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Adsorption of thallium using tangerine peels and exploitation from the waste in an eco-friendly manner

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ABSTRACT

Heavy metals are classified as environmentally hazardous materials, due to their toxicity to humans and other living organisms. Given the involvement of these metals in various human activities, it has become necessary to include them within international and local standards, to ensure the safety of both humans and the environment. The present study aimed to achieve the sustainability principle by investigating the ability of tangerine peels, as a readily available and low-cost material, to remove the toxic element thallium from contaminated aqueous solutions. Batch adsorption technique was used at different design parameters of acidity, temperature, contact time, initial concentration, adsorption dose and agitation speed. The obtained results showed that tangerine peels have a remarkable ability to recover thallium (III) ions from polluted water with an efficiency of 82.4% and an adsorption capacity of approximately 2 $mg.g^{-1}$ at initial concentration, adsorbent dosage, contact time, pH, agitation speed, and temperature of 80 ppm, 4.5 g, 120 min, 6, 350 rpm, and 25 °C, respectively. Morphological examinations indicated that the tangerine peels suffered from many changes due to thallium adsorption, as their surface area decreased by 83.5%, functional groups decreased significantly, and obvious changes in the surface structure occurred, as indicated by BET, FT-IR and SEM tests, respectively. The isothermal study showed that the best model to represent the experimental data is the Langmuir model, while the pseudo-second-order model is the closest to represent the results kinetically. Thermodynamically, adsorption is characterized as chemical, exothermic, and of decreasing randomness, in addition to being spontaneous at all studied temperatures. For the safe and comprehensive disposal of residual toxic waste, its use as a cheap and effective rodenticide has been studied, by mixing the waste at a rate of 10–25% with the diet used to feed laboratory rats. These residues caused mortality ranging from 50–100% of the animals exposed to the test in all experimental groups, which confirms the toxic effect of this metal and the necessity of providing effective and economical manners for getting rid of it.

Keywords: aqueous solution, thallium, batch adsorption, low-cost adsorbent, pesticide, and ZRL.

INTRODUCTION

Heavy metals are defined as a group of chemical elements that are characterized by their large atomic mass and high density, which is usually greater than 5 grams per cubic centimeter. According to the periodic table, they are often located in the middle to lower section of the table within the transition categories and beyond (Khaleel et al., 2022). They may be found naturally in the Earth's crust, or they can be found in low concentrations in many ecosystems. Heavy elements have complex atomic structures, giving them distinctive properties such as the ability to form multiple chemical bonds and relative stability in chemical composition (Abdulhammed and Alhamd, 2024). They are often not easily reactive with their surroundings, as they have specific operating properties that affect their interactions with other materials, whether in liquid or solid state. These elements include metals such as lead, mercury, cadmium, arsenic, chromium, zinc, iron, thallium, nickel, and others (Ali and Abbas, 2020). Some of these metals are needed by the organism in very small quantities to support its vital functions, such as copper, iron, and zinc (Al-Hermizy et al., 2022), and some are used in medical applications, such as platinum, or cosmetic applications, such as antimony (Ali et al., 2020a), most of these elements are harmful to the environment and toxic to humans and cause serious diseases such as cancer, even in low concentrations, such as lead, cadmium, mercury, chromium, cobalt, thallium, nickel, arsenic, and others (Ali et al., 2024). Despite these dangerous effects of heavy metals, it is impossible to dispense with them, because they are used in many industrial, technical and medical fields due to their unique physical and chemical properties that are not found in other materials (Khaleel et al., 2022). For example, iron is used in steel and construction, while copper is essential for electrical wiring due to its high conductivity. Zinc is used to protect metals from corrosion through galvanization, and lead is a key component in batteries. Heavy, precious metals such as gold and platinum are used in electronics, jewelry, and the manufacture of chemical catalysts (Abbas et al., 2021). In medicine, heavy metals such as barium are used in imaging the digestive system, while mercury is used in conventional thermometers, and vanadium and nickel are used as catalysts in many chemical processes (Khudair et al., 2024). Therefore, dealing with these metals requires careful management, which involves monitoring their concentrations in different ecosystems and providing safe and economical ways to dispose of them to avoid their negative environmental and health effects (Ali et al., 2024). Among these dangerous heavy metals is thallium due to its high toxicity. Thallium is a heavy chemical metal, its chemical symbol is Tl, its atomic number is 81, its density is 11.85 g/cm³ at room temperature, and it is characterized by its blue-gray color and its softness similar to lead. It is also characterized by its high sensitivity to light and its distinctive refractive properties (Alalwan et al., 2018). It is considered one of the minerals that belong to the group of post-transition elements in the periodic table. Thallium is used in several industrial and technological fields, such as the production of electronics, optical glass, lenses, optical fibres, in nuclear medicine examinations, metal alloys and in the manufacture of highly sensitive measuring devices, such as thermoelectric meters and sensors (Genchi et al., 2021). The lethal dose of thallium for human is 15 mg per kilogram of body weight. This dose is very low, as consuming 1.5 gram of thallium is enough to kill a person weighing 100 kg (Al Hammouri et al. 2011). This is what makes thallium a very toxic element. Thallium has the ability to accumulate in biological tissues, mainly affecting the central nervous system and the gastrointestinal tract (Fujihara and Nishimoto, 2024). When humans are exposed to it through inhalation, ingestion, or skin contact, it can cause symptoms such as nausea, vomiting, diarrhea, and peripheral nerve damage (Al Hammouri et al., 2011). Over time, thallium poisoning can lead to hair loss, with significant hair loss being seen 1 to 3 weeks after exposure. Poisoning can also cause kidney damage, with deterioration of kidney function possible in cases of chronic poisoning (Gad, 2024). Also, chronic thallium poisoning can lead to serious health problems that may even lead to death in cases of acute poisoning, as high doses are expected to lead to death within weeks or even days if not treated quickly and effectively (Fujihara and Nishimoto, 2024). Thallium toxicity poses significant threats to wildlife and ecosystems, with accumulation in living organisms resulting in acute and chronic toxic effects, degrading biodiversity and ecosystem viability (Genchi et al., 2021). This can be observed by monitoring the lethal dose, which for rats and mice ranges between 15–27 mg/kg of body weight, while it ranges between 15 mg/kg of body weight in dogs, 12–30 mg/kg body weight in rabbits and is 4 mg/kg of body weight in cats. As for insects and bees, the dose is very low, such that 0.5 mg/kg of body weight is sufficient to kill them (Gupta, 2018). Given the importance of thallium in various industrial activities on the one hand, and its danger to human life, living organisms and the environment in general on the other hand, its concentration must be monitored continuously and accurately and methods must be developed to treat the environmental elements contaminated by it, the most important of which are surface and groundwater, as is the case with other heavy metals (Alalwan et al., 2018). There are many methods and techniques used in treating water contaminated with heavy metals, aiming to remove or reduce the concentration of them to safe levels, such as ion exchange, chemical precipitation, reverse osmosis, electrocoagulation, sand filtration, membrane filtration, electrochemical filtration, thermal desorption, magnetic treatment, adsorption and others (Abbas et al., 2020). Among all the above methods, the promising adsorption technology is one of the most effective and easy to apply for treating water contaminated with heavy metals (Hameed and Abbas, 2024). Adsorption is defined as a physical or chemical process in which one substance (called the adsorbate) interacts with the surface of another substance (called the adsorbent) such that the molecules of the adsorbate stick to the surface of the adsorbent (Maddodi et al., 2020). This process occurs due to intermolecular forces such as van der Waals forces, electrostatic interactions, or chemical bonds. This method is flexible in dealing with a wide range of pollutants at different concentrations, both high and low. In addition, the adsorption process does not require complex equipment or high costs, nor does it require large areas or high energy consumption, making it an economical and practical option that contributes to reducing operating costs in the long term (Alwan et al., 2021). The most famous adsorbents that have shown high ability to treat polluted environments are activated carbon (Abbas and Alalwan, 2019), alumina (Shadhan et al., 2024), and zeolite (Khudair et al., 2024), due to their unique properties such as their distinctive surface structure and high surface area. However, the high cost of producing these media, their need for continuous reactivation, and the loss of some of their weight with each reactivation process prompted specialists to search for suitable and economical alternatives that serve the same purpose (Alhamd et al., 2024d). Among the most important and best alternatives were agricultural and some industrial wastes, as they are available materials, have low toxicity, low cost, and are characterized by a suitable structure and surface area (Ali and Abbas, 2020). The most important types of agricultural waste widely used in water treatment are banana peels (Abdullah et al., 2023), watermelon rinds (Abbas and Nussrat, 2020), lemon peels (Alsarayreh et al., 2024), mandarin peels (Alhamd et al., 2024a), orange peels (Hasan et al., 2021), eggshells (Ali et al., 2020a), rice husks (Alalwan et al., 2018), algae (Abbas et al., 2019b), water-hyacinth (Hashem et al., 2021), aluminum foil (Ghulam et al., 2020), pomegranate peels (Ali et al., 2024b), almond shells (Hameed et al., 2025), wasted tea leaves (Al-Ali et al., 2023), buckthorn leaves (Hameed and Abbas, 2024), and sunflower seed shells (Abdulkareem et al., 2023). Some of these wastes have been converted into nanomaterials characterized by high surface area and developed surface structure, such as silica nanoparticles (Ali et al., 2024a) and magnesium oxide nanoparticles (Alminshid et al., 2021). These promising wastes have been shown to be capable of removing various types of pollutants with considerable efficiency such as dyes (Alalwan et al., 2021), organic pollutants (Abbas et al., 2019b), acids (Abbas and Abbas, 2014), inorganic toxins (Alalwan et al., 2020), nutrient enrichment elements (Abbas, 2015), water hardness (Ibrahim et al., 2021), pesticides (Ali et al., 2018), pharmaceutical drugs (Ibrahim et al., 2020a), and sulfurous materials (Abbas and Ibrahim, 2020). In addition, agricultural wastes were highly efficient in treating media contaminated with various heavy elements such as selenium (Alsarayreh et al., 2024), cadmium (Alhamd et al., 2024b), copper (Rajaa et al., 2023), antimony (Ali et al., 2023), nickel (Ali et al., 2021), thallium (Alalwan et al., 2018), cobalt (Abbas and Abbas, 2013a), molybdenum (Abbas and Abbas, 2013b), boron (Abbas and Abbas, 2013c), chromium (Hashem et al., 2021), lithium (Abbas et al., 2021), etc. As these materials have shown their efficiency in treating polluted aquatic environments, they have also been excellent in treating soil (Abbas et al., 2019a) and crude oil (Abbas and Ibrahim, 2020) of organic pollutants and heavy metals. Although waste, which is often toxic, accumulates after the adsorption process is completed, the application of the sustainable approach represented by the concept of zero residue level has transformed these harmful residues into materials that can be disposed of through utilization (Ali et al., 2024b). These wastes can be used to prepare effective and cheap pesticides for rats (Ibrahim et al., 2020b) and rabbits (Al-Latif et al., 2023), produce important chemicals such as acetone (Abbas et al., 2022b), bioethanol (Hamdi et al., 2024), reinforcement of concrete (Abbas et al., 2022a), or prepare soil fertilizer (Abbas, 2015). The aim of the present study is focus on investigate the use of tangerine peels as a readily available and low-cost adsorbent for the treatment of aqueous solutions contaminated with the toxic metal thallium using a batch-type adsorption unit and under different operating conditions. In addition, studying the isothermal, kinetic and thermodynamic behavior of adsorption, the study aims to identify the morphological effects that occur to the adsorbent material as a result of thallium adsorption. Finally, the possibility of safe and economic disposal of toxic residues by converting them into a cheap and effective rodenticide is investigated, reaching the concept of zero residue level, and applying the sustainable approach in waste management.

METHODOLOGY

Tangerine peels

The source of tangerine peels utilized in this investigation was the domestic use of tangerine fruit produced from citrus groves in Al-Miqdadiyah district, located 40 km east of Baqubah and 90 km northeast of Baghdad. The gathered peels underwent thorough washing several times with tap water to remove any type of impurities, followed by additional rinsing with distilled water. Subsequently, the cleaned peels were naturally air-dried for three days in sunlight before being subjected to a 120-minute treatment in a hot air oven at 50 °C until the weigh is constant. Finally, the dried peels were storing in amber jars at laboratory conditions until ready for use. Figure 1 shows the Iraqi tangerine peels used in the present study.

Figure 1. Iraqi tangerine peels used in the present study

Calibration curve

The calibration curve employed for the determination of thallium ions in aqueous solutions was prepared by spectroscopic technique using the atomic absorption spectroscopy (AAS). Firstly, several known concentrations of thallium solutions, ranged between 0–80 ppm, were prepared using double distilled water, after that at a wavelength of 258 nm, the absorbance of each concentration was measured 3–5 times until an almost identical absorbance result was obtained, in order to reduce the experimental error of the obtained results. Then, the data obtained from different concentrations of thallium ions were plotted against the absorbance corresponding to each concentration, to produce the calibration curve used in the present study, which is shown in Figure 2.

Stock solution

In order to override the potential interference with other heavy metals and various compounds present in real wastewater, the effectiveness of tangerine peels in recovering thallium ions was evaluated using carefully prepared laboratory-based simulated aqueous solutions. These solutions were created with known thallium concentrations, from diluting the stock solution to

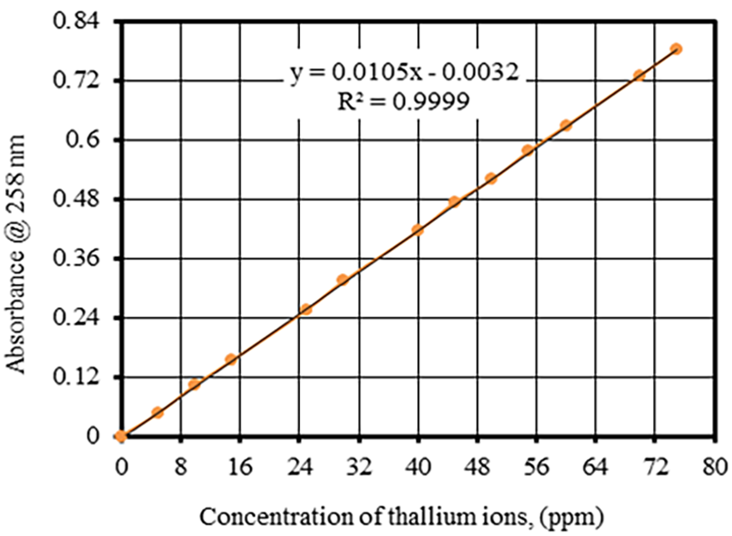

Figure 2. Calibration curve of thallium ions used in the present study

ensure accurate assessment of the adsorption process. Taking into account all safety guidelines for handling toxic materials, a stock solution of 1000 ppm thallium concentration was prepared by dissolving exactly 2.1746 g of thallium nitrate trihydrate of the chemical formula $Tl(NO_3)_3.3H_2O$ supplied by Alfa Aesar (purity ≥ 99.5%) in 1 liter of double distilled water, using continuous stirring in an electric stirrer for 20 minutes at 100 rpm and at laboratory temperature. The calibration curve, prepared previously, was used to estimate the concentration of thallium ions in the prepared stock solution, and the result was consistent with the preparation method. The produced stock solution was poured in Duran® amber Borosilicate glass laboratory bottle with plastic screw cap of suitable capacity and keep in dry place and out of light.

Adsorption unit used

The adsorption experiments of thallium metal using tangerine peels as a low-cost adsorbent were conducted in a batch mode unit. A desired concentration of thallium metal was prepared by diluting the stock solution to the require one. Various operating parameters including pH, agitation speed, initial concentration, adsorbent dose, contact time, and temperature were studied. The pH of the solution was controlled using 0.1 N potassium hydroxide (NaOH) and 0.1 N hydrochloric acid (HCl) solutions. The range of parameters tested were varied among 1–10, 100–500 rpm, 1–90 ppm, 0.5–6.0 g, 10–180 minutes, and 20–50 °C for pH, agitation speed, initial concentration, dose of tangerine peels, contact time, temperature, respectively. The experiments designed by adding 100 cm^3 of the thallium solution of desired concentration and pH value, to a sealed conical flask of appropriate capacity. The flask was then placed in a water bath shaker, and the experiment commenced by setting the required agitation speed. The experiment duration was determined by the predefined contact time. After completion, the solution was filtered using 0.45 μm Whitman filter paper, and then by vacuum filtration apparatus (JOANLAB VP-10L), after separated the tangerine peels from the slurry. The remaining concentration of thallium metal in the treated solution was measured using AAS device and calibration curve. The thallium percentage removal was calculated via Equation 1, while the adsorption capacity of the tangerine peels was obtained from Equation 2.

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

$$q = \frac{V}{1000} \frac{(C_\circ - C_f)}{m} \quad (2)$$

where: $\%R$ – the removal efficiency of thallium metal; C_o – initial concentration (ppm); C_f – final concentration (pmm); q – the adsorption capacity of tangerine peels for thallium metal, expressed in (mg/g); V – the volume of the solution used (ml); and m – the mass of tangerine peels exploiting in each experiment (g).

RESULTS AND DISCUSSION

Characterization of adsorbent medium (tangerine peels)

Specific surface area determination (S_{BET})

Surface area serves as a crucial parameter in assessing the operational attributes of catalysts, adsorbents, and porous materials. In this investigation, the surface area of unprocessed tangerine peels employed as an adsorbent was determined. The assessment involved nitrogen gas physical adsorption-desorption analysis at a consistent temperature matching the boiling point of liquid nitrogen (-77K). The resultant adsorption-desorption isotherm, as shown in Figure 3, revealed a characteristic IV category curve, indicating the presence of mesoporous structures and slit-like pores. Initially, the adsorption process saturated the material's micropores (at P/P° = 0.34513), followed by multilayered filling of mesopores with nitrogen gas. Notably, the measured specific surface area of the virgin tangerine peels was moderate, reaching 9.421 m^2/g. Several factors contribute to this moderate surface area. The porous nature of tangerine peels, characterized by voids and interstitial spaces, significantly contributes to the available surface area for adsorption. Furthermore, the cellulose component enhances the porous structure, augmenting the accessible surface area. The presence of lignin also influences the material's overall porosity and structure, potentially contributing to the surface area. After adsorption the surface area decreased to 1.552 $m^2.g^{-1}$, which means there is 83.5% of area was exploited in adsorption process. The observed significant reduction in the surface area

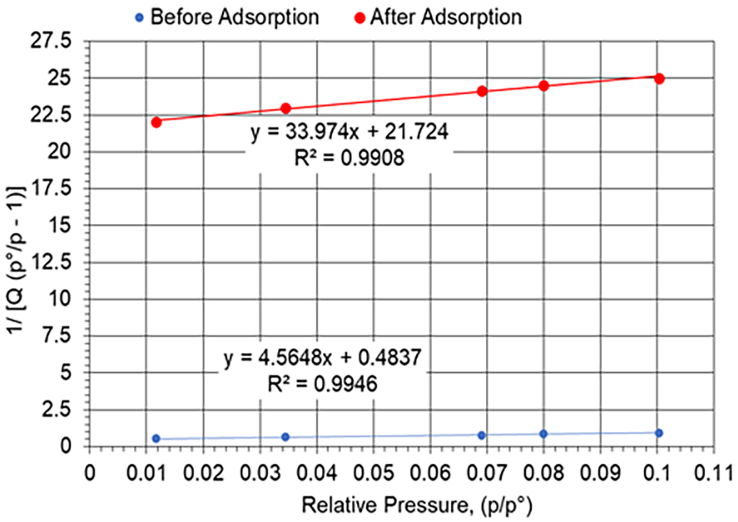

Figure 3. Adsorption-desorption isotherm plot of tangerine peels

of the tangerine peel adsorbent, from 9.421 m²/g before adsorption to 1.552 m²/g after adsorption, can be attributed to the effective adsorption of thallium ions onto the surface and within the pores of the adsorbent. This process likely results in pore blockage and the coverage of the surface-active sites, reducing the accessible surface area for further adsorption. The initial surface area reflects the inherent porosity and availability of active sites on the raw tangerine peels. Following adsorption, the captured thallium ions may form a layer on the surface and occupy internal pores, diminishing the total accessible area. Such a substantial decrease is consistent with high adsorption efficiency and the strong interaction between the adsorbent and the thallium ions, which may involve physical adsorption, chemisorption, or a combination of both mechanisms. These results further highlight the efficacy of tangerine peels as a potential adsorbent for heavy metal removal.

Fourier transfer infrared (FTIR) test

Figure 4 shows the FTIR test of tangerine peels before and after the adsorption process, and indicates the changes that occurred in the surface functional groups as a result of the interaction of the adsorbent with thallium ions. The spectra show a number of notable changes in the positions and intensities of the spectral peaks, indicating chemical and/or physical interactions between the tangerine peels and thallium ions. In the spectrum of tangerine peels before adsorption, characteristic peaks in the range 3688–2877

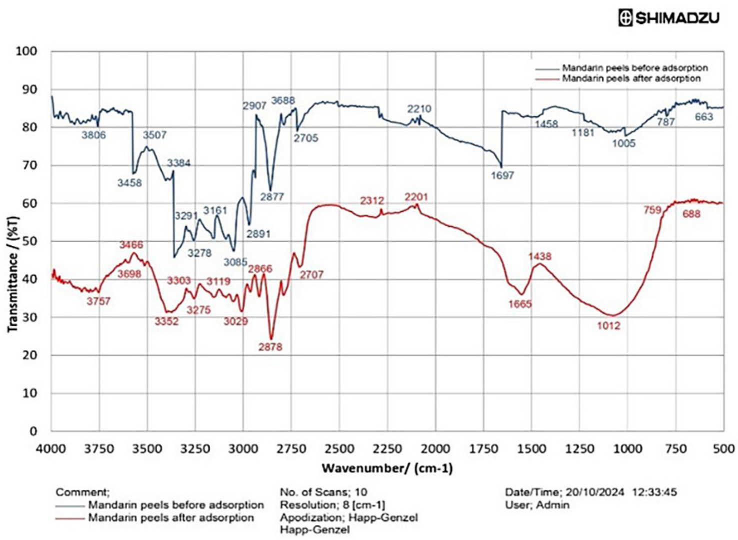

Figure 4. FTIR of tangerine peels, before and after adsorption of thallium ions

cm^{-1} can be observed, which reflect the stretching vibrations of hydroxyl groups (-OH). These peaks reflect the surface hydrophilic or hydroxyl nature of the shells. Peaks at 1697 cm^{-1} were also observed, indicating the presence of carbonyl groups (C = O), which may be attached to organic compounds such as acids or carbohydrates. In addition, peaks appear in the range 1458–1181 cm^{-1}, which are associated with $-CH_3$ and $-CH_2$ vibrations, while peaks at 1005–663 cm^{-1} reflect bonds such as C-O or aliphatic bonds. After adsorption, the spectrum shows a clear change in the range 3698–2866 cm^{-1}, where a decrease in the intensity of the peaks and a slight shift in their positions are observed. This change indicates partial consumption of hydroxyl groups (-OH) during the reaction with thallium ions. Furthermore, new peaks appear at 2312 cm^{-1} and 2201 cm^{-1}, indicating the formation of new bonds with the adsorbate. The carbonyl band (1665 cm^{-1}) also showed a significant change in position and intensity, indicating modification of the functional bonds of this group as a result of its interaction with thallium. In addition, the peaks at 1438 cm^{-1} and 1012–688 cm^{-1} reflect the influence of other functional groups, such as C-H and C-O, on the adsorption process. These results demonstrate that the spectral changes between tangerine peels before and after adsorption reflect strong interactions between surface functional groups and thallium ions. The interactions of hydroxyl and carbonyl groups are the most obvious, as the decrease in the intensity of their peaks and the appearance of new peaks reflect the association of ions with these active sites.

Scanning electron microscopy (SEM) test

Figures 5 a and 5 b show the scanning electron microscope (SEM) images. It's clear the changes in the surface structure of tangerine peels before and after thallium adsorption. Figure (5a) shows that the virgin tangerine peels before adsorption have a cohesive fibrous surface structure, and contain small to medium-sized pores distributed almost uniformly. These pores represent the active sites that facilitate the binding of thallium ions. The apparent fibrous nature emphasizes the presence of structural components such as cellulose, hemicellulose, and lignin, which are known to provide active functional groups such as hydroxyl (-OH) and carboxyl (-COOH). These functional groups contribute to improve the performance of the adsorption process through chemical interactions that occur through hydrogen bonds or ion exchange. After adsorption, Figure 5b records clear changes in the surface structure, as the surface becomes rougher, with noticeable accumulations of adsorbed ions appearing. In addition, some pores can be observed to be blocked and others to be missing, indicating that thallium ions have been effectively trapped within these pores or on the outer surface. These changes reflect the full utilization of the active sites during the adsorption process. Furthermore, the presence of clusters and precipitates indicates the chemical interaction between thallium ions and functional groups on the surface. This interaction can be explained by covalent or ionic bonds between thallium and the active sites. From the above, it is clear that the changes in the surface structure indicate the occurrence of complicated physical

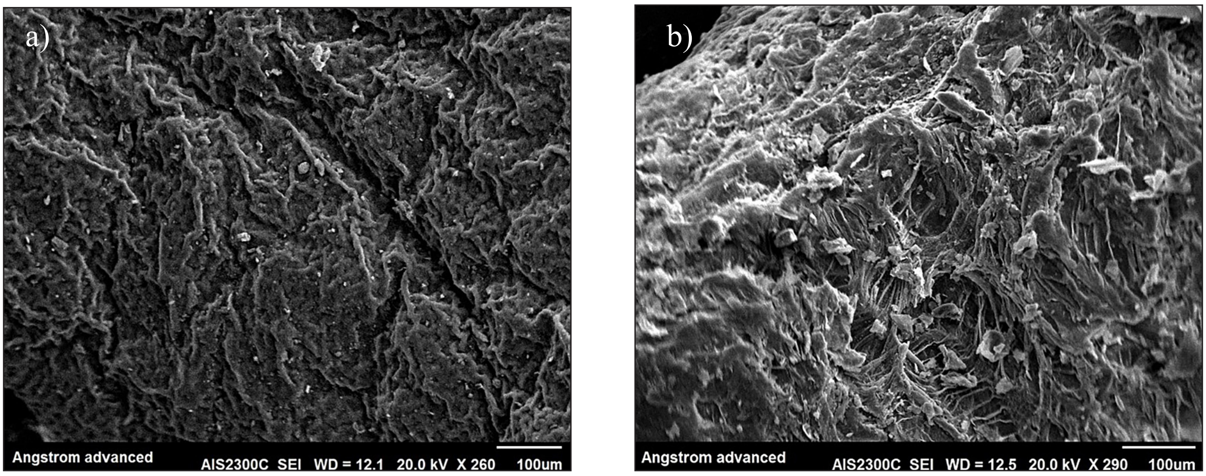

Figure 5. (a) FT-IR of tangerine peels before adsorption of thallium ions (b) FTIR of tangerine peels after adsorption of thallium ions

and chemical interactions during the adsorption process. Physically, the high porosity contributes to increasing the surface area available for the adsorption of pollutants, which enhances the adsorption efficiency. Chemically, the functional groups present in the chemical structure of the peels allow direct interactions with thallium ions, such as chemical bonding or ion exchange. The remarkable difference between the two forms confirms the effectiveness of tangerine peels as a natural, environmentally friendly mediator for the treatment of water contaminated with heavy metals.

Operating parameters affecting on thallium adsorption

pH impact

Figure 6 explains the influence of pH variations on the removal efficiency of thallium ions from simulated aqueous solutions employing tangerine peels as the adsorbent. The investigation of pH effect as a design parameter, was studied within the range from 1 to 10, while maintaining constant values for other operational conditions: 1 ppm, 180 minutes, 1.0 g, 300 rpm, and 20 °C for initial concentration, contact time, adsorbent dose, agitation speed, and temperature, respectively. As evident in Figure 6, the removal efficiency demonstrates a gradual, consistent, and nearly proportional augmentation with increasing the pH of solution, starting at 8% at pH 1 and peaking at 41% at pH 6. This pattern is explicable by the positively charged surface of the adsorbent resulting from H^+ ions at lower pH levels. This positive charge induces a substantial repulsion force between the adsorbent surface and diffusing Tl^{+3} ions in the solution, leading to a reduction in removal efficiency. Moreover, the elevated concentration of hydrogen ions in the solution competes with thallium ions for the accessible active sites on the surface of tangerine peels. In contrast, higher pH levels alleviate the positive charge on the adsorbent surface, thereby diminishing resistance to Tl^{+3} ion adsorption and consequently augmenting efficiency. Notably, as the pH value surpasses 6 (from 7–10), two observations were documented. Firstly, removal efficiency demonstrated a rapid and pronounced increase until reaching its optimum value. Secondly, the precipitation of thallium ions at the base of the experimental flask was observed. This phenomenon indicates that the increase in removal efficiency beyond 41% is a result of a precipitation process rather than adsorption. During this precipitation process, thallium ions persist in the solution, despite constrained diffusion, allowing removal efficiency to reach its maximum. It’s essential to note that this behavior does not signify the actual elimination of the target ions; instead, it merely neutralizes their activity. If there are variations in ambient conditions causing a decrease in pH values, there is a risk of these ions reintroducing contamination to the solution, thereby initiating a cycle of pollution. This result contradicts the fundamental objective of this study, which aims for a lasting purification of contaminated water rather than a transient treatment. Conversely, the adsorption method ensures a more permanent

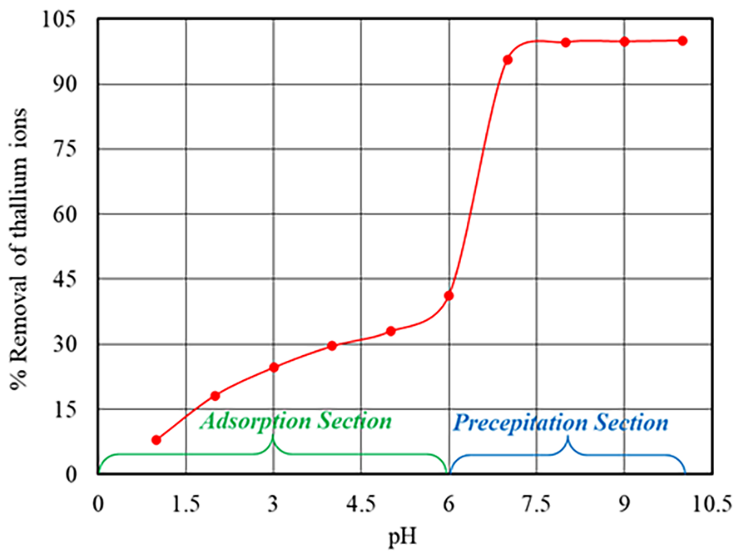

Figure 6. pH impact on thallium ions removal using tangerine peels

removal of thallium ions as they become securely bound to the functional groups located at active sites distributed on the surface of the adsorbent medium. This result contradicts the fundamental objective of this study, which aims for a lasting purification of contaminated water rather than a transient treatment. Conversely, the adsorption method ensures a more permanent removal of thallium ions as they become securely bound to the functional groups located at active sites distributed on the surface of the adsorbent medium. This result agrees with (Hasan et al., 2021).

Agitation speed impact

The agitation speed is one of the most important factors to be studied to know the behavior of the adsorption media, as it is always related to the concept of diffusivity. Therefore, the effect of this variable on the efficiency of the treatment process was studied within a range of 100–500 rpm, while the values of the acidity function, initial concentration, contact time, and adsorbent dose were fixed at 6, 1 ppm, 180 minutes, 1.0 g, respectively and at laboratory temperature. As illustrated in Figure 7, changing the agitation speed values has a pronounced and direct effect on the efficiency of thallium removal from simulated aqueous solutions when utilizing tangerine peels as the adsorption material. Notably, the removal efficiency was increased from 9.5% to 45.56% when the agitation speed increases from 100 to 350 rpm, respectively. At lower agitation speeds (100–350 rpm), the increased movement and mixing in the solution enhance the contact between thallium ions and the active sites on the surface of the tangerine peels (Abbas et al., 2019b). This facilitates effective adsorption, leading to higher removal efficiency. The agitation aids in minimizing boundary layer resistance, ensuring more efficient mass transfer of thallium ions from the solution to the adsorbent surface. However, beyond the optimal agitation range, the removal efficiency diminishes. This reduction can be attributed to several factors. Excessive agitation might lead to the detachment of previously adsorbed thallium ions from the active sites on the surface of tangerine peels. Additionally, very high agitation speeds (400–500 rpm) can cause particles to collide with each other, resulting in agglomeration and decreased interaction between thallium ions and the adsorbent surface. The reduction in removal efficiency observed at 400–500 rpm, reaching nearly 20%, suggests that the benefits of enhanced mass transfer at higher agitation speeds are outweighed by the negative impacts of ion desorption and particle agglomeration. Under these conditions, a singular outcome emerges wherein repulsive forces take precedence over sorption sites on the surface of the absorbent material. Consequently, there is a decline in the attraction between the thallium ion and the tangerine peels. Therefore, 350 rpm was chosen as the ideal speed for the following adsorption experiments. Similar results obtained by (Khudair et al., 2024).

Initial concentration impact

The investigation explored the removal efficiency within a concentration range of 1–90 ppm by varying the initial concentration of thallium

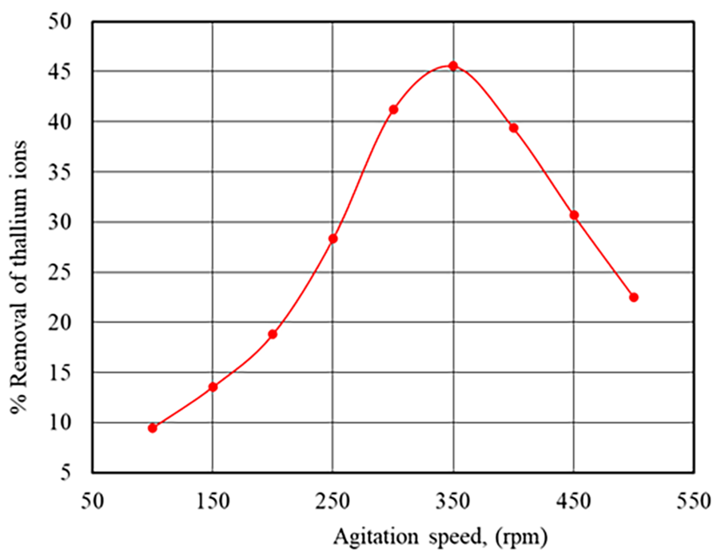

Figure 7. Agitation speed impact on thallium ions removal using tangerine peels

ions in simulated aqueous solutions. The study maintained fixed values for other operational factors: pH at 6, contact time at 180 minutes, adsorbent dose at 1 g, agitation speed at 350 rpm, and laboratory temperature. The results indicated an inverse relationship between removal efficiency and initial concentration. Specifically, the efficiency decreased from 45.56% to 15% as the concentration increased from 1 to 90 ppm. Conversely, the adsorption capacity of tangerine peels exhibits a gradual increase, reaching its maximum at 72 ppm concentration. Elevating the initial concentration results in a greater mass of Tl^{+3} within a constant aqueous solution volume, intensifying competition due to the stability of the adsorbent dose. The adsorbent maintains a fixed surface area with stable active sites featuring finite functional groups capable of bonding with a specific number of thallium ions. As the concentration increases, the presence of unadsorbed Tl^{+3} ions rise, leading to a reduction in efficiency. Figure 8 depicts the impact of varying initial concentrations on the adsorption efficiency of thallium ions from aqueous solutions using tangerine peels. A study by (Abdullah et al. 2023) yielded results consistent with those obtained in the present investigation.

Adsorbent dose impact

The quantity of adsorption medium plays a pivotal role in any adsorption process, making the determination of the optimal dose crucial for achieving maximum removal efficiency of the adsorbent material. This consideration is essential in the examination of surface phenomena, particularly in studies focused on adsorption. To assess the impact of the adsorption dose on treatment efficiency, a series of laboratory experiments were conducted under constant operating conditions, including a pH of 6, an initial concentration of 80 ppm, an agitation speed of 350 rpm, a contact time of 180 minutes, and a temperature of 20 °C. The studied range of adsorbent doses varied from 0.5 to 6 g of tangerine peels. The results depicting the influence of the adsorbent dose are presented in Figure 9. This finding indicates a direct correlation between the adsorbent dose and the removal efficiency. As elucidated in the previous discussion on the effect of initial concentration, the adsorbent material possesses a specific surface area per unit mass. An increase in the adsorbent dose results in an augmented surface area in contact with the contaminated solution, providing additional active sites capable of adsorbing more thallium ions. With the stability of the initial concentration, indicating a constant mass of dispersed thallium in the solution, the likelihood of thallium ions reaching the active sites becomes higher. Consequently, ion adsorption increases with the dose increment. Figure 9 further illustrates that the adsorption efficiency stabilizes at 89.6% without variation beyond 5.5 g of tangerine peels. This phenomenon is attributed to the adsorption process reaching an equilibrium state, signifying that the substance is incapable of adsorbing any additional amount of thallium ions

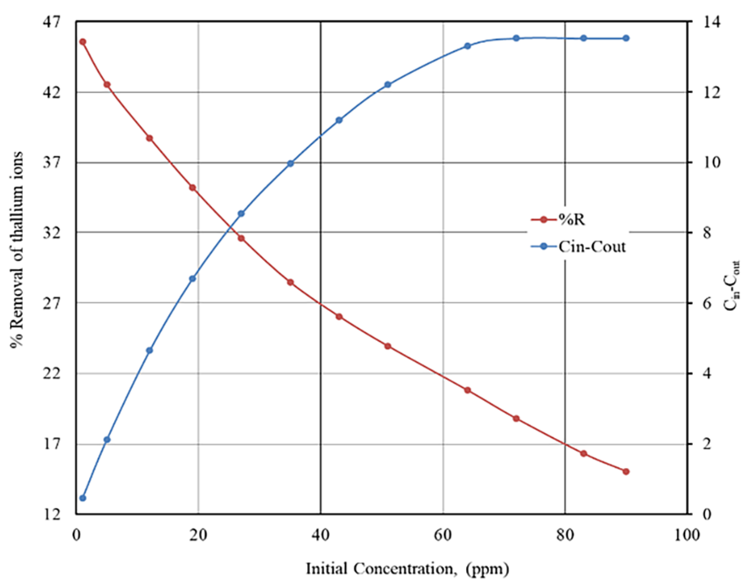

Figure 8. Initial concentration impact on thallium ions removal using tangerine peels

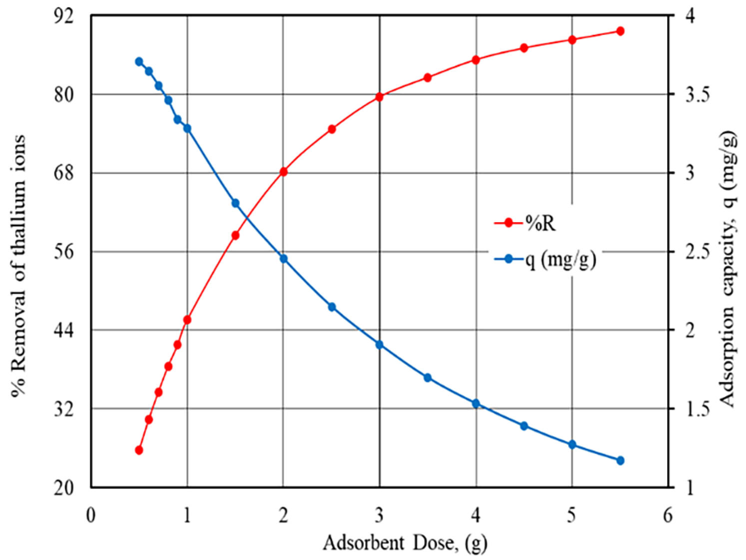

Figure 9. Adsorbent dose impact on thallium ions removal using tangerine peels

due to saturation. Comparable findings have been documented by (Abbas et al., 2021).

Contact time impact

The optimal duration required for achieving the highest removal efficiency of thallium ions was ascertained through a series of experiments conducted at laboratory temperature. All other design parameters, namely pH 6, initial concentration of thallium ions 72 ppm, adsorbent dose 5.5 g, and agitation speed 350 rpm, remained constant. Figure 10 illustrates the results obtained by varying the contact time within the range of 10 to 180 minutes. The results clearly indicate that an increase in contact time has a pronounced effect on enhancing the efficiency of the treatment process. The percentage of removal exhibited an increase from 14.46% to 89.6% with the extension of contact time from 10 minutes to 120 minutes, indicating a direct correlation between treatment time and efficiency within this interval. This observed trend is ascribed to the prolonged contact time, allowing thallium ions an extended duration for interaction with the adsorbent. Holding all other variables at their optimal levels, this extended contact period elevates the probability of thallium ions accessing active sites on the surface of adsorbent. Consequently, the potential for ion adsorption intensifies, leading to an enhanced removal efficiency. Beyond the 120-minute mark, it is noteworthy that the removal rate stabilizes, signifying the adsorption process reaching equilibrium and the incapacity to capture additional molecules under the prevailing operating conditions. This consistent finding aligns with the results reported by (Ghulam et al. 2020).

Temperature impact

The elucidation of important thermodynamic properties in any physical or chemical process, such as adsorption, necessitates a thorough examination of temperature effects (Figure 11). This exploration allows for the determination of the spontaneity of adsorption on the adsorbent material's surface. The influence of temperature on the efficiency of the removal process was scrutinized within a temperature range of 20–50 °C, with all other operational parameters maintained at their optimal values. Figure 12 conveys that the adsorption process is exothermic, evidenced by a reduction in removal efficiency with an increase in temperature. The pinnacle of removal efficiency, recorded at 89.6%, was attained under standard laboratory temperature conditions. This result can be ascribed to the weak forces governing the adsorption process. Within the specified temperature range, an elevation disrupts the intermolecular forces that link thallium ions. This disturbance on the adsorption surface facilitates their release, prompting the ions to re-enter the aqueous solution and thereby diminishing adsorption efficiency. Notably, the decline in efficiency becomes markedly pronounced with escalating temperature, indicating an accelerated liberation of particles from their bonds with the tangerine peel surface. It is plausible that the temperature

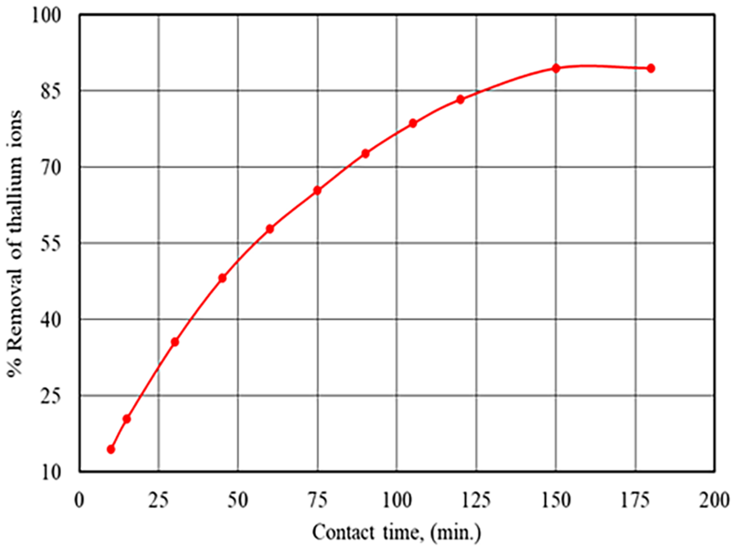

Figure 10. Contact time impact on thallium ions removal using tangerine peels

increase enhances the kinetic energy of adsorbed thallium ions, providing them with the requisite energy to break free from surface forces and re-enter the aqueous solution. This pattern implies that van der Waals forces govern the adsorption, with the rate of desorption surpassing the adsorption rate, characterizing the process as predominantly physical. These findings align consistently with various studies, including the work of (Ibrahim et al., 2021).

Characterization of thallium adsorption demeanor using tangerine peels

Characterizing the adsorption behavior is an essential element for understanding how adsorbents interact with contaminants in adsorption systems. This is achieved through the integration of three studies, namely isothermal, kinetic, and thermodynamic studies. Isothermal study is used to analyze the distribution of adsorbents between solid and liquid phases, providing clearly insights into the adsorbent capacity and adsorption mechanism. Kinetic study, on the other hand, contribute to determining the adsorption rates, mechanisms, and pathways followed by the process. In addition, thermodynamic study highlights the nature of interactions in terms of energy and stability, enabling the evaluation of adsorption efficiency under different conditions and enhancing the overall understanding of this process.

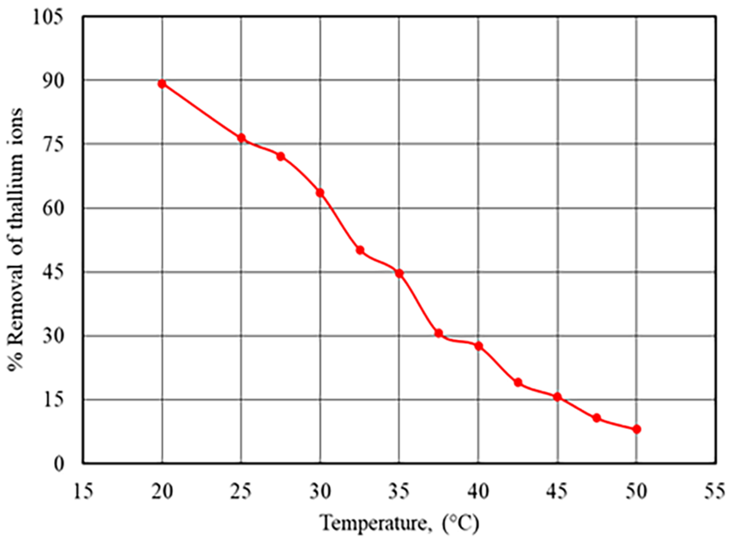

Figure 11. Temperature impact on thallium ions removal using tangerine peels

Adsorption isothermal study

Isothermal study is considered as an essential tool for understanding and characterizing adsorption behavior, as it focuses on studying the relationship between the amount of adsorbed material on the surface of the adsorbent and its concentration in the solution at equilibrium, under a constant temperature. This study provides a deep understanding of the adsorption mechanism and the factors affecting it, such as the nature of the adsorbent and the properties of the adsorbent, including the surface area and the nature of the active sites. It also helps to determine the type of adsorption, whether it is physical based on van der Waals forces or chemical based on the formation of stronger bonds between the adsorbent and the adsorbed molecules. To understand this process systematically, several isothermal models have been developed that help interpret experimental data (Shadhan et al., 2024). The Langmuir model is one of the most widely used models, as it assumes that adsorption occurs on a homogeneous surface with active sites of equal energy, and that each site can accommodate only one molecule, which means that adsorption is limited to a single layer of molecules, which makes it ideal for representing simple adsorption. On the other hand, the Freundlich model focuses on adsorption on heterogeneous surfaces. This model assumes that the energy of active sites varies widely, allowing for multilayer adsorption, making it suitable for representing more complex systems. The Temkin model provides additional insight by focusing on the effect of interactions between adsorbent molecules and the adsorbent. This model assumes that the adsorption energy is not constant, but rather decreases gradually with increasing adsorbent amount, due to changes in the surface nature and interactions between adsorbent molecules and the adsorbent (Ali et al., 2024). These models help to explain adsorption behavior accurately, but in different ways, allowing for the evaluation of adsorbent efficiency and the optimization of adsorption performance. Table 1 shows the general and linear mathematical formulas for the isothermal models used to clarify the adsorption of thallium ions using tangerine peels.

Figures 12–14 and Table 2 present the outcomes of applying various isothermal models to the experimental data for thallium ion adsorption using tangerine peels as a cost-effective adsorbent. The analysis clearly indicates that the Langmuir model aligns most closely with the experimental results, as evidenced by its high correlation coefficient (R^2 = 0.9993), slightly outperforming the Freundlich model (R^2 = 0.8913) and Temkin model (R^2 = 0.9956) models. This result suggests that adsorption occurs as a monolayer on a uniform surface, where all adsorption sites possess the same energy level, was confirmed by SEM analysis, which revealed that the tangerine peels exhibit an organized and homogeneous surface with uniformly sized pores.

Adsorption kinetics study

Kinetic isotherm study is considered as an important element in the characterization of adsorption behavior, as it aims to understand the adsorption rates and the mechanisms controlling the transfer of adsorbent from the solution to the surface of the adsorbent (Ali et al., 2024). This study

Table 1. Details of isothermal models

Isotherm model	Form of model's equation		Slop term	Intercept term	Augmented parameter
	General	Linear			
Langmuir	$q_e = \frac{q_{max}.K_L C_e}{1+K_L C_e}$	$\frac{1}{q_e} = \frac{1}{q_{max}K_L}\frac{1}{C_e} + \frac{1}{q_{max}}$	$\frac{1}{q_{max}K_L}$	$\frac{1}{q_{max}}$	$R_L = \frac{1}{1+K_L C_e}$
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e$	$\frac{1}{n}$	$\ln K_F$	-
Temkin	$q_e = \frac{RT}{b}\ln K_T C_e$	$q_e = \frac{RT}{b}\ln K_T + \frac{RT}{b}\ln C_e$	$\frac{RT}{b}$	$\frac{RT}{b}\ln K_T$	-

Note: q_e – adsorption capacity at equilibrium state (mg.g^{-1}), C_e – equilibrium adsorbed concentration (mg.g^{-1}), q_{max} – maximum adsorption capacity of Langmuir model (mg.g^{-1}), K_L – constant of Langmuir adsorption isotherm model, expressed the binding sites (l.mg^{-1}), R_L – separation factor in Langmuir model (dimensionless), K_F – constant of Freundlich adsorption isotherm model (mg.g^{-1}).(l.mg^{-1})$^{1/n}$, n – intensity of the adsorption in Freundlich model (dimensionless), K_T: Temkin isotherm equilibrium binding constant (l.mg^{-1}), R – universal gas constant (8.3144 J.mol^{-1}.K^{-1}), b – constant in Temkin isotherm model (dimensionless), and T – absolute temperature (K).

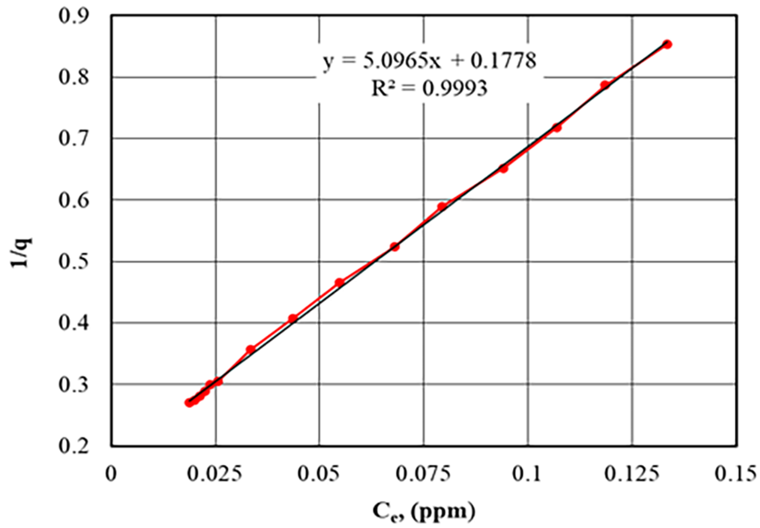

Figure 12. Langmuir isotherm model

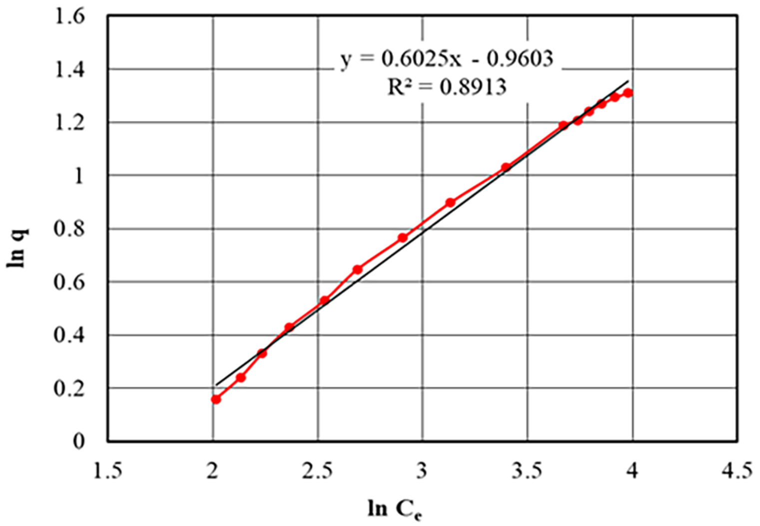

Figure 13. Freundlich isotherm model

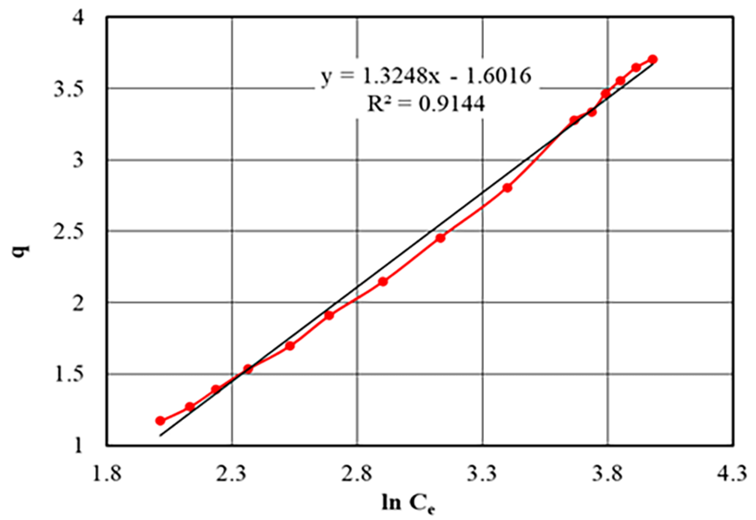

Figure 14. Temkin isotherm model

Table 2. Constants of isothermal models used in the current study

Langmuir isotherm model				Freundlich isotherm model			Temkin isotherm model		
q_{max}	K_L	R_L	R^2	K_F	n	R^2	K_T	b	R^2
5.6243	0.0349	0.2848	0.9993	1.8267	1.0413	0.8913	0.2985	3.2290	0.9144

focuses on determining the time required to reach equilibrium, which helps to improve the adsorption efficiency and identify the factors affecting its speed, such as the properties of the adsorbent, the size of the molecules, and the concentration of the adsorbent. Kinetic models are based on different hypotheses that explain the mechanisms governing adsorption. The pseudo-first-order kinetic model assumes that the adsorption rate depends primarily on the concentration of the adsorbent remaining in the solution, which means that adsorption is directly affected by the number of molecules available on the surface and the surroundings. On the other hand, the pseudo-second-order kinetic model assumes that the adsorption rate depends on the interaction between the adsorbent molecules and the active sites, which indicates that adsorption is more closely related to the availability of active sites on the surface of the adsorbent. The intra-particle diffusion model focuses on the effect of internal transport of adsorbed molecules within the pores of the adsorbent, making it suitable for describing systems where the transport process within the material is the velocity limiting factor (Shadhan et al., 2024). Table 3 shows the differential and linear mathematical formulas for the kinetics models used to describe the adsorption of thallium ions using tangerine peels. Figures 15–17 and Table 4 present the results of applying three kinetic models to the

Table 3. Details of kinetic models

Kinetic model	Form of model's equation		Slop term	Intercept term
	Differential	Linear		
Pseudo first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$-k_1$	$\ln q_e$
Pseudo second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t$	$\frac{1}{q_e}$	$\frac{1}{k_2 {q_e}^2}$
Intra-particle diffusion	–	$q_t = k_P t^{0.5} + I$	k_P	I

Note: q_e – adsorption capacity at equilibrium state (mg.g^{-1}), q_t – adsorption capacity at any time (mg. g^{-1}), k_1 – first order rate constant (min^{-1}), k_2 – second order rate constant (g mg^{-1} min^{-1}), k_p – rate constant in intra-particle diffusion model (mg g min$^{-0.5}$), and I – thickness of boundary layer (mg.g^{-1}).

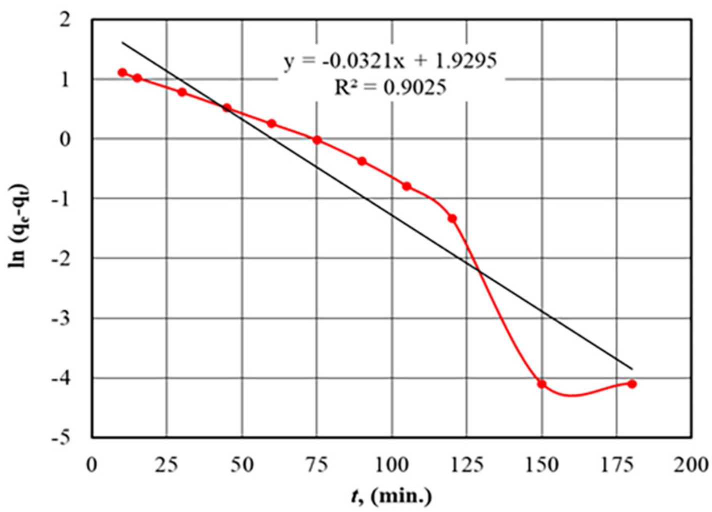

Figure 15. Pseudo first order kinetic model

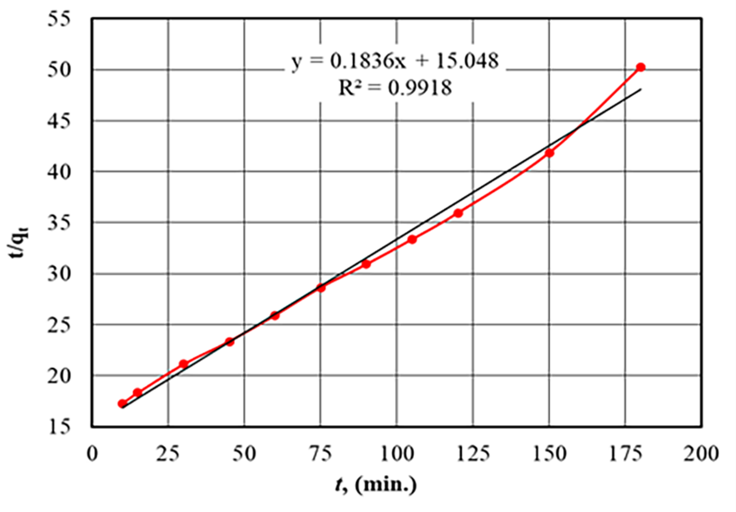

Figure 16. Pseudo second order kinetic model

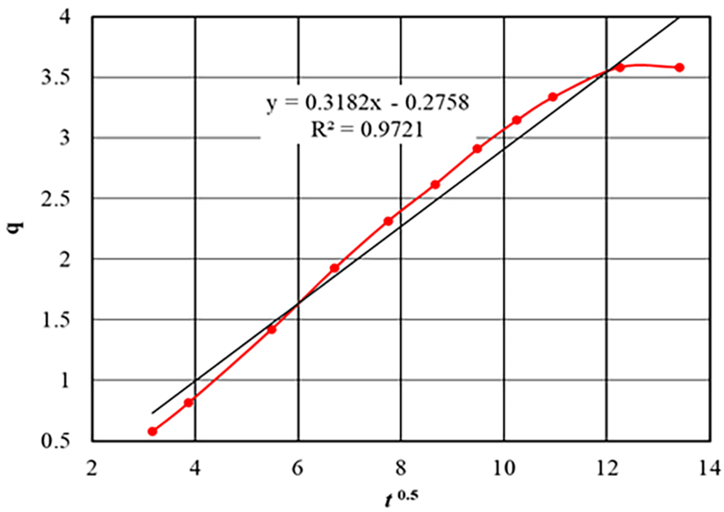

Figure 17. Intra-particle diffusion kinetic model

Table 4. Constants of kinetics models

Pseudo first order			Pseudo second order			Intra-particle diffusion		
k_1	q_e	R^2	k_2	q_e	R^2	K_p	I	R^2
0.0321	6.886	0.9025	0.00224	5.4466	0.9918	0.3182	- 0.2758	0.9721

experimental data for thallium ion adsorption using tangerine peels as a low-cost adsorbent. The data clearly indicate that the pseudo-second-order kinetic model aligns most closely with the experimental results compared to the pseudo-first-order kinetic model and the intra-particle diffusion model, as evidenced by correlation coefficients of 0.9918 and 0.9721, respectively. According to the pseudo-second-order model's assumptions, the adsorption rate of thallium primarily depends on the concentration of available adsorbent in the solution. This implies that the adsorption process is significantly influenced by the number of accessible active sites on the adsorbent surface. This explanation is supported by the agitation speed results, which demonstrate that the highest adsorption efficiency occurs at an optimal speed of 350 rpm -a moderate rate- indicating that the movement of thallium ions toward the active sites requires a concentration gradient. Furthermore, no boundary layer film was observed to hinder the ions' access to the adsorbent surface. In contrast, the pseudo-first-order kinetic model showed a weaker fit to the experimental data, with a correlation coefficient (R^2) of 0.9025.

Adsorption thermodynamic study

The thermodynamic analysis of adsorption seeks to evaluate the energy changes involved in the process and to understand the interactions between the adsorbent and the adsorbate. This analysis involves determining key thermodynamic parameters, such as the change in Gibbs free energy (ΔG), which indicates the spontaneity of the process. Adsorption occurs spontaneously when ΔG has a negative value. Additionally, the change in enthalpy (ΔH) is calculated to reveal whether energy is absorbed or released during the adsorption process (Shadhan et al., 2024). A negative ΔH signifies exothermic adsorption, while a positive ΔH denotes endothermic adsorption. The third parameter, the change in entropy (ΔS), provides insight into the degree of randomness or disorder in the system post-adsorption. A positive ΔS indicates an increase in disorder at the surface. These thermodynamic parameters are calculated using adsorption data collected at various temperatures, and the Van't Hoff equation, as shown in Equation 3, is applied to determine ΔH, ΔS, and ΔG based on the adsorption equilibrium constants at different temperatures.

$$\Delta G = \Delta H - T\Delta S \tag{3}$$

$$k_d = -\frac{\Delta H}{\mathbb{R}}\frac{1}{T} + \frac{\Delta S}{\mathbb{R}} \tag{4}$$

where: k_d – adsorption equilibrium coefficient (–); $\mathbb{R}$ – universal gas constant (8.3144 J/mol.K); T – absolute temperature (K); ΔH – Enthalpy change (kJ/mol); ΔS – Entropy change (J/mol.K); ΔG – Gibbs free energy (kJ/mol).

The logarithmic distribution coefficient (ln k_d) plotted against (1/T) in Figure 18, as outlined in Equation 4, was utilized to calculate the thermodynamic parameters ΔH and ΔS from the slope and intercept, respectively. Table 5 presents the results of thallium ion adsorption using tangerine peels as a cost-effective adsorbent. The process is evidently spontaneous, as demonstrated by the negative values of ΔG^o. The negative ΔH^o confirms that the adsorption is exothermic within the temperature range of 20–50 °C, indicating that higher temperatures enhance adsorption efficiency. This improvement is likely due to the formation of additional active sites on the adsorbent surface and the increased rate of pore diffusion. Moreover, the adsorption is chemical in nature, as suggested by the enthalpy values. The negative ΔS reflects decrease randomness at the solid/solution interface during the adsorption. These findings are consistent with results reported by (Alhamd et al., 2024a).

Benefit from the toxic residue of tangerine peels

After ending the practical experiments of adsorption of thallium ions on tangerine peels as a low-cost adsorbent, thallium-loaded tangerine peels accumulated as toxic residues, that must be disposed of in a safe and inexpensive manner, to

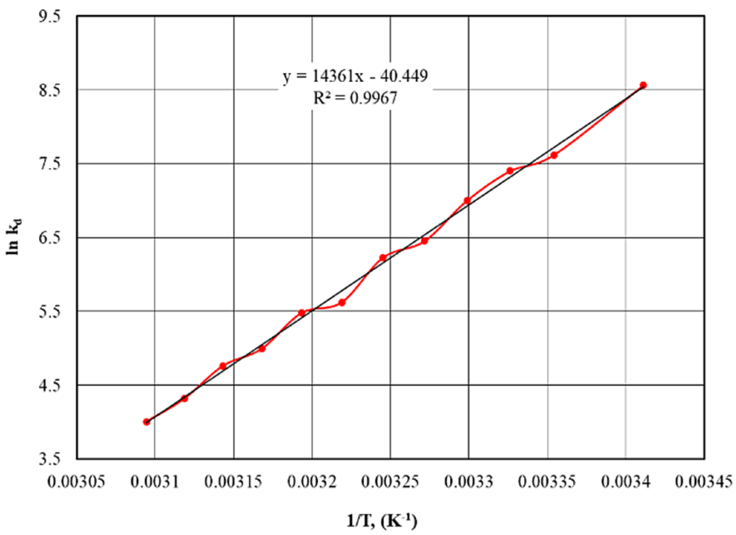

Figure 18. Thermodynamic behavior for Tl^{+3} adsorption using tangerine peels

Table 5. Thermodynamic parameters of Tl^{+3} adsorption using tangerine peels

Temperature, (K)	ΔH (kJ/mol)	ΔS (J/mol·K)	ΔG (kJ/mol)
20	-119.404	-337.975	-20.3267
25			-18.6369
27.5			-17.7919
30			-16.947
32.5			-16.1021
35			-15.2571
37.5			-14.4122
40			-13.5673
42.5			-12.7223
45			-11.8774
47.5			-11.0324
50			-10.1875

achieve the main study objective of reaching zero residues and achieving a sustainable approach to treating contaminated solutions. The introduction of thallium-laden tangerine peels as a food for rapidly breeding rodents was investigated, and the possibility of using these toxic residues to prepare an effective and low-cost rodenticide was studied. The effect of these residues on laboratory albino rats (Sprague Dawley type), of scientific name *Rattus norvegicus domestica*, was tested by mixing the toxic residues with the diet provided to them according to the method described by (Alalwan et al., 2020). Initially, a suitable number of standard cages for raising rats were prepared. The cages were made of plastic, measuring 30 × 50 × 20 cm, covered with metal mesh covers, and their floors were covered with sawdust to a height of 3–5 cm. In laboratory conditions suitable for living in terms of ventilation, with 12 hours of lighting using a standard lamp (Panasonic 15W B22 LED Bulb) of 10–15 watts power, and a temperature between 23–25 °C ± 2 °C, the animals were placed in equal and proportional numbers of males and females inside each cage. The animals were cared for, provided with drinking water and diet, and were placed under observation for 10 days, to ensure that they did not suffer from any disease or health condition or were pregnant (for females). The cages were cleaned and sterilized with disinfectants and detergents daily, and during the cleaning period the animals were transferred to cages similar in terms of living conditions, to provide a safe and healthy environment for the rats to obtain guaranteed results. 30 Sprague Dawley rats (15 males and 15 females) were selected to carry out the practical experiments. Their ages ranged between 20–24 weeks and their weights ranged between 180–230 g. They were divided into 5 groups, with 6 animals per group, where the number of males was equal to the number of females in each group. The first group was the control group (CG), where its animals were fed with the regular diet and pure water only, while the rats in the second group (PG) were fed with the regular diet mixed with washed and clean virgin tangerine peels in different proportions ranging from 10–25% of the diet weight, in addition to pure water. Groups 3–5 (EG1-EG3) were the experimental groups, because their animals were treated with toxic waste. In addition to drinking water, the rats in the experimental groups were fed tangerine peels loaded with thallium in the same proportions used with the animals in the second group. The results showed that animals in groups 3–5 suffered from numerous deaths ranging from 50–100% of rats fed the diet mixed with the toxic substance, while animals in groups 1 and 2 did not suffer from any significant deaths. In addition, the time to death was inversely proportional to the ratio of thallium-loaded tangerine peels mixed in, the higher the ratio, the shorter the time to death of the animals. In general, symptoms of thallium poisoning in rats appeared within 24–48 hours and the time to death ranged from 3 to 7 days depending on the ratio of thallium-loaded peels mixed in the rats' diet and the gender of animal. Calculations for the half-lethal dose (LD_{50}), representing the amount of toxin needed to lethally affect half of the subjects in the tested animals (rats in this study), were conducted. Notably, no fatalities were observed in the control groups. The LD_{50}, expressed as the toxin amount (in mg) per body weight (in kg) of deceased animals, was determined to be 16.50 (mg/kg) for males and 15.74 (mg/kg) for females. These values are consistent with the cited literature which was 15 mg/kg (Gupta, 2018).

CONCLUSIONS

Tangerine peels, a prevalent agricultural waste, exhibit exceptional adsorption properties, rendering them a promising material for environmental applications. Thallium adsorption by tangerine peels manifests a notable dependence on pH, adsorbent dosage, and contact time. The optimal sorption conditions were identified at pH 6, initial concentration of 72 ppm, agitation speed of 350 rpm, contact time of 120 min, temperature of 20 °C and adsorbent dosage of 5.5 g. The morphological examinations showed that the initial surface area of tangerine peels is 9.421 m^2/g, and the adsorption occupied 83.5% of this area, according to BET surface area analysis. Furthermore, the adsorbent medium having an organized and homogeneous surface according to SEM test and multiple functional groups according to FTIR test. The Langmuir isotherm model emerged as the most fitting model for thallium removal, boasting a high correlation coefficient of $R^2 = 0.9993$. Kinetic studies revealed that the pseudo-second-order model best elucidated the adsorption process. Furthermore, the adsorption proved to be spontaneous, exothermic, and characterized by low entropy, with respective values of -20.3267 kJ/mol.K, -119.404 kJ/mol, and -337.975 J/mol at 20 °C. As one way to move towards sustainability, toxic residues from tangerine peels were tested as a rodenticide, by mixing them with the feed of laboratory rats (Rattus norvegicus domestica). The test results were promising, as mortality rates were proportional to the percentage of waste consumed, confirming the achievement of the concept of zero residue level. This study highlights the potential of tangerine peels as an efficient adsorbent for wastewater treatment, achieving remarkable removal rates of up to 89.56% for Tl^{+3}. Additionally, tangerine peels stand out as a practical and cost-effective option for wastewater treatment, owing to the widespread availability of this waste material.

Acknowledgments

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REFERENCES

1. Abbas F.S., Abdulkareem W.S., Abbas M.N. (2022a). Strength development of plain concrete slabs by the sustainability potential of lead-loaded rice husk (LLRH). *Journal of Applied Engineering Science, 20*(1), 160–167. https://doi:10.5937/jaes0-32253
2. Abbas M.N. (2015). Phosphorus removal from wastewater using rice husk and subsequent utilization of the waste residue. *Desalination and Water Treatment, 55*(4), 970–977. https://doi.org/10.1080/19443994.2014.922494
3. Abbas M.N., Abbas F.S. (2013a). Iraqi rice husk potency to eliminate toxic metals from aqueous solutions and utilization from process residues. *Advances in Environmental Biology, 7*(2), 308–319. https://www.aensiweb.com/old/aeb/2013/308-319.pdf
4. Abbas M.N., Abbas F.S. (2013b). The Predisposition of Iraqi rice husk to remove heavy metals from aqueous solutions and capitalized from waste residue. *Research Journal of Applied Sciences, Engineering and Technology, 6*(22), 4237–4246. https://www.maxwellsci.com/html/rjaset.6.3539.html
5. Abbas M.N., Abbas F.S. (2013c). The feasibility of rice husk to remove minerals from water by adsorption and avail from wastes. *Research Journal of Applied Sciences, WSEAS Transactions on Environment and Development, 9*(4), 301–313. http://www.wseas.org/multimedia/journals/environment/2013/145715-140.pdf
6. Abbas M.N., Abbas F.S. (2014). Application of rice husk to remove humic acid from aqueous solutions and profiting from waste leftover. *WSEAS Transactions on Biology and Biomedicine, 11*(9), 62–69. http://www.wseas.us/journal/pdf/biology/2014/a025708-124.pdf
7. Abbas M.N., Alalwan H.A. (2019). Catalytic oxidative and adsorptive desulfurization of heavy naphtha fraction. *Korean Journal of Chemical Engineering, 12*(2), 283–288. http://doi.org/10.9713/kcer.2019.57.2.283
8. Abbas M.N., Ali S.T., Abbas R.S. (2020). Rice husks as a biosorbent agent for Pb^{+2} ions from contaminated aqueous solutions: A review. *Biochemical and Cellular Archives, 20*(1), 1813–1820. https://doi.org/10.35124/bca.2020.20.1.1813
9. Abbas M.N., Al-Madhhachi A.T., Esmael S.A. (2019b). Quantifying soil erodibility parameters due to wastewater chemicals. *International Journal of Hydrology Science and Technology, 9*(5), 550–568. http://doi.org/10.1504/IJHST.2019.10016884
10. Abbas M.N., Al-Tameemi I.M., Hasan M.B., Al-Madhhachi A.T. (2021). Chemical removal of cobalt and lithium in contaminated soils using promoted white eggshells with different catalysts. *South African Journal of Chemical Engineering, 35*, 23–32. https://doi.org/10.1016/j.sajce.2020.11.002
11. Abbas M.N., Ibrahim S.A. (2020). Catalytic and thermal desulfurization of light naphtha fraction. *Journal of King Saud University - Engineering Sciences, 32*(4), 229–235. https://doi.org/10.1016/j.

jksues.2019.08.001

12. Abbas M.N., Ibrahim S.A., Abbas Z.N., Ibrahim T.A. (2022b). Eggshells as a sustainable source for acetone production. *Journal of King Saud University - Engineering Sciences, 34*(6), 381–387. https://doi.org/10.1016/j.jksues.2021.01.005
13. Abbas M.N., Nussrat T.H. (2020). Statistical analysis of experimental data for adsorption process of cadmium by watermelon rinds in continuous packed bed column. *International Journal of Innovation, Creativity and Change, 13*(3), 124–138. https://www.ijicc.net/images/vol_13/Iss_3/13321_Abbas_2020_E_R.pdf
14. Abbas M.N., Al-Hermizy S.M.M., Abudi Z.N., Ibrahim T.A. (2019a). Phenol biosorption from polluted aqueous solutions by *Ulva lactuca* alga using batch mode unit. *Journal of Ecological Engineering, 20*(6), 225–235. https://doi.org/10.12911/22998993/109460
15. Abd ali I.K., Ibrahim T.A., Farhan A.D., Abbas M.N. 2018. Study of the effect of pesticide 2,4-D on the histological structure of the lungs in the albino mice (*Mus musculus*). *Journal of Pharmaceutical Sciences and Research, 10*(6), 1418–1421. https://www.jpsr.pharmainfo.in/Documents/Volumes/vol10Issue06/jpsr10061822.pdf
16. Abd Ali I.K., Salman S.D., Ibrahim T.A., Abbas M.N. (2024). Study of the teratogenic effects of antimony on liver in the adult rabbit (*Oryctolagus cuniculus*). *Advancements in Life Sciences, 11*(2), 462–469. http://dx.doi.org/10.62940/als.v11i2.2773
17. Abd Al-Latif F.S., Ibrahim T.A., Abbas M.N. (2023). Revealing potential histological changes of deltamethrin exposure on testicular Tissue in albino rabbits (*Oryctolagus cuniculus*). *Advancements in Life Sciences, 10*, 4, 619–626. http://dx.doi.org/10.62940/als.v10i4.2323
18. Abdulkareem W.S., Aljumaily H.S.M., Mushatat H.A., Abbas M.N. (2023). Management of agro-waste by using as an additive to concrete and its role in reducing cost production: impact of compressive strength as a case study. *International Journal on Technical and Physical Problems of Engineering (IJTPE), 15*(1), 62–67. http://www.iotpe.tabaelm.com/IJTPE/IJTPE-2023/IJTPE-Issue54-Vol15-No1-Mar2023/9-IJTPE-Issue54-Vol15-No1-Mar2023-pp62-67.pdf
19. Abdullah W.R., Alhamadani Y.A.J., Abass I.K., Abbas M.N. (2023). Study of chemical and physical parameters affected on purification of water from inorganic contaminants. *Periodicals of Engineering and Natural Sciences, 11*(2), 166–175. http://dx.doi.org/10.21533/pen.v11i2.3508
20. Al Hammouri, F., Darwazeh, G., Said, A. Abu Ghosh, R. (2011). Acute thallium poisoning: Series of ten cases. *Journal of Medical Toxicology, 7*, 306–311. https://doi.org/10.1007/s13181-011-0165-3
21. Al-Ali S.I.S., Abudi Z.N., Abbas M.N. (2023). Modelling and simulation for the use of natural waste to purified contaminated heavy metals. *Journal of the Nigerian Society of Physical Sciences, 5*(1), 1143. https://doi.org/10.46481/jnsps.2023.1143
22. Alalwan H.A., Abbas M.N., Abudi Z.N., Alminshid A.H. (2018). Adsorption of thallium ion (Tl^{+3}) from aqueous solutions by rice husk in a fixed-bed column: Experiment and prediction of breakthrough curves. *Environmental Technology and Innovation, 12*, 1–13. https://doi.org/10.1016/j.eti.2018.07.001
23. Alalwan H.A., Abbas M.N., Alminshid A.H. (2020). Uptake of cyanide compounds from aqueous solutions by lemon peel with utilising the residue absorbents as rodenticide. *Indian Chemical Engineer, 62*(1), 40–51. https://doi.org/10.1080/00194506.2019.1623091
24. Alalwan H.A., Mohammed M.M., Sultan A.J., Abbas M.N., Ibrahim T.A., Aljaafari H.A.S., Alminshid A.A. (2021). Adsorption of methyl green stain from aqueous solutions using non-conventional adsorbent media: Isothermal kinetic and thermodynamic studies. *Bioresource Technology Reports, 14*, 100680. https://doi.org/10.1016/j.biteb.2021.100680
25. Alhamd S.J., Abbas M.N., Manteghian M., Ibrahim T.A., Jarmondi K.D.S. (2024a). Treatment of oil refinery wastewater polluted by heavy metal ions via adsorption technique using non-valuable media: cadmium ions and buckthorn leaves as a study case. *Karbala International Journal of Modern Science (KIJOMS), 10*(1), 1–18. https://doi.org/10.33640/2405-609X.3334
26. Alhamd S.J., Abbas M.N., Al-Fatlawy H.J.J., Ibrahim T.A., Abbas Z.N. (2024b). Removal of phenol from oilfield produced water using non-conventional adsorbent medium by an eco-friendly approach. *Karbala International Journal of Modern Science (KIJOMS), 10*(2), 191–210. https://doi.org/10.33640/2405-609X.3350
27. Al-Hermizy S.M.M., Al-Ali S.I.S., Abdulwahab I.A., Abbas M.N. (2022). Elimination of zinc ions (Zn^{+2}) from synthetic wastewater using lemon peels. *Asian Journal of Water, Environment and Pollution, 19*(5), 79–85. https://doi.org/10.3233/AJW220073
28. Ali G.A.A., Abbas M.N. (2020). Atomic spectroscopy technique employed to detect the heavy metals from Iraqi waterbodies using natural bio-filter (*Eichhornia crassipes*) thera dejla as a case study. *Systematic Reviews in Pharmacy, 11*, 9, 264-271. https://doi.org/10.31838/srp.2020.9.43
29. Ali G.A.A., Ibrahim S.A., Abbas M.N. (2021). Catalytic adsorptive of nickel metal from Iraqi crude oil using non-conventional catalysts. *Innovative Infrastructure Solutions, 6*(7), 1–9. https://doi.org/10.1007/s41062-020-00368-x

30. Ali S.A.K., Abudi Z.N., Abbas M.N., Alsaffar M.A., Ibrahim T.A. (2024). Synthesis of nano-silica particles using *Eucalyptus globulus* leaf extract and their innovative application as an adsorbent for malachite green dye, *Russian Journal of Applied Chemistry, 97*(1), 2–14. https://doi.org/10.1134/S1070427224010099
31. Ali S.A.K., AL-Kaabi Z., Kasim M.N., Abbas M.N., Ibrahim T.A. (2023). Remediation of antimony from aqueous solutions by adsorption technique: Isothermal, Kinetic and Thermodynamic Studies. *Indian Journal of Environmental Protection, 43*(14), 1316–1325, (Conference 2023). https://www.e-ijep.co.in/43-14-1316-1325/
32. Ali S.A.K., Almhana N.M., Hussein A.A., Abbas M.N. (2020a). Purification of aqueous solutions from toxic metals using laboratory batch mode adsorption unit antimony (V) ions as a case study. *Journal of Green Engineering (JGE), 10*(11), 10662–10680.
33. Ali S.T., Qadir H.T., Moufak S.K., Al-Badri M.A.M., Abbas M.N. (2020b). a statistical study to determine the factors of vitamin D deficiency in men: the City of Baghdad as a model. *Indian Journal of Forensic Medicine & Toxicology, 14*(1), 691–696. https://doi.org/10.37506/ijfmt.v14i1.132
34. Ali S.T., Shahadha R.W., Abdulkareem W.S., Abbas M.N. (2024). Available low cost agro-waste as an efficient medium to eliminate heavy metal contamination using sustainable approach achieving zero residue level, *Journal of Ecological Engineering, 25*(10), 160–175. https://doi.org/10.12911/22998993/191945
35. Alminshid A.H., Abbas M.N., Alalwan H.A., Sultan A.J., Kadhome M.A. (2021). Aldol condensation reaction of acetone on MgO nanoparticles surface: An *in-situ* drift investigation. *Molecular Catalysis, 501*, 111333. https://doi.org/10.1016/j.mcat.2020.111333
36. Alsarayreh, A.A., Ibrahim, S.A., Alhamd S.J., Ibrahim T.A., Abbas M.N. (2024). Removal of selenium ions from contaminated aqueous solutions by adsorption using lemon peels as a non-conventional medium. *Karbala International Journal of Modern Science (KIJOMS), 10*(4), 511–531. https://doi.org/10.33640/2405-609X.3375
37. Alwan E.K., Hammoudi A.M., Abd I.K., Abd Alaa M.O., Abbas M.N. (2021). Synthesis of cobalt iron oxide doped by chromium using sol-gel method and application to remove malachite green dye. *NeuroQuantology, 19*(8), 32–41 http://doi:10.14704/nq.2021.19.8.NQ21110
38. Fujihara J., Nishimoto N. (2024). Thallium – poisoner's poison: An overview and review of current knowledge on the toxicological effects and mechanisms. *Current research in toxicology, 6*, 100157. https://doi.org/10.1016/j.crtox.2024.100157
39. Gad S.C. (2024). Thallium. Encyclopedia of Toxicology (Fourth Edition), 9, 19–23. https://doi.org/10.1016/B978-0-12-824315-2.00668-0
40. Genchi G., Carocci A., Lauria G., Sinicropi M.S., Catalano A. (2021). Thallium use, toxicity, and detoxification therapy: An overview. *Applied Sciences, 11*(18), 8322. https://doi.org/10.3390/app11188322
41. Ghulam N.A., Abbas M.N., and Sachit D.E. (2020). Preparation of synthetic alumina from aluminium foil waste and investigation of its performance in the removal of RG-19 dye from its aqueous solution. *Indian Chemical Engineer, 62*(3), 301–313. https://doi.org/10.1080/00194506.2019.1677512
42. Gupta R.C. (2018). Chapter 47 - non-anticoagulant rodenticides. veterinary toxicology: *Basic and Clinical Principles*, (Third Edition), 613–626. https://doi.org/10.1016/B978-0-12-811410-0.00047-7
43. Hamdi G.M., Abbas M.N., Ali S.A.K. (2024). Bioethanol production from agricultural waste: A review. *Journal of Engineering and Sustainable Development, 28*(2), 233–252. https://doi.org/10.31272/jeasd.28.2.7
44. Hameed A.S., Alsarayreh A.A., and Abbas M.N. (2025). Applying of zero residue level concept in integrated management of toxic and solid wastes as a sustainable approach. *Ecological Engineering & Environmental Technology, 25*(1), 353–378. https://doi.org/10.12912/27197050/196409
45. Hameed W.A., and Abbas M.N. (2024). Dyes adsorption from contaminated aqueous solution using SiO_2 nanoparticles prepared from extracted tree leaves. *Journal of Ecological Engineering, 25*(7), 41–57. https://doi.org/10.12911/22998993/187921
46. Hasan M.B., Al-Tameemi I.M., Abbas M.N. (2021). Orange peels as a sustainable material for treating water polluted with antimony. *Journal of Ecological Engineering, 22*(2), 25–35. https://doi.org/10.12911/22998993/130632
47. Hashem N.S., Ali G.A.A., Jameel H.T., Khurshid A.N., Abbas M.N. (2021). Heavy metals evaluation by atomic spectroscopy for different parts of water hyacinth (*Eichhornia Crassipes*) plants: banks of Tigris River and Al-Zuhairat Village sites. *Biochemical and Cellular Archives, 21*(2), 3813–3819. https://connectjournals.com/03896.2021.21.3813
48. Ibrahim S.A., Hasan M.B., Al-Tameemi I.M., Ibrahim T.A., Abbas M.N. (2021). Optimization of adsorption unit parameter of hardness remediation from wastewater using low-cost media. *Innovative Infrastructure Solutions, 6*(4), Article number: 200. https://doi.org/10.1007/s41062-021-00564-3
49. Ibrahim T.A., Mahdi H.S., Abbas R.S., Abbas, M.N. (2020a). Study the effect of ribavirin drug on the

histological structure of the testes in albino mice (*Mus musculus*). *Journal of Global Pharma Technology, 12*(2),142-146. http://www.jgpt.co.in/index.php/jgpt/article/view/3233

50. Ibrahim T.A., Mohammed A.M., Abd ali I.K., Abbas M.N., Hussien S.A. (2020b). Teratogenic effect of carbamazepine drug on the histological structure of testes in the albino mouse (*Mus musculus*). *Indian Journal of Forensic Medicine & Toxicology, 14*(4), 1829–1834. https://doi.org/10.37506/ijfmt.v14i4.11809
51. Khaleel L.R., Al-Hermizy, S. M., Abbas, M.N. (2022). Statistical indicators for evaluating the effect of heavy metals on samaraa drug industry water exposed to the sun and freezing. *Tropical Journal of Natural Product Research, 6*(12), 1969–1974. http://www.doi.org/10.26538/tjnpr/v6i12.12
52. Khudair S.Y., Alsarayreh, A.A., Abbas M.N. (2024). Adsorption of vanadium from Iraqi crude oil on nano zeolite and alum sludge. *Journal of Engineering and Sustainable Development (JESD), 28*(6), 762–769. https://doi.org/10.31272/jeasd.28.6.9
53. Maddodi S.A., Alalwan H.A., Alminshid A.H., Abbas M.N. (2020). Isotherm and computational fluid dynamics analysis of nickel ion adsorption from aqueous solution using activated carbon. *South African Journal of Chemical Engineering, 32*, 5–12. https://doi.org/10.1016/j.sajce.2020.01.002
54. Rajaa N., Kadhim F.J., Abbas M.N., Banyhussan Q.S. (2023). The improvement of concrete strength through the addition of sustainable materials (agro-waste loaded with copper ions). *3rd International Conference for Civil Engineering Science (ICCES 2023)*, IOP Conf. Series: Earth and Environmental Science, 1232, 012038, 9. http://doi.org/10.1088/1755-1315/1232/1/012038
55. Shadhan Z.J., Alhamd S., Abbas M.N. (2024). Recovery of vanadium element from wastewater of petroleum refineries using effective adsorbent: Mathematical approach via isothermal, kinetics and thermodynamic simulation. *Al-Qadisiyah Journal for Engineering Sciences (QJES), 17*(3), 211–219. https://doi.org/10.30772/qjes.2024.145441.1069