which enhances the mass transfer rate and accelerates the surface reaction (adsorption). By setting other operating conditions, namely temperature and agitation speed, the adsorption process begins, and then the mixture is left to agitate continuously for a specified period of time. After the reaction period has elapsed, the solution is separated from the solid phase using filter paper (Whatman™ No.1 of 110 mm diameter), firstly and then using a filtration equipment (Filtering Kit 250 ml, Vacuum Pump with Gauge, KT3003-3 Science Lab Supplies/UK) to obtain a clear solution that is used to analyze the remaining concentration of thallium heavy metal cation. In this study, the recovery efficiency of thallium cations was investigated under the influence of contact time, agitation speed, temperature, initial concentration of thallium, pH, and dosage of pistachio shell. The design parameters studied ranged from 10-180 min, 100-500 rpm, 25-50 °C, 1-90 ppm, 4-12, and 1-5.5 g, respectively. After the specified time for the experiment has completed, the unit is automatically shut down, and the samples are carefully extracted, filtered, and the concentration of unadsorbed thallium cations is recorded using an AAS device and a pre-prepared calibration curve. The adsorption efficiency is determined by applying Equation (1), while Equation (2) is used to obtain the adsorption capacity of pistachio shells (Ibrahim et al., 2025a).

$$\%R = 100 \times \left( \frac{C_o - C_f}{C_o} \right) \quad (1)$$

$$q = \frac{V(C_o - C_f)}{m} \quad (2)$$



**Figure 2:** Adsorption-desorption isotherm of pistachio shells

Finally, the possibility of a portion of thallium cations being absorbed or trapped within the very deep pores cannot be ignored. This obstructs the access of the N<sub>2</sub> gas used to measure the BET surface area to these pores. This is reflected in the analysis results, as these areas are not included in the effective surface area. Based on the above, this sharp decrease in surface area is a natural result of the reactions that occur during the adsorption process and largely reflects the efficiency of pistachio shells in trapping thallium cations and the intensity of the interaction occurring at their surface (Alhamd et al., 2024a).

### 3.1.2 FT-IR Analysis

Figure 3 shows the FT-IR analysis of the adsorbent before and after adsorption of thallium cations. The blue curve represents pistachio shells before adsorption, while the red curve represents pistachio shells after

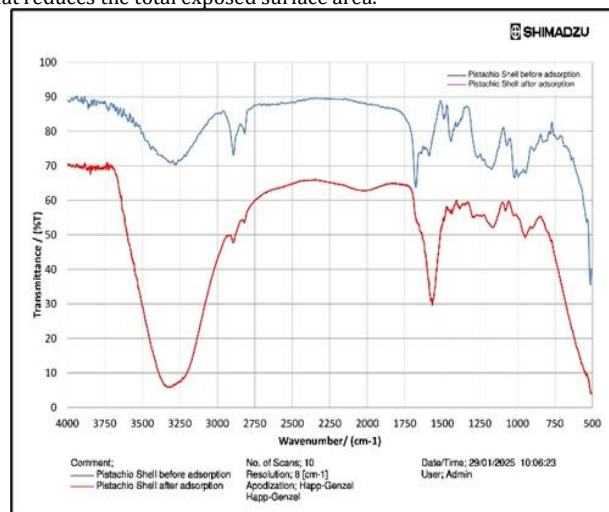
Where: %R: removal efficiency of thallium metal; C<sub>o</sub>: initial concentration of thallium (ppm); C<sub>f</sub>: final concentration of thallium (ppm); q: adsorption capacity of pistachio shells, expressed in (mg/g); V: volume of the solution (l); and m: the mass of pistachio shells exploiting in each experiment (g).

## 3.RESULTS AND DISCUSSION

### 3.1 Morphological Studies Of Pistachio Shells Due To Thallium Adsorption

#### 3.1.1 BET surface area

The surface area of the pistachio shells used in the present study, before and after adsorption of thallium cations, was measured using Micromeritics Co., USA and surface area analyzer, Qsurf M1, Thermo CO., USA) devices, while the adsorption-desorption isotherm curve of adsorption media shows in the Figure 2 (ASAP 2020). The results obtained from the BET test of surface area, indicate that the virgin pistachio shells had a surface area of 19.216 m<sup>2</sup>/g, while after adsorption the measured surface area of the shells treated with solution of thallium cations was estimated to be slightly higher than 1.0 m<sup>2</sup>/g, which confirms that the surface properties were strongly affected, and that changes occurred in the structural feature of the adsorption medium. This decrease can be explained by several mechanisms, including that treatment with contaminated solutions has led to saturation of the active sites of pistachio shells surface, resulting in intense adsorption of thallium cations. These cations occupy available active sites on the surface of the material, either through chemical bonds or physical forces. Over time, the adsorbed thallium cations penetrate the internal pores of the pistachio shells, leading to the closure or blockage of a large number of micro- and medium-sized pores, thus reducing the active surface area. Also, there is a possibility that there will be a change in the morphological or structural of the adsorbent material as a result of treatment with thallium cations, especially since pistachio shells are of an organic or semi-organic nature, and thus are sensitive to chemical changes, which may lead to a partial collapse in their porous structure or a change in their structural arrangement, which reduces the active area. In addition to the above, there may be an additional possibility of redistribution of the material particles or the occurrence of agglomeration as a result of operating conditions such as temperature, adsorption time, or the nature of the chemical medium, as these conditions lead to the particles coming together and gathering in a way that reduces the total exposed surface area.

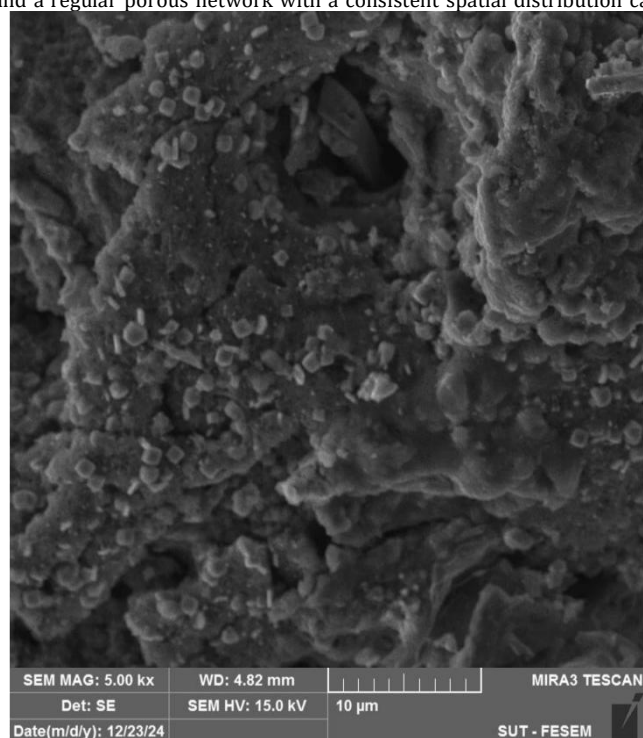


**Figure 3:** FT-IR spectrum of pistachio shells before and after adsorption. The blue curve shows very fine details of the functional groups in the adsorbent. At 3425 cm<sup>-1</sup>, a broad, symmetric peak appears, indicating the presence of extended hydroxyl (O-H) bonds, with a light transmittance of 72%, indicating the presence of abundant free hydroxyl groups on the surface. At 2920 and 2850 cm<sup>-1</sup>, two sharp peaks appear, representing the symmetric and asymmetric stretching vibrations of the C-H bonds in the alkyl groups, with a transmittance of 85% and 88%, respectively. The prominent peak at 1635 cm<sup>-1</sup> (65% transmittance) is due to the C=O bond in the carbonyl or aromatic C=C groups, while the peak at 1385 cm<sup>-1</sup> (78% transmittance) represents C-H bond bending vibrations. In the 1200-1000 cm<sup>-1</sup> region, a series of peaks appear at 1150 cm<sup>-1</sup> (82% transmittance), 1075 cm<sup>-1</sup> (79% transmittance), and 1025 cm<sup>-1</sup> (81% transmittance) which are attributed to the C-O bond stretching vibrations in ethers, alcohols, and phenols. Together, these

functional groups form an ideal network for metal binding via multiple mechanisms. In contrast, the red curve shows profound changes in spectral properties after adsorption (Alhamd et al., 2024b). The peak at 3425 cm<sup>-1</sup> had a transmittance decrease of 58% and a narrower width, indicating the participation of hydroxyl groups in the formation of coordination complexes with the metal. The peaks at 2920 and 2850 cm<sup>-1</sup> completely disappeared, indicating the involvement of alkyl groups in the adsorption process. The peak at 1635 cm<sup>-1</sup> had a transmittance decrease of 42% and shifted to 1610 cm<sup>-1</sup>, while the peak at 1385 cm<sup>-1</sup> completely disappeared. In the lower region, new functional peaks appeared at 875 cm<sup>-1</sup> (65% transmittance), 620 cm<sup>-1</sup> (58% transmittance), and 540 cm<sup>-1</sup> (53% transmittance), representing M–O–H, M–O, and M–O–M vibrations (where M is the adsorbed metal), respectively. The peaks in the 1200–1000 cm<sup>-1</sup> region underwent dramatic changes, with the transmittance of the peak at 1150 cm<sup>-1</sup> decreasing to 68%, and a new peak appeared at 1045 cm<sup>-1</sup> (72% transmittance), representing the C–O–M bond. These changes confirm the occurrence of complex chemical interactions between functional groups and metal ions (Mahmood et al., 2025).

### 3.1.3 SEM Test

Figure 4a shows a scanning electron microscope (SEM) examination of pistachio shells before adsorption of thallium cation. The shells are characterized by a homogeneous surface with a fairly uniform structure, and a regular porous network with a consistent spatial distribution can



**Figure 4a:** SEM image of pistachio shells before adsorption of thallium ions

## 4. ADSORPTION EXPERIMENTS

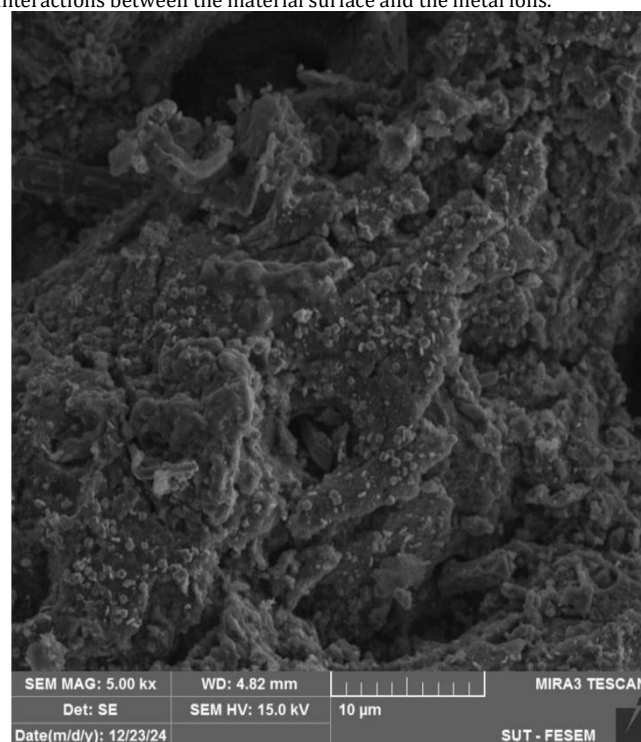
### 4.1 Effect Of Changing The Acidity Of Polluted Solution

Due to the importance of the acid function in any adsorption process, this variable was studied in this investigation within a range of 4–12, based on the results obtained from point of zero-charge pH<sub>pzc</sub> experiments. The other operational parameters were constant at 1 g of pistachio shells, a time of 180 minutes, an agitation speed of 250 rpm, and the initial concentration of thallium cations was 1 ppm, at room temperature. Figure 5 shows the relationship between the pH's varying of the solution and the removal percentage of thallium cations by pistachio shells. It is noted that the removal efficiency increases sharply with the increase in pH value. The removal starts very low at a pH of approximately 4, and remains so until it reaches a value of 7. Then it begins to suddenly increase until it reaches the ideal removal at a pH of approximately 9, and remains almost constant after this point without change. These results reflect the nature of the interaction between the surface of pistachio shells and adsorbed thallium cations under the influence of changing hydrogen ion concentration in the aqueous medium. They are directly related to the surface charge behavior of the adsorbent and the change in the nature of the chemical compounds of thallium within the studied pH range. At low pH values, the medium is more acidic, causing the surface

be observed. The pores appear to be of closely spaced sizes, ranging from approximately 0.5–200 μm, with sharp, well-defined edges, indicating the crystallinity of the adsorbent. The surface appears free of impurities or

unwanted deposits, with fine protrusions that increase the effective surface area. This fine microstructure provides a large number of active

binding sites, including surface functional groups and negatively charged regions that will contribute to the attraction of heavy metal ions. The surface also exhibits good mechanical cohesion between its constituent nanoparticles, ensuring structural stability during the adsorption process. Figure 4b shows a scanning electron microscope (SEM) examination of pistachio shells after adsorption of thallium cation. The image reveals a clear transformation in the surface composition of the material after adsorption. A nearly continuous layer of adsorbed metal particles is observed, covering approximately 60–70% of the original surface area. The deposits appear in irregular shapes, ranging from spherical (200–500 nm in size) to lamellar (approximately 100 × 200 nm in size). The distribution of the adsorbed particles follows a heterogeneous pattern, with regions of high mineral concentrations corresponding to the most active adsorption sites. A change in the surface topography is also observed, with many of the original porous features disappearing, and fine nano-cracks (50–100 nm wide) appearing, resulting from the tensile stresses generated by the adsorption reactions (Abed et al., 2025b). These changes confirm the occurrence of strong physicochemical interactions between the material surface and the metal ions.



**Figure 4b:** SEM image of pistachio shells after adsorption of thallium ions

of the pistachio shells to be saturated with protons (H<sup>+</sup>), providing a positive charge that hinders the adsorption of thallium cations due to electrostatic repulsion. Furthermore, there is competition between protons and thallium cations for the active sites available on the surface of pistachio shells, which reduces the adsorption efficiency. As the pH value increases, the surface functional groups of pistachio shells gradually begin to lose protons, which causes the surface charge to gradually become negative. Thus, electrostatic attraction forces arise between the negatively charged surface of the adsorbent and the positive metal cations, which greatly enhances the adsorption. This can be explained by the fact that the surface charge of the adsorbent reaches a nearly neutral state in the intermediate range of acidity, which reduces the electrostatic repulsion barriers and facilitates the adsorption process. Also, the high pH promotes a reduction in the concentration of protons in the solution, which limits competition for active sites and leaves the field open for thallium cations to bind to the surface. In basic circumstances, pH greater than 7, the removal percentage increases dramatically, perhaps due to the precipitation of thallium cations via the formation of insoluble hydroxides rather than adsorption. This hypothesis can be confirmed by the observation of a precipitate at the bottom of the experimental flask. Therefore, the optimum pH for the removal of the maximum amount of thallium cations using pistachio shells is 7 (Gadooa et al. 2025).

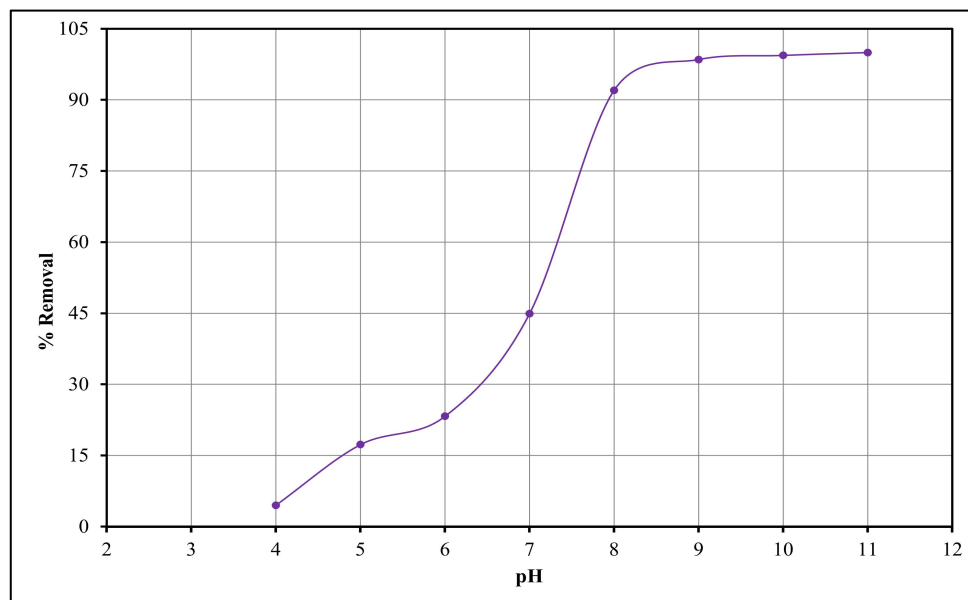


Figure 5: pH effect on thallium adsorption

#### 4.2 Effect of changing the agitation speed of polluted solution

Agitation speed is a key factor in enhancing adsorption efficiency in the initial stages of the reaction, and choosing an optimal speed that ensures maximum removal without damaging the adsorbent structure is essential in the design of any adsorption-based treatment unit. Figure 6 shows the relationship between the agitation speed and the removal rate of thallium ions from the contaminated aqueous solution using 1 g of pistachio shells, neutral acidity (pH=7), 1 ppm initial concentration of thallium cations, 3 hours contact time, and room temperature. It is clearly shown that the removal efficiency increases gradually with increasing agitation speed from 100 rpm up to about 350 rpm, and then stabilizes at a removal ratio of approximately 54%. This behavior reflects the direct effect of the agitation process in improving the adsorption efficiency by reducing the external resistance to mass transfer between the solution and the surface of the pistachio shells. At low speeds, the movement of molecules is relatively slow, which limits the efficiency of transporting thallium cations to the active binding sites on the surface of the material, and thus the removal percentage is low. As the agitation speed increases, the degree of distribution and mixing between thallium cations and the surface of

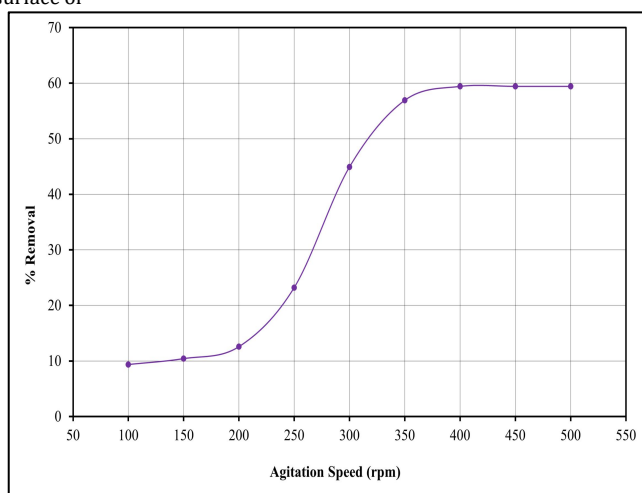


Figure 6: Shaking effect on thallium adsorption

#### 4.3 Effect Of Changing The Initial Concentration Of Polluted Solution

At constant values of pistachio shell dosage, contact time, agitation speed, and pH at 1 g, 180 min, 7, and 350 rpm, respectively, the effect of varying the initial concentration of thallium cations within the range of 1-90 ppm was studied. The results shown in Figure 7 indicate an inverse relationship between the initial concentration of thallium cations in the aqueous solution and the percentage removal using pistachio shells, where it is clear that increasing the thallium concentration from 1 to 90 mg/L leads to a gradual decrease in the removal efficiency from about 53.4% to about 16.5%, respectively. This behavior can be explained by several interrelated considerations related to the dynamics of the surface

pistachio shells increases, which contributes to improving the chances of direct contact between the two parties, and accelerates the transfer of target ions through the static boundary layer surrounding the pistachio shell particles, which leads to a gradual increase in the adsorption. Higher speeds also ensure that thallium cations do not precipitate or accumulate at the bottom of the flask, helping to keep the adsorbent surface area available for the reaction. The ratio reaching a near-steady value after a speed of 350 rpm indicates that a dynamic equilibrium state has been reached, such that further agitation does not lead to further improvement in adsorption. This may mean that all active sites have become occupied or that the adsorption process has become limited by internal factors such as diffusion within micropores or structural limitations of the adsorbent. On the other hand, the stability at higher speeds indicates that the increased agitation did not cause any negative effects, such as degrading the material's physical structure or reducing its effectiveness through separation or corrosion. These results confirm that the optimum speed for achieving maximum removal of thallium ions from contaminated aqueous solutions using pistachio shells as an adsorbent is 350 rpm (Ibrahim et al., 2025a).

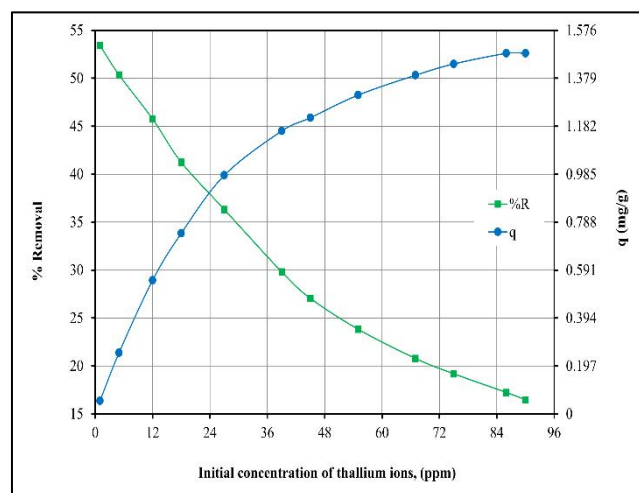


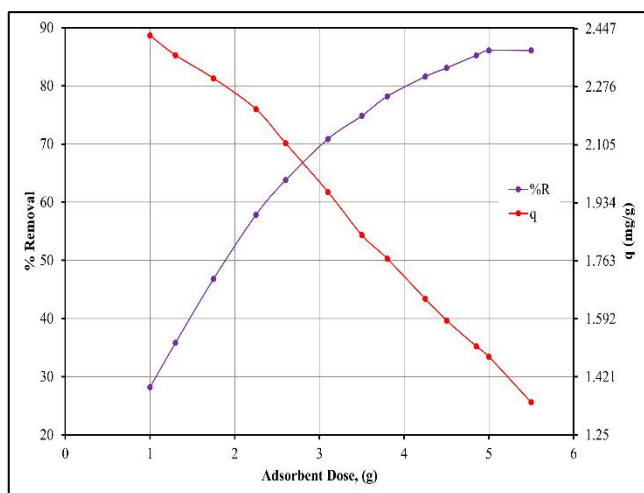
Figure 7: Concentration effect on thallium adsorption

interaction and the adsorption mechanism. At low initial concentrations, the ratio of the thallium cations number to the number of available active sites on the surface of the pistachio shells is small, which means that almost all of the contaminating cations find their opportunity to bind to the active sites spread across the adsorbent surface, and thus the removal efficiency will be high. When the initial concentration of thallium cations in the solution is high, the number of available ions greatly exceeds the number of active sites, which leads to rapid surface saturation and an insufficient number of sites for complete adsorption, thus reducing the removal rate. Also, the presence of a high concentration of ions can generate a state of internal competition between cations for surface sites, which contributes to reducing the

binding efficiency. In addition, high concentrations lead to increased repulsion between cations close to each other on the surface of the material, which may hinder the stability of the adsorption process and reduce the effectiveness of capturing new ions. It is also possible that an increase in the concentration of thallium cations leads to an increase in the strength of the loose ions in the solution, which may affect the stability of the adsorption layer surrounding the pistachio shell particles, and increase the ability of the ions to return to the solution (desorption), especially if the binding forces between the adsorbent and the element are relatively weak. Furthermore, the decreased removal percentage at high concentrations may be due to internal diffusion restrictions within the pores, as a large increase in the number of ions may block the entrances to the micropores or delay the arrival of ions at the active sites within the porous structure of the material. The results confirm that the optimum initial concentration of thallium cations is 86 ppm, given that the adsorption capacity remains constant at this concentration (Abed et al., 2025b).

#### 4.4 Effect Of Changing The Adsorbent Dosage Of Pistachio Shells

Determining the effective dosage of the adsorbent is a critical issue in any adsorption experiment. Therefore, the behavior of this critical variable was determined at 7, 350, 25 °C, 86 ppm, and 3 h for pH, agitation rate, temperature, initial thallium concentration, and contact time, respectively. The pistachio shell dosage range studied was 1–5.5 g. Figure 8 shows the effect of pistachio shell dosage (in grams) on thallium removal efficiency (%R) and adsorption capacity (q) of the adsorbent. Increasing the dosage from 1 g to 5.5 g results in a gradual increase in removal efficiency from approximately 28.2% to 86.05%, with a clear stabilization in the percentage removal after a dosage of approximately 5 g. This behavior can be explained by the direct effect of increasing the amount of adsorbent on the number of active sites available for adsorption of thallium cations, as small doses provide a limited number



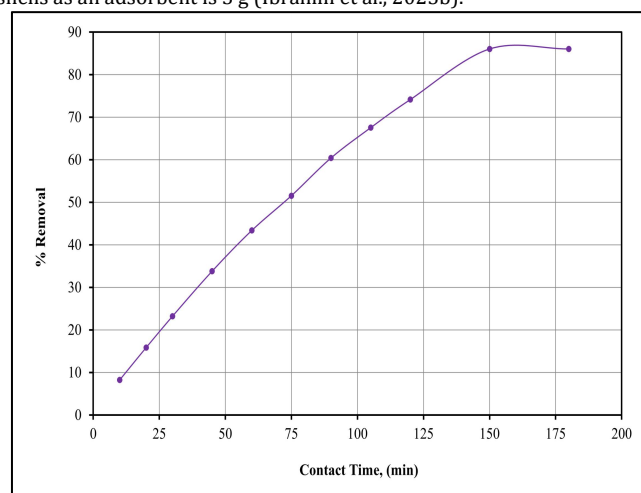
**Figure 8:** Dosage effect on thallium adsorption

#### 4.5 Effect Of Changing Contact Time Of Adsorption Unit

Contact time is an essential factor in determining adsorption efficiency, and the selection of the appropriate time should be based on achieving the highest possible percentage removal without wasting time or energy, to achieve the economic feasibility of the treatment process with efficient time efficiency. Figure 9 shows the effect of contact time on the removal efficiency of thallium cations using pistachio shells at 7, 350 rpm, 86 ppm, 5 g, and 25°C for pH, agitation speed, initial concentration of thallium, pistachio shell dosage, and temperature, respectively. It is noted that the removal rate increases gradually over time, starting from approximately 8.2% at the 10th minute, reaching approximately 86.05% at the 150th minute, and then stabilizing without any further increase at the 180th minute. The adsorption process begins at a high speed in its early stages, due to the availability of a large number of active sites on the surface of the adsorbent, which allows for rapid binding of contaminated thallium ions from the solution. During this early stage, the high percentage removal is attributed to the large concentration difference between the liquid and solid phases, which creates a strong incentive for the immediate transfer of cations to the surface of the pistachio shells. Over time, these sites gradually fill up, and the reaction rate slows down due to the decreasing number of empty sites and the accumulation of adsorbed ions on the surface. This creates an increasing electrical repulsion that may limit the binding of further thallium cations. Furthermore, the remaining thallium cations in the solution need longer time to reach the internal sites within the micropores, which slows the adsorption process during the transition phase. Approximately 150 minutes, the process

of surface sites capable of capturing contaminated cations, leading to low adsorption efficiency due to the

insufficiency of these sites compared to the number of cations available in the solution. As the dose increases, the number of particles and available active sites increases, which increases the chances of the heavy metal being bound to the surface of the material, thus increasing the removal efficiency. Increasing the dose also contributes to reducing competition between ions for active sites, improving the surface distribution of ions, and increasing the total surface area exposed to interaction. However, it is noted that after a certain dose, specifically at 5 g, the increase in the removal efficiency becomes very small or almost non-existent. This indicating that a state of surface saturation or equilibrium has been reached, as most of the thallium cations in the solution have actually been dealt with, and there is no longer a sufficient amount of them to occupy the new sites provided by the increase in the dose. Therefore, adding more adsorbent does not lead to an actual improvement in the removal efficiency. Furthermore, this behavior can be attributed to the occurrence of flocculation or partial overlap between the adsorbent particles at high doses, which may lead to a reduction in the actual available effective surface area, despite the increase in the total mass, due to the overlap or aggregation of particles in a way that limits the exposure of some active sites. The concentration balance between the solid and liquid phases also plays a role in determining the maximum adsorbable limit, as the amount of the remaining element in the solution becomes small at high doses, which reduces the adsorption drive across the concentration difference. On the other hand, the adsorption capacity (q) exhibits an opposite behavior, decreasing with increasing dosage. This is because the number of adsorbed cations is distributed over a larger amount of adsorbent, reducing the specific efficiency per gram. Therefore, according to the obtained results, the optimal dosage that achieves the highest removal efficiency of thallium ions using pistachio shells as an adsorbent is 5 g (Ibrahim et al., 2025b).



**Figure 9:** Time effect on thallium adsorption

reaches equilibrium, where the adsorption-desorption rates are equal, and the pistachio shells become nearly saturated, unable to adsorb any additional thallium cations dispersed in the solution to continue increasing the overall percentage removal. The stability of the efficiency at this point indicates that the optimal contact time has been achieved, and any further increase in time will not lead to a significant improvement in performance. It is also possible that there are limitations in internal transport within the small pores, or that some active sites have become unavailable due to agglomeration or accumulation of previous cations, which would explain the stability of performance at the final values. Therefore, these results confirm that 150 minutes is the optimal time for achieving maximum adsorption efficiency for thallium cations using pistachio shells as an adsorbent (Alsarayreh et al., 2025a).

## 5. CONCLUSIONS

Given the extreme toxicity of thallium, its removal or reduction in various types of water is of paramount importance and must be continuously pursued. This study proposed the idea of utilizing pistachio shells, a non-conventional type of agricultural waste, as an adsorbent to remove thallium cations from contaminated aqueous solutions. The results of the laboratory-scale study were promising, as pistachio shells demonstrated a high ability to recover thallium cations, with an efficiency exceeding 86%. Maximum efficiencies of treatment were achieved at various operating conditions of temperature, pH, time, agitation speed, pistachio shell dosage, and initial thallium concentration, respectively. These values were 25 °C, 7, 150 min, 350 rpm, 50 g/L, and 86 ppm. The

accumulation of thallium cations led to significant changes in the structural feature and surface area of pistachio shells, with adsorption resulting in the disappearance or displacement of several functional groups and a surface area reduction of more than 95%. Therefore, this low-cost material opens up new horizons in the field of environmental treatment and water purification, especially if its use is expanded to treat other pollutants, or if the possibility of its reactivation or utilization as a raw material in other industrial or environmental fields is studied in economical and non-expensive ways.

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