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Experimental and theoretical study on chromium adsorption by tangerine peels with isotherm, kinetic and thermodynamic insights

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ABSTRACT

Citrus peels, a common agricultural waste, a sustainable and available resource for innovative and environmentally friendly uses. This study investigated the ability of tangerine peels as an adsorbent to recover hexavalent chromium ions from polluted aqueous solutions. The treatment process was carried out under different operating conditions using laboratory adsorption unit of batch mode. The operating conditions ranges studied were 20–50 °C, 10–180 min, 1–10 ppm, 100–500 rpm, 1–8, for temperature, contact time, initial concentration of chromium, agitation speed, pH, and adsorbent dosage, respectively. The obtained results showed that the adsorption efficiency is directly proportional to all variables except the initial concentration, while it increases with the increase of the pH, until it reaches a certain limit and then begins to decrease. 72.4% was the highest treatment efficiency and was achieved at a value of 4 for the acidity function, 350 rpm for the agitation speed, 8 ppm for the initial concentration, 5 g of adsorption medium, 120 min adsorption time, and 50 °C temperature. The results of FTIR analysis showed that the tangerine peels contain multi-functional groups responsible for capturing chromium ions and the surface area of the raw peels decreased by 93% after adsorption, indicating that this material is highly effective in adsorption of heavy metals in general and chromium in particular.

Keywords: Tangerine peels, batch adsorption, hexavalent chromium, aqueous solutions, and removal

INTRODUCTION

Agricultural waste includes residues from crop production, animal husbandry, and food industries, and its type and volume vary based on agricultural productivity and crop type (Riseh et al., 2024; Bala et al., 2023). Among these, plant-based residues such as wheat straw, rice straw, corn stalks, and especially fruit and vegetable peels—including citrus peels—are produced in large amounts worldwide (Ogbu and Okey, 2023). In countries like China, India, and the U.S., agricultural waste reaches hundreds of millions of tons annually (Hashem et al., 2021; Singh et al., 2024). Citrus peels, particularly from oranges, lemons, and tangerines, form a significant portion of this waste. For example, Brazil alone produces over 8 million tons of orange peel annually (Rocha et al., 2023), and in North Africa and the Middle East, large volumes of citrus peel are generated due to intensive fruit processing industries (Beshara et al., 2024). Despite their abundance and potential value, these peels are often discarded or burned, contributing to pollution through greenhouse gas emissions and water contamination (Hawal et al., 2021). However, citrus peels contain valuable compounds like limonene, hesperidin, pectin, and essential oils, making them suitable for industrial reuse (Maqbool et al., 2023). Researchers have explored the potential of citrus peels as low-cost adsorbents for wastewater treatment due to their zero-toxicity and high availability (Russo et al., 2021; Abbas and Nussrat, 2020). For instance, Akinhanmi et al. (2020) reported a maximum cadmium adsorption capacity of 128.23 mg/g using orange peels under

optimal conditions (pH 5.5, 240 ppm Cd^{2+}, 45 °C, 2 h), with adsorption following the Langmuir isotherm and pseudo-first-order kinetics. Similarly, Hasan et al. (2021) found that acid-treated orange peels achieved 98% efficiency in antimony removal compared to 72% for raw peels.

In multi-component systems, dyes can enhance heavy metal adsorption via complexation. Giraldo et al. (2022) showed that untreated orange peels effectively adsorbed both methylene blue (0.7824 mmol/g) and cadmium (0.2884 mmol/g), with Langmuir isotherms fitting the data best. Batista et al. (2025) demonstrated that NaOH-treated tangerine peels significantly improved methylene blue adsorption (328 mg/g), nearly tripling the capacity of untreated peels, with modified peels showing entropy-driven adsorption behavior ($\Delta H = -3$ J/mol for raw peels). Other researchers have focused on converting citrus waste into high-surface-area carbon materials. De Tuesta et al. (2022) used tangerine peels activated with iron (III) chloride to produce hydrothermal carbon with a surface area of 104 m^2/g, while untreated peels yielded 287 m^2/g. These materials achieved nickel adsorption capacities of up to 16.5 mg/g under optimal batch conditions. Kang et al. (2024) developed high-performance activated carbon from tangerine peels using hydrothermal and dry carbonization, achieving surface areas between 1530–3375 m^2/g and removing up to 76% of methylene chloride from water. Building on these findings, the present study explores the use of tangerine peels as a sustainable, low-cost adsorbent for hexavalent chromium (Cr^{+6}) removal from aqueous solutions. This research focuses on optimizing operational parameters and characterizing the adsorption process through isotherm, kinetic, and thermodynamic models, with surface morphology analysis before and after treatment.

EXPERMINTAL WORK

Adsorbent

In the present study, tangerine peels, of Egyptian origin, were used as an available and low-cost adsorbent, and prepared according to the method describes in (Alhamd et al. 2024). Tangerine peels, shown in Figure 1, were collected from household consumption for one month, washed several times using an excess of tap water to remove any impurities or dirt that may be stuck to them, and then washed once using distilled water. The washed peels were dried in two stages, the first was natural drying stage, where they were spread out in the open air for 3 days at a temperature ranging between 40–45 °C in a clean place, while the other drying stage was carried out using a drying oven at a temperature of 60 °C, to ensure that the peels did not char and crushed After drying they were sieved to particle size 0.5 mm, and used as an adsorben. The oven drying process continued until the weight of the peels is constant. The dried peels were stored in glass amber jars in a clean, dry and dark place, away from sunlight until use, where they were used without any additional treatment. (Zainab and Hayder, 2022).

Calibration curve

It is an indispensable and obligatory tool during experiments involving adsorption to properly and reliably ascertain the adsorbate's concentration in contaminated solutions by measuring it, since it is relied upon in converting the values accessed through measurements made with a spectroscopy technique to actual concentrations. The calibration curve is the fundamental foundation upon which the adsorbent's efficiency utilized in removing the adsorbate is gauged. In preparation for this critical tool of the present work, a series of standard solutions containing known and predetermined concentrations of hexavalent chromium ions were prepared, after which the absorbance of every concentration was taken with an atomic absorption spectrophotometer (AAS) at a wavelength of 425.4 nm, and thereafter the absorbance

Figure 1. Tangerine peels used in this study

was plotted versus the standard concentrations on a graph, whereupon linear regression analysis was used to yield a mathematical equation representing the relationship between concentration and absorbance, as shown in Figure 2. Such an equation is subsequently employed in determining the concentration of samples whose chromium concentration is unknown, given their measured value of absorbance. The calibration curve not only provides a means of quantifying the concentration, but also a means of estimating the data quality and instrument sensitivity, as the correlation coefficient (R2) measures the accuracy of the linear relationship between absorbance and concentration. Besides, the calibration curve offers a method of detecting any discrepancy or deviation in the measurements to ensure the data acquired is credible in determining the efficiency of tangerine peels in chromium removal from contaminated aqueous solutions (Ali et al., 2020).

Stock solution of hexavalent chromium metal

For interference solution of other metals and compounds known and unknown that may be present in actual water, hexavalent chromium adsorption experiments were carried out using lab-prepared aqueous solutions of known concentration of chromium. Stock solution refers to a high and precise concentration of the heavy metal to be studied under adsorption experiments and is pre-prepared to act as the benchmark in preparing different concentrations of the solutions required during the experiment, through the process of adhering to dilution steps. The role of the stock solution for the current study is to provide an appropriate reference for determining the efficacy of tangerine peels in the adsorption of hexavalent chromium ions from water solutions because it ensures the accuracy and credibility of the experimental data. For the manufacture of the required stock solution, bright orange granular crystal, sodium dichromate dihydrate of chemical structure ($Na_2Cr_2O_7.2H_2O$) supplied by Yucheng CHEM-China with a purity of not less than 98.5% was used as a supplier of Cr^{+6} ions. 1000 ppm stock solution of hexavalent chromium ion was prepared by dissolving 11.75 g of sodium dichromate dihydrate in the necessary quantity of distilled water using a stirrer at 150 rpm and laboratory temperature for 30 minutes (Almhana et al., 2020, 2022). After ensuring that all the quantity was dissolved, the volume was completed to one liter in a volumetric flask using distilled water and stored in a dry and cool place to prevent contamination or evaporation at room temperature. To conduct adsorption experiments under different operating conditions, samples of the stock solution were used to prepare other solutions with diluted concentrations by serial dilution using distilled water. This process allows experiments to be conducted and the adsorption efficiency to be evaluated under precise conditions, making the obtained results highly reliable.

Batch adsorption unit

It is a device widely used in laboratory studies to evaluate the efficiency of adsorbents in removing heavy metals or other pollutants from

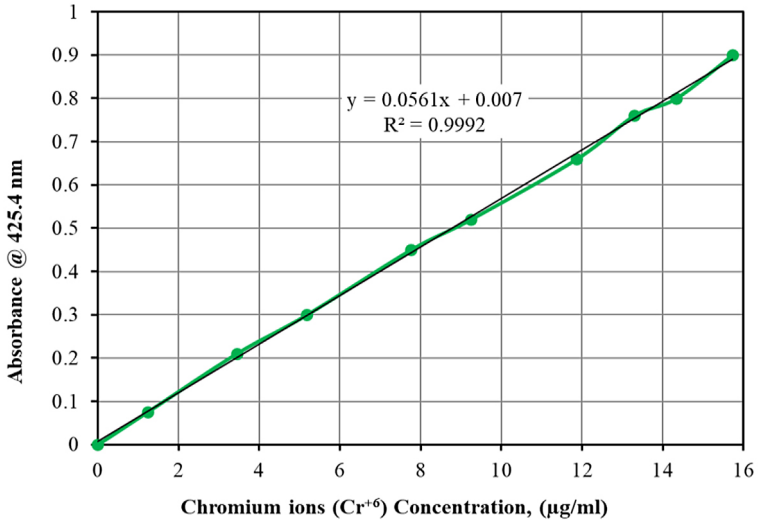

Figure 2. AAS Calibration curve of Cr^{+6} ions

aqueous solutions. In the present study, the adsorption unit basically consists of a water bath shaker containing laboratory vessels of suitable size in which the tangerine peels are mixed with the solution contaminated with hexavalent chromium ions under controlled conditions such as temperature, pH, agitation speed, and pollutant concentration. Adsorbent is added to the chromium-contaminated solution in specific doses to study the effect of adsorbent quantity on removal rate. Stirring is done using mechanical water bath stirrer to ensure homogeneous distribution of adsorbent and to enhance contact between adsorbent surface and target ions. Samples are collected at regular intervals for analysis of the remaining chromium concentration using atomic absorption spectrometry (AAS) based on a previously prepared calibration curve. The unit is based on the principles of surface adsorption where chromium ions move from the solution to the surface of the tangerine peels due to chemical or physical attraction forces (determined from the results of the experimental adsorption process). The batch adsorption unit is characterized by its ease of use, flexibility in adjusting operating conditions, and its effectiveness in studying the factors affecting the adsorption process. The results obtained from this unit are of great importance in designing larger units to treat polluted water effectively. The ranges of variables studied to determine the ability of tangerine peels to remove hexavalent chromium ions from contaminated aqueous solutions were 1–8, 100–500 rpm, 1–10 ppm, 10–180 min, 20–50 °C for pH, agitation speed, initial concentration of hexavalent chromium ions, adsorbent dosage, contact time, and temperature, respectively. The efficiency of tangerine peels to recover hexavalent chromium ions was evaluated using the Equation 1, while the adsorption capacity was determined using the relation (2).

$$q_e = (C_o - C_f)\frac{V}{m} \ldots \quad (1)$$

$$\%R = \frac{C_o - C_e}{C_o} \ldots \quad (2)$$

where: q_e – the amount of hexavalent chromium ion removal per unit of tangerine peels at equilibrium, (mg.g^{-1}), C_o and C_f – initial, and final concentrations of Cr^{+6} (mg.l^{-1}), V – volume of experimental solution, (l), m – mass of tangerine peels, (g), $\%R$ – removal percentage of hexavalent chromium ion from polluted solution.

RESULTS AND DISCUSSION

FTIR test

The Fourier transform infrared spectra before and after adsorption shows significant changes reflecting the nature of the chemical interactions that occurred between the tangerine peels and the hexavalent chromium ions. In the spectrum before adsorption, as in Figure 3, a peak at approximately 3400 cm^{-1} stands out, indicating the stretching vibrations of the hydroxyl group (O-H), indicating

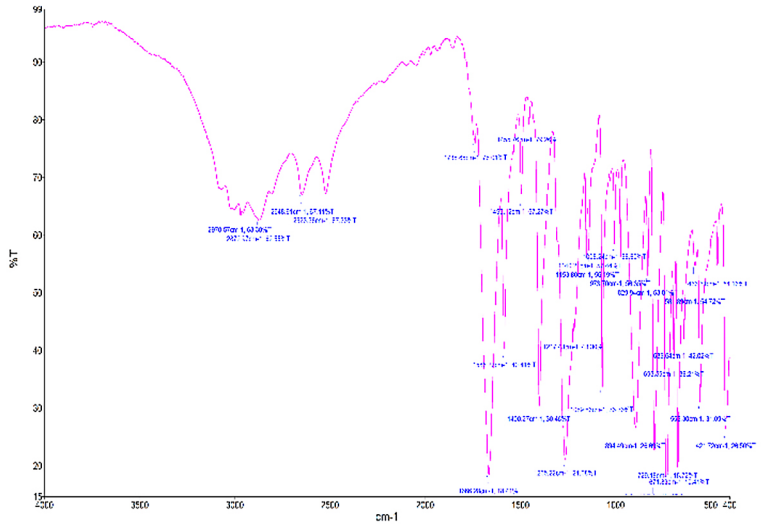

Figure 3. FTIR spectra of tangerine peels before adsorption of Cr^{+6}

the presence of strong hydrogen bonds and polar functional groups contributing to the interaction. Peaks at 2900–2970 cm^{-1} are associated with aliphatic C-H vibrations, indicating the presence of organic components such as cellulose and hemicellulose, while the peak at 1730 cm^{-1} indicates the presence of carbonyl (C=O) vibrations in carboxyl or ester groups. Peaks at 1600–1450 cm^{-1} are due to vibrations of double bonds (C=C) in aromatic compounds such as lignin, while peaks at 1050–1150 cm^{-1} indicate C-O vibrations in carbohydrates or ethers (Alwan et al., 2021). Figure 4 is the FTIR spectra during adsorption where the band at 3400 cm^{-1} shows reduced intensity or positional shift, attributed to the engagement of hydroxyl groups to bond with hexavalent chromium ions. The peaks in the range 2900–2970 cm^{-1} did not vanish and were not greatly changed in intensity, showing negligible interactions of C-H bonds. The 1730 cm^{-1} peak reduced in intensity or shifted towards lower wavelengths upon interaction of carbonyl with hexavalent chromium ions, whereas peaks at 1600–1450 cm^{-1} showed significant changes reflecting the participation of aromatic compounds in adsorption. Apart from this, changes also occurred at the maximum 1050–1150 cm^{-1}, where intensity decreased or was shifted due to association of C-O groups with hexavalent chromium ions. Finally, new peaks or shifts were observed in the fingerprint region (ranged between 500–900 cm^{-1}), indicating development of new complexes or bonds between the tangerine peel surface and the hexavalent chromium ions (Jadooa et al., 2025). These advancements highlight the aspect that the tangerine peels possess multi active functional groups such as hydroxyl and carbonyl, which functioned successfully in aiding the process of adsorption, hence proving their remarkable effectiveness in removing the hexavalent chromium metal from the polluted water solutions

Specific surface area

The Brunauer-Emmett-Teller (BET) technique was used to quantify the surface area of the peels of the tangerine, both after and before the adsorption of hexavalent chromium ions. The analysis suggested that the surface area of the tangerine peels before adsorption was 16.25 m^2/g, while the chromium-treated peels, after adsorption, recorded a significantly lower surface area of 1.14 m^2/g. The significant decrease in tangerine peels following treatment with hexavalent chromium-contaminated solutions is definite proof of the occupation of active sites and pores on the surface of the material by hexavalent chromium ions. This result indicates that the process of adsorption was carried out effectively, as most of the functional groups and pores in active sites dispersed on the surface were used, as per the high efficacy of the peels as an adsorbent. When this result is compared to the FTIR test, surface area reduction is attributed to the apparent changes on the peaks on the active functional groups (Alhamd et al., 2024). For example, the broad peak of hydroxyl (O-H) at 3400 cm^{-1} showed a clear loss of intensity after adsorption, indicating interaction with chromium ions through the production of hydrogen bonds or

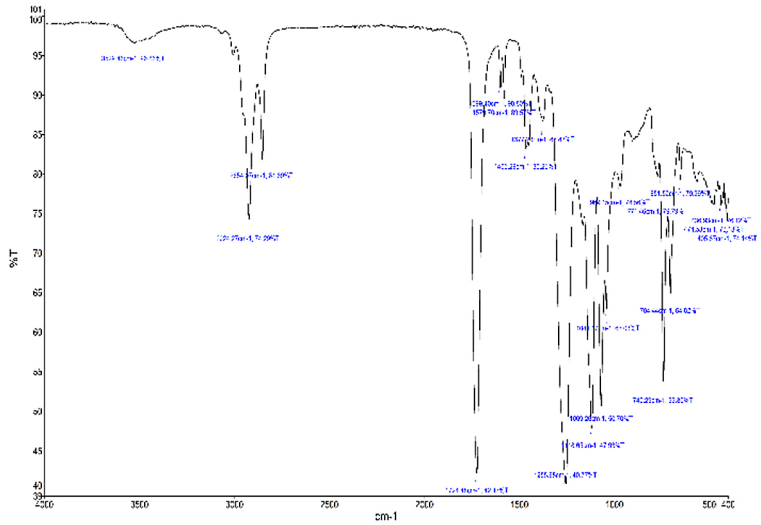

Figure 4. FTIR spectra of tangerine peels after adsorption of Cr^{+6}

surface complexes. Similarly, the carbonyl band (C=O) at 1730 cm^{-1} showed a minor shift in its position due to its involvement in the process of adsorption by electrostatic attraction or through the formation of covalent bonds. In addition, the changes in the fingerprint region (500–900 cm^{1}) indicate the formation of new bonds between the chromium ions and the peels' surface, such as M-O (metal-oxygen) bonds, confirming the interaction of the adsorbed element with the active sites in the material. From a scientific perspective, the decrease in surface area is due to the micropores becoming clogged and filled with hexavalent chromium ions, which reduces the number of pores available to absorb more ions. These results indicate that the adsorption was not limited to the outer surface but also extended to the inner pores, demonstrating the effectiveness of the tangerine peels in exploiting the available adsorption sites. Correlation between the surface results and FTIR analysis highlights the strong chemical interaction between the tangerine peels and chromium ions, making this material an excellent candidate for adsorption applications in water treatment. The results support the hypothesis that the adsorption occurs via a dual mechanism involving chemical interactions and physical interference, which enhances the efficiency of the material in removing Cr^{+6} ions from aqueous solutions.

Changing the acidity of the solution

The acid function experiments were carried out within a range of 1–8, keeping all other variables constant at 300 rpm, 5 ppm, 1 g, 180min, 50 °C for agitation speed, initial chromium concentration, tangerine peels dosage, contact time, and temperature, respectively. The results showed that the adsorption capacity of chromium is clearly affected by the acidity function (pH) of the solution, as it follows a non-linear pattern that reflects the effect of chemical and electrostatic interactions between the surface of the tangerine peels and hexavalent chromium ions, as shown in Figure 5. At pH 1, the percentage removal is low (8.58%) due to the strong competition between hydrogen ions (H^{+}) present in high concentration for the active sites of the adsorbent surface, which reduces the ability of the adsorbent to adsorb hexavalent chromium ions. With increasing the value of pH to 4, the percentage removal increases significantly to reach a peak of 42.81%, which can be explained by the reduction of hydrogen ion concentration and the increase of negative charge on the surface of the material, which enhances the electrostatic interactions between the surface of the material and positive chromium ions. At pH above 4, the percentage removal gradually decreases, reaching 30.31% at pH = 5 and 19.48% at pH = 6. This decrease may be due to the formation of insoluble compounds i.e. precipitation by chromium ions in the solution or to the reduction of effective interactions due to the change in the nature of the surface charges. At pH above 6, the removal rate decreases significantly to 5.34% at pH = 8, as the surface of the peels becomes less reactive due to the decrease in suitable active sites or due to the change in the nature of the metal ions in the solution. These results confirm that the acid function is

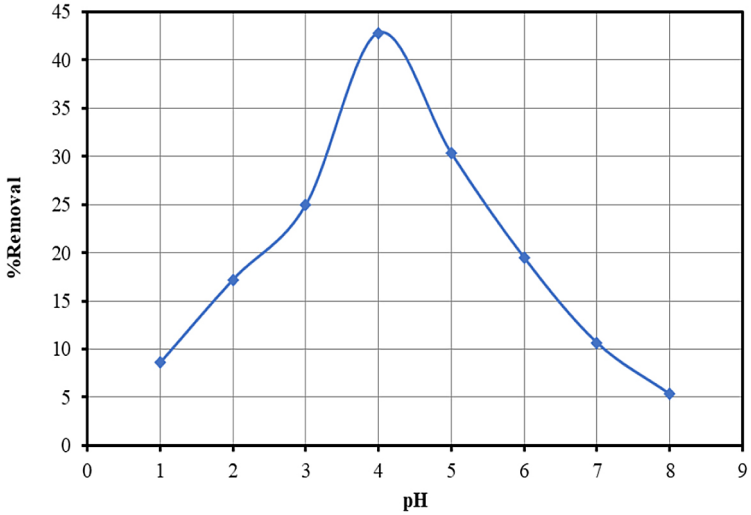

Figure 5. Effect of pH on the adsorption of Cr^{+6}using tangerine peels

an important factor that greatly affects the adsorption mechanism, with the optimum pH value being determined at 4 to achieve the maximum efficiency of heavy metal removal (Enkhtuya et al., 2024).

Changing the agitation speed of the solution

Tests for agitation speed were carried out at 100–400 rpm by keeping all other conditions constant at 4, 5 ppm, 1 g, 180 min, 50 °C for pH, initial chromium concentration, tangerine peels dosage, contact time, and temperature, respectively. The obtained results plotted in Figure 6 indicate that the increase in agitation speed has a positive effect on chromium percentage removal (%R) to a certain point because the percentage increased from 5% at 100 rpm to 51.71% at 350 rpm. This increase is since increasing the agitation speed acts to improve the good distribution of the tangerine peels in the solution, which increases the chances of the Cr^{+6} ions coming into collision with the active sites on the surface of the adsorbent. The higher agitation speed also reduces the thickness of the diffusion layer surrounding tangerine peels, enhancing the rate of mass transfer between the material surface and solution. At 400 rpm, the percent removal, however, is maintained at 51.71%, which is an equilibrium stage where all the active sites on the surface are fully saturated, and a further increase in agitation speed is no longer favorable to the adsorption. This stability might be because of centrifugal forces at high stirring speeds, capable of reducing the effective contact time between ions and adsorbent (Jadooa et al., 2025). In general, results show that the agitation speed plays a vital part in accelerating the adsorption process up to the surface saturation stability point. Therefore, 350 rpm is the optimum value for achieving the maximum efficiency of removing hexavalent chromium ions from contaminated aqueous solutions.

Changing the initial concentration

Initial concentration experiments were conducted within the range of 1–8.5 ppm, keeping all other variables constant at 4, 350 rpm, 1 g, 180 min, 50 °C for pH, agitation speed, tangerine peels dosage, contact time, and temperature, respectively. Figure 7 shows that the initial concentration of Cr^{+6} has a dual effect on both the removal ratio (%R) and the adsorbed concentration (C_{ads}) on the surface of the tangerine peels. Initially, at low concentrations (1–2 ppm), %R is high (77.20% at initial concentration of 1 ppm) due to the abundance of active sites on the surface of the adsorbent medium compared to the number of metal ions present in the solution. With increasing initial concentration of heavy metal ions, the percentage removal gradually decreases to 36.72% at initial concentration of 8.5 ppm. This decrease is explained by the saturation of the active sites on the surface, where the excess number of ions in the solution becomes un-adsorbable due to the limited adsorption capacity of the material, resulting in a decrease in the relative removal efficiency. In contrast, the C_{ads} shows an increasing trend with increasing initial concentration, starting from 0.772 mg/g at 1 ppm and reaching to

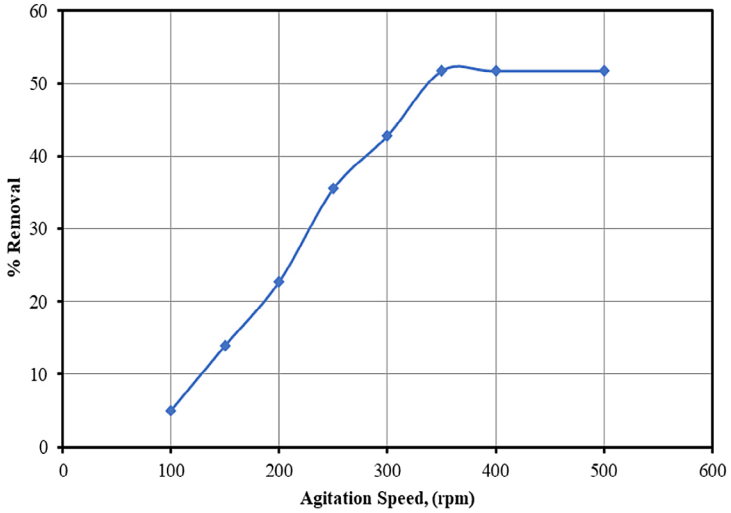

Figure 6. Effect of agitation speed on the adsorption of Cr^{+6}using tangerine peels

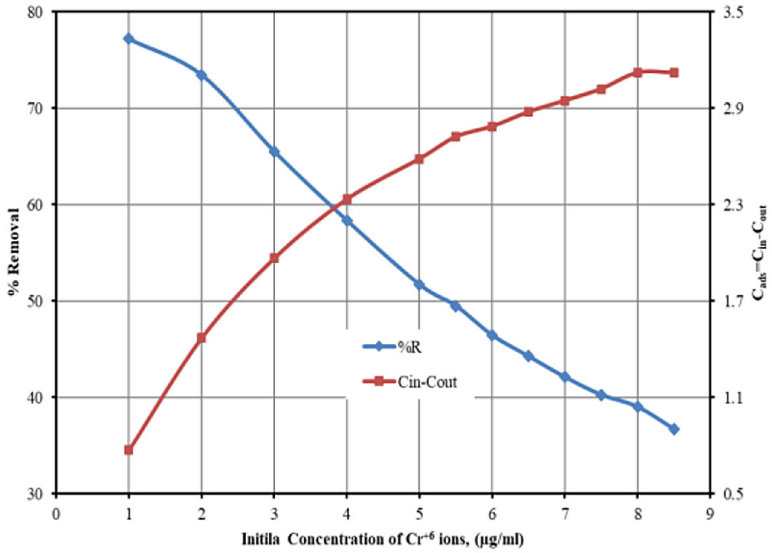

Figure 7. Effect of initial concentration on the adsorption of Cr^{+6}using tangerine peels

3.12 mg/g at 8.5 ppm. This increase is due to the increased availability of metal ions in the solution, which allows an increase in the amount of Cr adsorbed even with a decrease in the removal rate. This behavior reflects the nature of adsorption that follows a saturation curve, where the active sites are initially completely unsaturated, and as the concentration increases the amount of Cr increases until the maximum adsorption capacity is reached. The variation between %R and C_{ads} indicates that tangerine peels are acceptable and particularly effective at low concentrations, where the percentage removal is high, but they are still able to still higher concentrations by absorbing larger numbers of Cr^{+6} ions despite the low percentage removal (Liang et al., 2020). These results indicate that tangerine peels have reasonable adsorption capacity (as confirmed by results of FTIR and surface area tests) and show a balanced performance between percentage removal and adsorption capacity. Hence, the maximum concentration used in further experiments to determine the actual suitability of tangerine peels for treating Cr^{+6} contaminated solutions is 8 ppm.

Changing the dose of tangerine peels

The adsorption dose experiments were carried out within the range of 0.1–5.5 g, keeping all other variables constant at 4, 350 rpm, 8ppm, 180 min, 50 °C for pH, agitation speed, initial concentration of chromium, contact time, and temperature, respectively. Figure 8 shows the results obtained from the effect of increasing the dose of the adsorbent on the percentage removal of hexavalent chromium ions (%R) and the specific adsorption capacity (q) and reflects the relationship between the added mass of tangerine peels and the adsorption behavior. When the adsorbent dosage of tangerine peels was increased from 0.1 g to 5.5 g, the percentage removal (%R) increased from 8.59% to 72.38%, indicating that increasing the mass of tangerine peels provides more active sites that can interact with the hexavalent chromium ions in the solution. However, the data show that the removal ratio starts to level off after the dosage of 4.5 g, where it remains at 72.38%, indicating that most of the ions are saturated with the available active sites and there are not enough ions in the solution to benefit from the additional dosage increase. As for the specific adsorption capacity (q), it gradually decreases with increasing the dosage of tangerine peels from 0.69 mg/g at 0.1 g to 0.1 mg/g at 5.5 g. This behavior is explained by the fact that as the dosage f tangerine peels increases, the amount of adsorbed chromium is distributed over a larger mass of the adsorbent, which reduces the number of ions adsorbed per unit mass of tangerine peels. In addition, increasing the dose leads to interference between the adsorbent particles and increases the probability of covering some active sites, which reduces their individual efficiency. According to the results obtained, at the values of operating factors, the optimal dose of tangerine peels should not exceed 5 g to achieve effective results. (Rane et al., 2019).

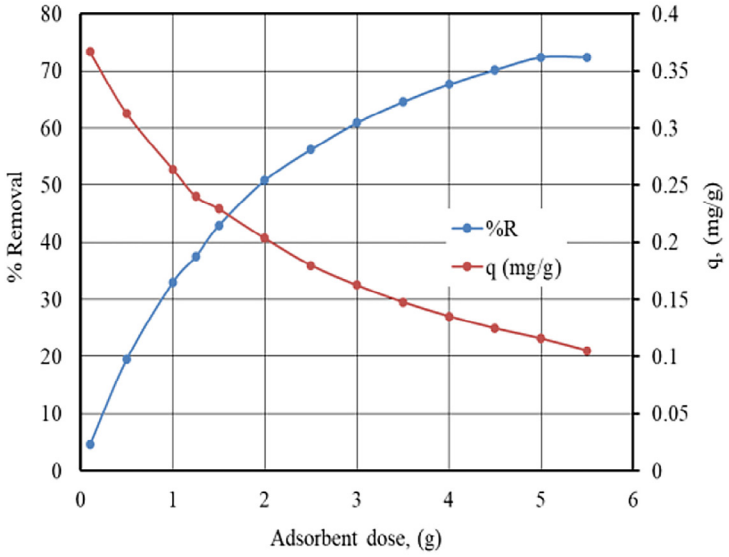

Figure 8. Effect of adsorbent dosage on the adsorption of Cr^{+6}using tangerine peels

Changing the contact time

Contact experiments were conducted over a period of 10–180 min, keeping all other variables constant at 4, 350 rpm, 8 ppm, 5 g, and 50 °C for pH, agitation speed, initial chromium concentration, tangerine peels dosage, and temperature, respectively. Figure 9 shows the relationship obtained from changing the contact time with the chromium removal efficiency. The results obtained clearly show the effect of time on the adsorption process, which is affected by several factors including the nature of the tangerine peels and the properties of chromium. Initially, at 10 min, the adsorption efficiency was very low, not excessed 9%, which can be attributed to the fact that the adsorbent has not yet fully reacted with the chromium ions, and therefore the available sites on the surface of the adsorbent are very few at the beginning of the reaction. As the reaction time increases, a gradual increase in the adsorption rate is observed. At 20 min, the percentage removal becomes 17.33%, and at 30 min, it was 25.43%, indicating that the adsorption began to take a more efficient direction, as the adsorption sites on the tangerine peels began to attract chromium ions faster. Between 45 and 90 min, the percentage removal increased more significantly from 36% to 60%. This rapid increase in adsorption can be explained by the increased exposure of the adsorbent to more hexavalent chromium ions, and the treatment process became more effective with the increasing number of adsorbed ions. Hexavalent chromium ions began to migrate to the smaller pores and more reactive areas on the surface of the tangerine peels, which accelerated the adsorption process. As time went on, the ability of the adsorbent to adsorb more heavy metal ions decreased, which reflected the increasing saturation on the surface of the tangerine peels. After 105 min, the removal efficiency reached 67.6%, and at 120 min the efficiency reached its maximum value of 72.4%, and remained stable at 150 min. This indicates that the tangerine peels have exactly reached the adsorption equilibrium, where the most reactive sites on the surface of the adsorption medium are almost filled with hexavalent chromium ions, and no more ions can effectively bind to the surface after this point. This slowdown in the increase after this period indicates that the interaction between chromium ions and tangerine peels faces limitations, which are often due to surface saturation or lack of available active sites for adsorption (Alwan et al., 2021). These results can be generally explained according to different adsorption models, such as the dynamic adsorption model, which shows that the adsorbent starts to react rapidly with the heavy element at first, and then the reaction becomes slower with time as the available areas for interaction shrink. According to the above data, 5 g is the optimum dose of tangerine peels required to achieve the highest adsorption of hexavalent chromium ions.

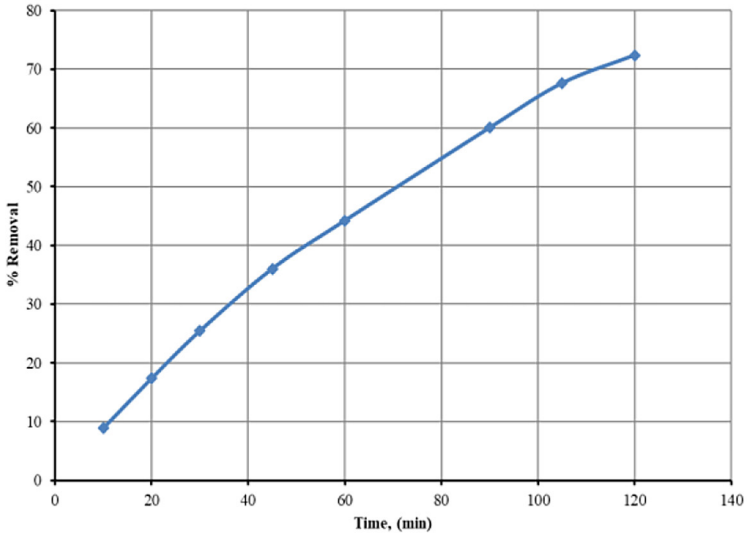

Figure 9. Effect of contact time on the adsorption of Cr^{+6}using tangerine peels

Changing the temperature of adsorption unit

Temperature experiments were conducted over a range of 20–50 °C with all other variables held constant: 4, 350 rpm, 8 ppm, 5 g, 120 min for pH, agitation speed, initial concentration of chromium, tangerine peels dosage, and temperature, respectively. As shown in Figure 10, the obtained results show the effect of temperature on the adsorption capacity of chromium ions using tangerine peels, where a significant increase in the adsorption rate can be observed with increasing temperature. At 20 °C, the percentage removal was 8%, indicating the limited ability of the adsorbent to recover hexavalent chromium ions at low temperatures. With increasing the temperature to 25 °C, a slight improvement in the percentage removal was observed to reach 11.6%, indicating the beginning of activation of the chemical and physical processes that support the adsorption of chromium metal ions. With increasing the temperature to 30 and 35 °C, the percentage removal began to increase significantly to reach 22.59% and 38.73%, respectively, reflecting the positive effect of high temperature on the interaction of hexavalent chromium ions with tangerine peels. This result may be attributed to the increase in the kinetic energy of adsorbed ions at higher temperatures, which allows for increased collisions between target ions and adsorption sites on the surface of tangerine peels, thus facilitating their adsorption (Abdić et al., 2018). Also, temperature

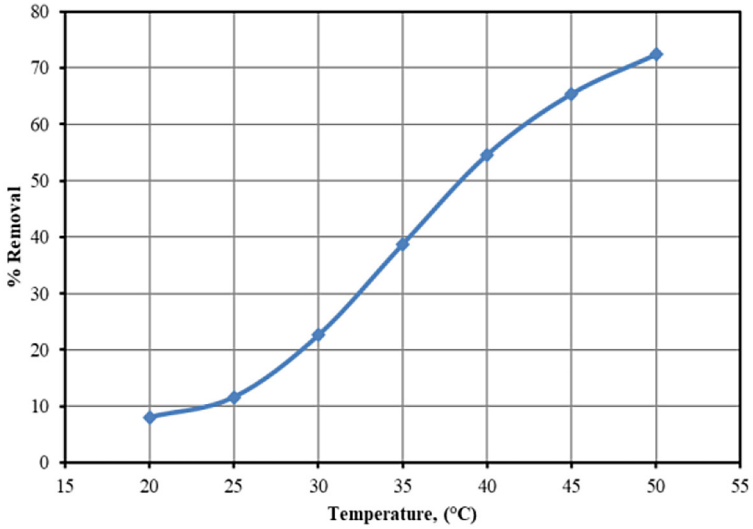

Figure 10. Effect of temperature on the adsorption of Cr^{+6}using tangerine peels

may contribute to the increase in pores on the surface of the peels or induce chemical reactions that may increase the ability of the adsorption medium to recover hexavalent chromium ions. When it was 40 °C and 45 °C, the percentage removed was 54.6% and 65.4%, respectively, and it was indicated that the process of reaction between chromium ions and tangerine peels under these temperatures is stronger. Such a significant increase in adsorption can be linked to the activation of the thermodynamic process, such as movement of molecules from the surface and to the surroundings, making the material more capable of adsorption under the circumstances of heat. There is also a possibility that the chemical reaction activity between chromium ions and tangerine peels is higher at high temperatures, making the adsorption capacity greater. Finally, at 50 °C, the adsorption efficiency had the maximum value of 72.39%, which indicates that the treatment process favors high temperature. This is likely due to the remarkable improvement of the structural composition and physical properties of tangerine peels at elevated temperature, facilitating easier adsorption of hexavalent chromium ions. This report is consistent with the assumption that high temperatures can cause changes in the structure of the adsorbent, such as pore opening and increasing the surface area available for adsorption, which all contribute to overall increased adsorption capacity (Khudair et al., 2024). Overall, the results confirm that temperature has a substantial effect on adsorption capacity as the performance of the tangerine peels in adsorption improves with an increase in temperature up to the maximum value of 50 °C, indicating that temperature is a significant factor for improving the ability of tangerine peels to adsorb hexavalent chromium ions (Shaikhiev et al., 2023).

Adsorption isotherm Shaikhiev

Isothermal research is regarded as one of the key principles of studying and learning the adsorption processes, as they aim to investigate the effect of the concentration of the adsorbate on the adsorbent surface at constant temperature. Such research is necessary in most environmental and industrial operations, such as purification of dirty water and air, as they aid in offering a complete view of how the molecules of adsorbents interact with adsorbents. There are some isothermal models that have been used to describe the behavior of the adsorption process, the most important one of which is the Langmuir model based on the assumption of having a homogeneous distribution of sites over the adsorbent surface where every site can adsorb a single molecule of the adsorbent. The Freundlich model is also considered to be one of the important models that are applied when there is a non-homogeneous configuration of sites in the adsorbent surface, considering the presence of the fact that the adsorbent molecules and adsorbent have strong as well as weak interactions. In addition, the Timken model is among the models that address the mechanical interactions between adsorbent molecules on the adsorbent surfaces because it is presumed that as adsorption increases, these interactions decrease. The models are based on basic assumptions such as homogeneous or heterogeneous distribution of adsorbent sites, adsorbent-adsorbate interaction, and effective molecule transport through the pores in the adsorbents (Shadhan et al., 2024). Table 1 presents the mathematical computation of the isothermal model equations used to examine the adsorption of hexavalent chromium ions by tangerine peels as an inexpensive adsorbent medium.

Figures 11–13 show the results of the isothermal analysis of the adsorption of Cr^{+6} ions using tangerine peels, while Table 2 shows the values of the isothermal model parameters used in the present study. These results exhibited significant data when analyzed using the Langmuir, Freundlich, and Temkin models, where the Langmuir model reflects that the adsorption occurs on a homogeneous surface with a maximum adsorption capacity of q_{max} = 2.611 mg/g, indicating a moderate ability of the adsorbent to adsorption. The equilibrium constant K_L = 0.02109 shows that the interaction between tangerine peels and Cr^{+6} ions is relatively weak, while the separation coefficient R_L = 0.8556 indicates that the adsorption process is moderately favorable. The correlation coefficient R^2 = 0.9992 confirms that this model is the most suitable for representing the data. In contrast, the Freundlich model assumes a heterogeneous surface and shows a relatively low adsorption capacity with a constant K_F = 0.056, while the intensity factor n = 1.0873 indicates that the adsorption is moderate and not intense. However, the coefficient of determination R^2 = 0.9988 shows a strong fit with the data, but less favorable than the previous model. The Empower model, which considers thermal effects, showed an equilibrium constant K_T = 0.9963 indicating

Table 1. Equations of isothermal models used in this study

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

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

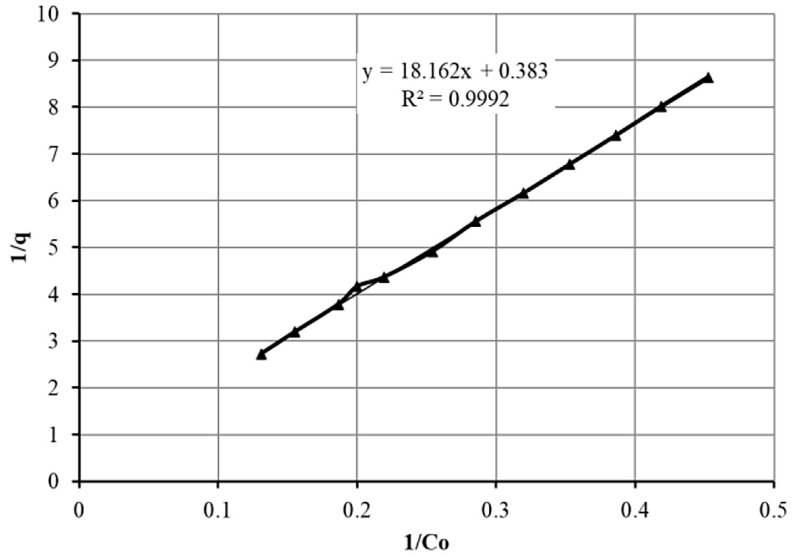

Figure 11. Langmuir Isotherm model of Cr^{+6} adsorption using tangerine peels

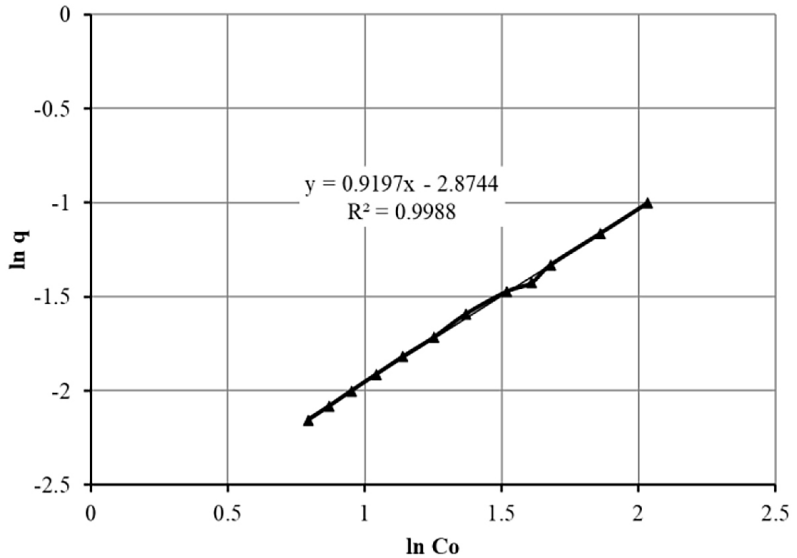

Figure 12. Freundlich isotherm model of Cr^{+6} adsorption using tangerine peels

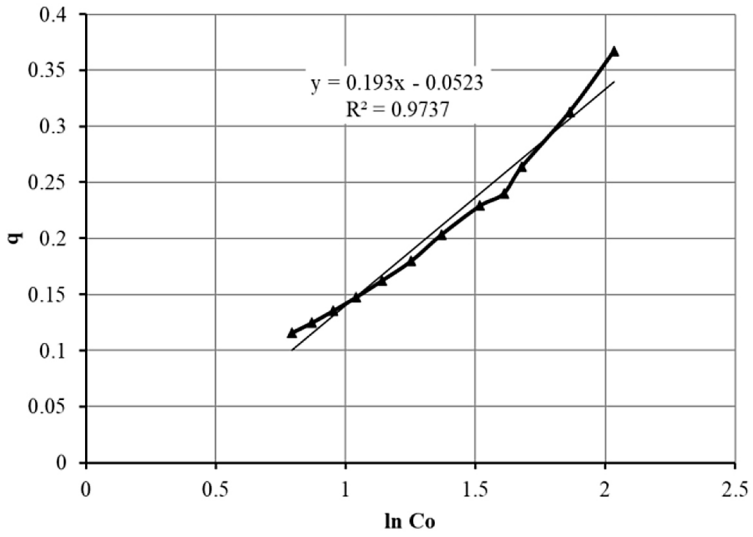

Figure 13. Temkin Isotherm model of Cr^{+6} adsorption using tangerine peels

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
2.611	0.02109	0.8556	0.9992	0.056	1.0873	0.9988	0.9963	13.9212	0.9737

a significant equilibrium in the process, and an energy constant b = 13.9212 reflecting relatively large thermal effects. However, the correlation coefficient R^2 = 0.9737 was the lowest compared to the other models, indicating that thermal effects are not the dominant factor in the adsorption process. In comparison, the Langmuir model was the most accurate in representing the data, indicating that the adsorbing surface is mainly homogeneous, followed by the Freundlich model, which reflects the properties of the heterogeneous surface. From these results, it can be concluded that the adsorbent has moderate capacity to adsorb heavy elements, and that the adsorption dynamics are mainly affected by the surface nature rather than thermal effects (Ugbe et al., 2014).

Adsorption kinetics

Kinetic study in adsorption processes is an important aspect used for under-standing the mechanisms of interaction of pollutants with sorbents and is necessary to determine the speed and efficiency of the processes, as well as the mechanisms that govern the adsorption of pollutants on the absorbent surface. This study contributes to improving the methods of effective removal of pollutants from water or air. There are many kinetic models used to describe the adsorption process. The most prominent of these models is the pseudo-first order model, which assumes that the adsorption process follows a dynamic based on rapid changes in concentration at the beginning and gradually reaches equilibrium, and its assumptions are since the interaction occurs only between the pollutant and the active surface of the absorbent material. As for the pseudo-second order model, it assumes that the adsorption process is linked to chemical interactions between the pollutant and the absorbent material, where it is assumed that the adsorption process depends on the ratio between the absorbed amount and the number of available active sites. While the Elovich model assumes that the adsorption process is affected by many factors and reflects the assumption that the interaction between the pollutant and the sorbent changes with time, where the adsorption process starts rapidly and then becomes slow with time due to the formation of an occupation layer near the active surface of the sorbent. On the other hand, the intra-particle diffusion model focuses on the assumption that the speed of the adsorption process is mainly affected by the internal diffusion of the pollutant within the structure of the sorbent, so that the slow movement of the pollutant within the

particles becomes the limiting factor in reaching equilibrium, and it is assumed that the adsorption of the pollutant occurs through its transfer from the surface to the interior of the sorbent (Shadhan et al., 2024). Table 3 shows the equations of the kinetic models used to describe the adsorption of hexavalent chromium ions using tangerine peels as a low-cost adsorption medium.

Figures 14–17 show the results of the kinetic analysis of the adsorption of Cr^{+6}ions using tangerine peels, while Table 4 shows the values of the kinetic models used in the present study. The obtained results indicate that the adsorption of Cr^{+6}ions by tangerine peels is attributed to multiple and complex dynamic mechanisms, as the values extracted from the four models reflect accurate information about the interactions and adsorption behavior. In the pseudo-first-order model, the adsorption rate constant $k_1 = 1.8437$ indicates the initial adsorption velocity, while the value $q_e = 0.975$ indicates the theoretical amount adsorbed at equilibrium, and the correlation coefficient $R^2 = 0.9422$ reflects moderate agreement with the data, indicating that the adsorption may not depend entirely on the concentration of target element ions. On the other hand, the pseudo-second-order model showed higher accuracy with a correlation coefficient $R^2 = 0.9915$, indicating that the adsorption is governed by a chemical reaction between the tangerine peels and the hexavalent chromium ions, where $k_2 = 0.0142$ reflects the relatively slow reaction rate and $q_e = 0.3268$ reflects the adsorption capacity at equilibrium, which seems lower than expected, indicating the limitations of this model in representing the data (Abdulrazak, 2016). The Elovich model, which is used to analyze

Table 3. Equations of kinetic models used in this study

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

Note: q_e – adsorption capacity of hexavalent chromium ions at equilibrium state (mg.g^{-1}), q_t – adsorption capacity of hexavalent chromium ions 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}), α – initial adsorption rate in Elovich model (mg g^{-1} min^{-1}), β – desorption constant in Elovich model (g mg^{-1}), k_p – rate constant in intra-particle diffusion model (mg g min$^{-0.5}$), and C – thickness of boundary layer (mg.g^{-1}).

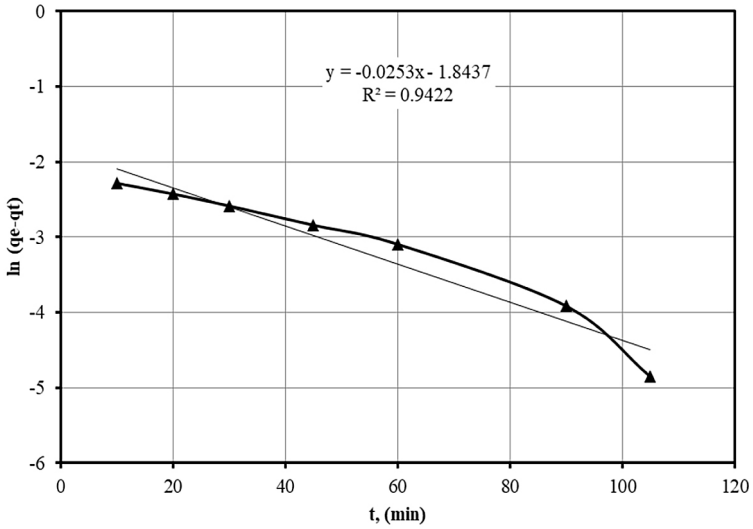

Figure 14. Pseudo first order model of Cr^{+6} adsorption using tangerine peels

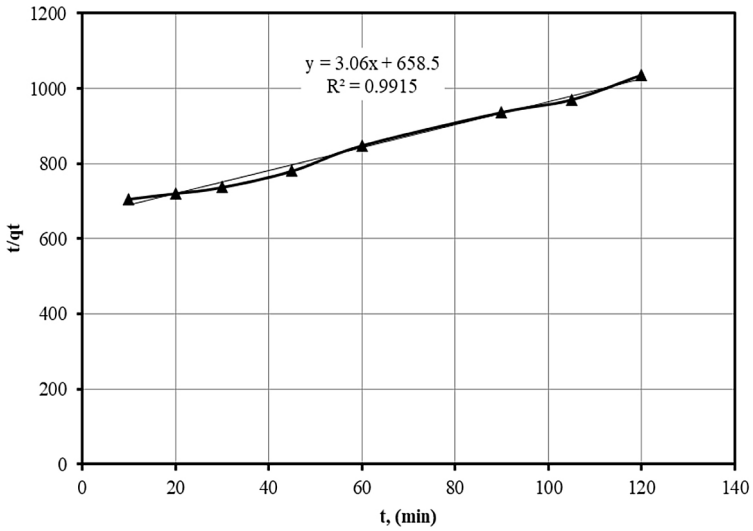

Figure 15. Pseudo first second model of Cr^{+6} adsorption using tangerine peels

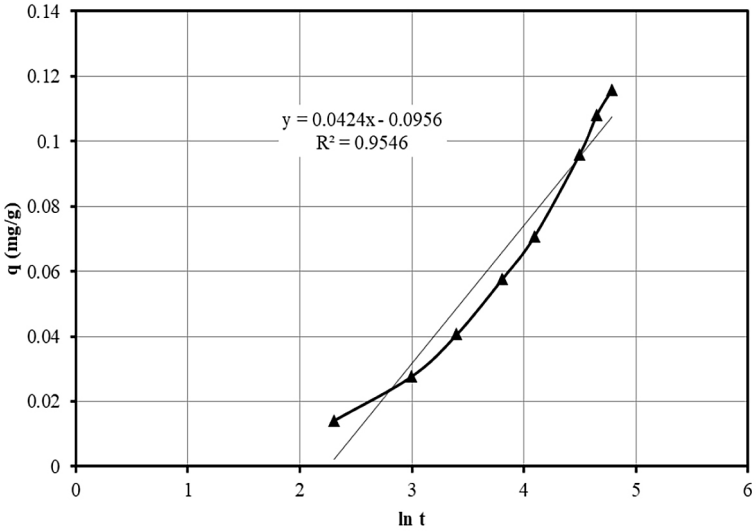

Figure 16. Elovich model of Cr^{+6} adsorption using tangerine peels

heterogeneous surfaces, showed that the initial adsorption rate was low $\alpha = 0.042$, and that adsorption required more energy $\beta = 23.585$ due to the structural challenges of the tangerine peels, with an acceptable fit to the data ($R^2 = 0.9546$). In contrast, the intraparticle diffusion model was the most accurate, with the correlation coefficient $R^2 = 0.9979$ reflecting an excellent fit, and the intrapore diffusion rate $k_p = 0.0134$ indicates an adsorption process governed by movement inside the pores of the material, while the negative value of $C = -0.0312$ expresses the effect of the fast initial diffusion that slows down with time due to the filling of the active sites. When comparing the models, it becomes clear that the intraparticle diffusion model describes the process more accurately, indicating that adsorption depends mainly on intrapore diffusion, while the pseudo-second-order model reflects the role of chemical interaction in enhancing the adsorption efficiency. The Elovich model supports the hypothesis that the surface is heterogeneous and contains sites with different energies. These results indicate that adsorption is a complex process governed by interconnected mechanisms including diffusion, chemical interactions, and the structural nature of the adsorbent (Lahieb et al.,2020).

Adsorption thermodynamic

Thermodynamic study in adsorption processes is a vital concept for understanding the interactions between the adsorbent and the pollutants in

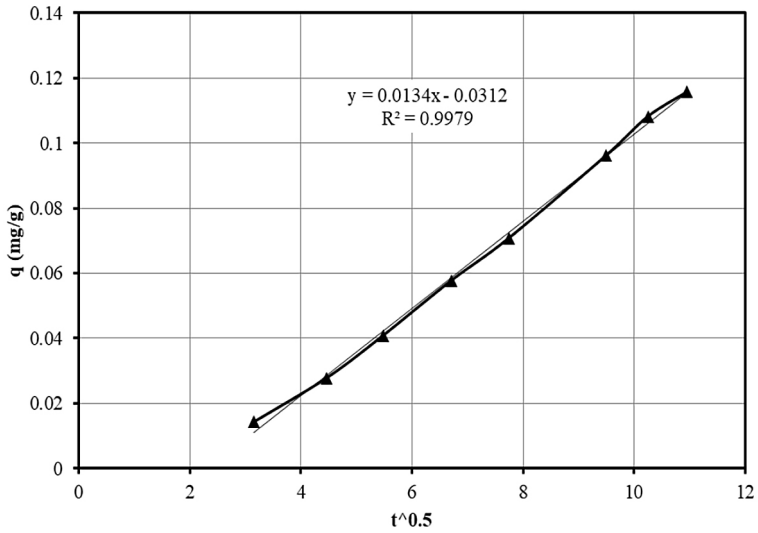

Figure 17. Intra-particle diffusion model of Cr^{+6} adsorption using tangerine peels

Table 4. Constants of kinetics models

Pseudo first order			Pseudo second order			Elovich model			Intra-particle diffusion		
k_1	q_e	R^2	k_2	q_e	R^2	α	β	R^2	k_P	C	R^2
1.8437	0.975	0.942	0.0142	0.3268	0.9915	0.042	23.585	0.9546	0.013	- 0.0312	0.9979

the system, as it helps in evaluating the energy required for the adsorption reaction and determining whether the process is feasible or sustainable in practice. This study is used to determine the direction of the process, whether it is a spontaneous process or not, and it also provides information about the extent to which environmental factors such as temperature affect the adsorption efficiency. By analyzing thermodynamic variables such as the change in entropy and free energy, it can be determined whether the process requires additional energy or if it is self-sustaining (Fajarwati et al., 2023). For example, if the adsorption process is preferred at high or low temperatures, this helps in determining the optimal conditions for the process. Thermodynamic study also contributes to understanding the nature of the interaction between the pollutant and the adsorbent, whether it is a physical or chemical interaction, which contributes to improving the design of adsorbents and choosing the most suitable ones for various environmental applications. In general, the thermodynamic behavior of the adsorption process is determined by calculating the thermodynamic functions through the Equations 3 and 4 (Ben Khalifa et al., 2019).

$$\Delta G = \Delta H - T\Delta S \ \ldots \quad (3)$$

$$ln\ ln\ k_{ad} = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R} \ \ldots \quad (4)$$

where: k_{ad} – adsorption equilibrium coefficient (–); 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).

Figure 18 represents the results of the comprehensive thermodynamic analysis of the adsorption process of hexavalent chromium ions from contaminated aqueous solutions using tangerine peels as a low-cost adsorbent, while Table 5 includes the values of the thermodynamic functions of the adsorption process. The distribution constant K_d reflects the preference of hexavalent chromium ions to move from the solution to the surface of tangerine peels, and the results showed a significant increase in the K_d values with increasing temperature, as it increased from 5 at 20 °C to 151.31 at 50 °C. This increase indicates that the adsorption is a thermally activated process, and that the efficiency of the adsorbent increases significantly at higher temperatures. The value of the enthalpy change ΔH is 95.5 KJ/mol, which is positive, meaning that the process is endothermic. This

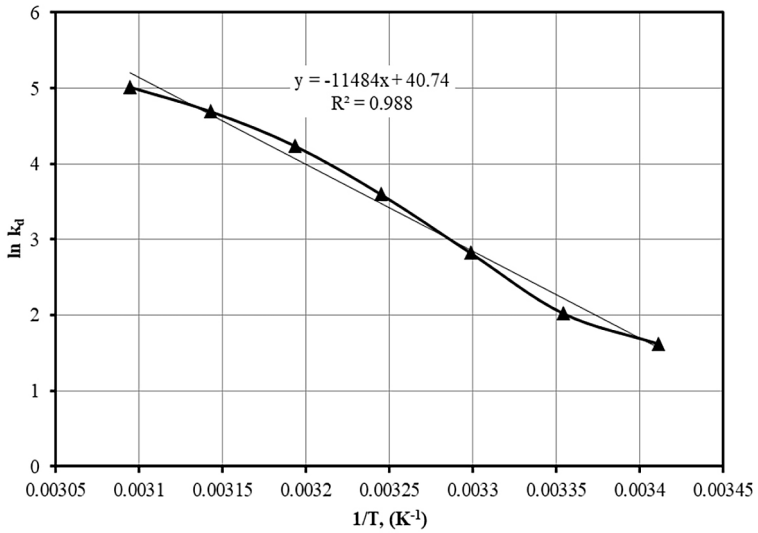

Figure 18. The relation between adsorption constant and temperature for Cr^{+6} adsorption using tangerine peels

Table 5. Thermodynamic functions of Cr^{+6} adsorption using tangerine peels

T(°C)	K_d	ΔH (KJ/mol)	ΔS (J/mol.K)	ΔG (KJ/mol)
20	5.0689	95.483	338.7312	-3.8158
25	7.591			-5.5094
30	16.849			-7.2031
35	36.497			-8.8967
40	69.501			-10.59
45	109.26			-12.284
50	151.31			-13.978

indicates that increasing the temperature provides the energy needed to overcome the energy barriers associated with the binding of ions to the surface of the adsorbent. This result is consistent with the common thermal behavior in chemical processes where higher temperatures facilitate the dissociation of the bonds between the heavy metal and the surrounding water molecules, thus enhancing its attachment to the surface of the adsorbent. The value of the entropy change ΔS is 338.7312 J/mol. K, which is strongly positive. This indicates a significant increase in the randomness or molecular freedom at the interface between the chromium ions and the tangerine peels during the adsorption process. This increase may be due to the replacement of water molecules attached to the adsorbent surface by chromium ions, as confirmed by the results obtained from the FTIR analysis, which leads to the liberation of these ions and their increased freedom in the solution. The free energy change values ΔG were all negative, confirming that the adsorption process is dynamically spontaneous at all studied temperatures. It is worth noting that the ΔG values became more negative with increasing temperature, changing from -3.8158 KJ/mol at 20 °C to -13.978 KJ/mol at 50 °C. This decrease indicates an increase in spontaneity and efficiency with increasing temperature, which is consistent with the high K_d values and confirms that the association between hexavalent chromium ions and the tangerine peels becomes more stable with increasing thermal energy. Overall, these results demonstrate that tangerine peels are highly efficient for the removal of hexavalent chromium ions, especially at high temperatures, where thermodynamic interactions support spontaneous and endothermic adsorption with increasing temperature (Tran et al., 2016).

CONCLUSIONS

The experimental results obtained from the present study showed a significant ability of tangerine peels as a low-cost adsorbent to recover

hexavalent chromium ions from contaminated aqueous solutions as one of the toxic and carcinogenic heavy metals. The available data showed that the adsorption efficiency of hexavalent chromium is directly proportional to the agitation speed, the dose of tangerine peels, the contact time and the temperature, where the percentage removal begins to gradually increase with the increase in the value of the operating factor, to a certain limit until reaching a constant value that does not change after that. As for the pH, the removal capacity starts to increase with increasing pH until it reaches the maximum value and then starts to decrease sharply at the last value of the operating range. While the efficiency was inversely proportional to the initial chromium concentration. The maximum removal efficiency was 72.4% and was achieved at pH = 4, agitation speed = 350rpm, initial chromium concentration = 8 ppm, contact time 120 min, tangerine peels dosage = 5 g, temperature = 50 °C, while the maximum adsorption capacity was 0.116 mg of hexavalent chromium per gram of tangerine peels. Morphological analyses showed that the tangerine peels possessed different functional groups that were responsible for the efficient adsorption performance, while the surface area decreased from 16.25 m^2/g before adsorption to 1.14 m^2/g after, indicating the effectiveness of this material as an adsorption medium, when the appropriate operating conditions are available. The adsorption behavior studies confirmed that the Langmuir model is the best in describing the isothermal adsorption process of chromium, while the intra-particle diffusion model was the closest to describing the data kinetically. Thermodynamically, the adsorption was spontaneous, exothermic and increasingly randomness, according to the enthalpy and entropy values which were 95.5 kJ/mol and 338.7 J/mol. K, respectively. These results indicate that the tangerine peels are a material of remarkable potential in treating polluted water, which makes it increasingly important to exploit and transform them from a worthless agricultural waste into a promising material in treating polluted aquatic media with tangible efficiency.

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