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Chemically Treated Pistachio Green Hull as an Effective and Economical Adsorbent for Cadmium Removal: Optimization and Mechanistic Insights

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Abstract
Nowadays, heavy metal contamination in water sources is a critical environmental concern directly related to human health, necessitating the development of sustainable and cost-effective remediation techniques. Traditional adsorbents are often expensive and less environmentally friendly, highlighting the need for alternative materials with high adsorption efficiency. This study proposes using pistachio green hull, an agricultural byproduct, in both untreated and chemically treated forms as an adsorbent for removing cadmium (Cd^{2+}) from aqueous solutions. Batch adsorption experiments were conducted using untreated, HNO_3-treated, NH_3/H_2O_2-treated, and acetone/H_2O_2-treated pistachio green hulls at an initial Cd^{2+} ions concentration of 20 mg/L. The adsorption kinetics, equilibrium isotherms, and pH dependence were analyzed to determine the adsorption efficiency and mechanism. The removal efficiencies for untreated, HNO_3-treated, NH_3/H_2O_2-treated, and acetone/H_2O_2-treated samples in laboratory scale were 68%, 55%, 88%, and 95%, respectively. Maximum adsorption occurred within a broad pH range of 4-9. The kinetic analysis revealed that Cd^{2+} adsorption follows a pseudo-second-order model, with rapid adsorption (<4 min). The adsorption isotherm followed the Langmuir model, suggesting monolayer adsorption, and electrostatic interactions were identified as a key mechanism. The findings demonstrate that pistachio green hulls, particularly after chemical modifications, serve as an effective and eco-friendly adsorbent for Cd^{2+} removal. This study contributes to advancing sustainable and low-cost solutions for heavy metal remediation.
Keywords: Adsorption, Cadmium, Chemical treatment, Isotherm, Pistachio green hull.

1. Introduction
The availability of drinkable water is one of the most significant worldwide challenges of the 21^{st} century. The rapid growth of contamination sources, especially industries, over time results in the release of alarming quantities of contaminants into large bodies of water, which affect the quality of drinking water. Heavy metals, pesticides, and microbial toxins are prevalent contaminants that are often found in drinking water systems (Saravanan et al., 2023). Nowadays, heavy metal contamination in aqueous environments is an extremely serious environmental issue owing to the severe damage it causes to ecosystems and human health (Gogoi et al., 2024; Santhosh et al., 2024). In this regard, the cost-effective and environmentally sustainable technologies for wastewater treatment are thus an absolute necessity currently.

A range of traditional techniques, such as ion exchange, precipitation, and coagulation-flocculation, have been utilized to eliminate heavy metals from aqueous solutions (Dorri et al., 2022; Sadeghi et al., 2014; Zeraatkar Moghaddam et al., 2019). These methods often suffer from drawbacks such as high cost, limited efficiency, and the generation of secondary pollutants. Amongst them, the adsorption treatment attracted significant attention due to its simplicity, low cost, low energy consumption, and high efficacy in removing heavy metals (Fiyadh et al., 2023; Karimi et al., 2022; Xue et al., 2023). In recent years, there has been growing interest in utilizing bio-adsorbents derived from waste biomass sources, which provide the dual environmental benefits of waste management and water treatment without toxicity or carbon footprints (Solangi et al., 2021). Their abundance, low cost, and eco-friendliness are additional attributes, that make them promising adsorbents (Joshi et al., 2023; Ramesh et al., 2023).

These byproducts present sustainable alternatives to traditional adsorbents. Several agricultural byproducts, husks, shells, and peels of different fruits, such as lemon, pomegranate, apple, papaya, grapefruit, pumpkin, peach, avocado, and others, have actively been studied for adsorptive wastewater treatment applications (Alsulaili et al., 2024; Nguyen et al., 2013). Surface activation was used as a modification technique to enhance the adsorption performance of biosorbents and improve their surface characteristics. Activation can additionally improve the contact area of the biosorbents with the sorbate species by removing impurities (Karić et al., 2022).

Pistachio is one of the most popular snacks and ingredients in various culinary dishes in the world, and it is mainly produced in the USA, Iran, and Turkey, with annual production surpassing one million tons. A considerable quantity of pistachio shells is generated as a by-product of the pistachio industry, given that the shell-to-pistachio ratio is approximately 45% (Deniz and Kepekci, 2016). Aside from the unsuitable application of complex and green pistachio hulls (shown in Fig. 1) for heating, their potential use as an adsorbent could benefit the management of these waste materials. For example, natural (Armagan and Toprak, 2015), modified hard shells (Foo and Hameed, 2011), and produced activated carbon from pistachio nut shells (Khan et al., 2015) were efficiently used for the adsorptive removal of dyes (Deniz and Kepekci, 2016). Biochar derived from pistachio green hull has recently been investigated as an efficient adsorbent for the removal of Cu^{2+} from water (Teğin et al., 2025).

Fig. 1. Pistachio shells

Pistachio green hulls contain a high concentration of organic compounds, polysaccharides, and functional groups, which are favourable for metal ion adsorption. Nevertheless, the existing body of research on the potential of modified pistachio green hulls as a sustainable, cost-effective, and readily available adsorbent for heavy metal removal is relatively scant.

Considering the environmental and biological risks associated with Cd^{2+} accumulation, developing low-cost, sustainable adsorbents like pistachio green hulls can significantly enhance the progress of eco-friendly remediation technologies (Bhattacharyya et al., 2024). The present study aims to comprehensively investigate the adsorption behavior of untreated and chemically treated pistachio green hulls for removing cadmium ions from aqueous solutions. This research specifically focuses on evaluating and comparing the removal efficiency of different treatments, optimizing the process by examining key factors such as chemical modification type, initial Cd^{2+} concentration, pH, contact time, and temperature, and ultimately providing deeper insights into the adsorption mechanism and kinetics using advanced modeling techniques.

2. Materials and Methods

2.1. Materials and synthesis procedure

This study was conducted at a laboratory scale to investigate the potential of pistachio green hulls as adsorbents for Cd^{2+} removal from aqueous solutions. The pistachio green hulls were collected from local pistachio trees in Birjand, South Khorasan, Iran.

The study involved four treatments: untreated pistachio green hull (control), HNO_3-treated hull, NH_3/H_2O_2-treated hull, and acetone/H_2O_2-treated hull. Each treatment was replicated three times to ensure reliability. $Cd(NO_3)_2{\cdot}4H_2O$ (Merck Co, Germany) was dissolved in deionized water to prepare the cadmium solution to achieve the desired initial concentration of 20 mg/L. All chemicals used in this study were of analytical grade.

The collected green hulls were washed several times with distilled water to remove dirt and water-soluble impurities, then dried in an oven at 120 °C for 6 hours. The dried materials were ground and sieved to obtain a particle size smaller than 63 µm (mesh no. 225). The sieved powder was rewashed with distilled water until the wash water became colorless, followed by re-drying.

For chemical modification, the dried powders were treated with one of the following solutions in a closed container for 30 minutes: HNO_3 solution, NH_3 (2 vol%)/H_2O_2 (2 vol%) mixture, or acetone (2 vol%)/H_2O_2 (2 vol%) mixture. The chemical treatments aimed to enhance surface functionality and improve adsorption performance (Hamdaoui, 2009). Finally, all prepared materials were stored in a desiccator until further use. Key operational parameters were investigated under controlled laboratory conditions to comprehensively evaluate the acetone/H2O2-treated pistachio green hull's adsorption performance.

These parameters included the type and dosage of chemical treatments, initial cadmium ion concentration, solution pH, contact time, and temperature. The effects of each parameter on the adsorption capacity and removal efficiency were systematically examined to optimize the adsorption process.

2.2. Boehm's titration

Chemical and thermal treatment processes produce some functional groups on the solid surface, influencing adsorption capability of adsorbents toward metal ions. Boehm titration was used to measure the surface functional groups quantitatively. In this regard, 0.5 g of sorbent was placed in flasks containing 50 mL of 0.05 N sodium bicarbonate, sodium carbonate, sodium hydroxide, and hydrochloric acid. The flasks were sealed and shaken for 24 h, then the solutions were filtered. Afterward, 10 mL of each solution was pipetted into a flask and titrated with 0.05N sodium hydroxide and/or hydrochloric acid, depending on the original solution. Based on the assumption that NaOH neutralizes carboxylic, lactonic, and phenolic groups, Na_2CO_3 neutralizes both carboxylic and lactonic groups, and $NaHCO_3$ neutralizes only the carboxylic group, the number of acidic groups on the adsorbent was computed. The amount of HCl that reacted with the adsorbent determined the number of surface basic sites. The acid/base strength difference governs the reaction between reagents and acidic oxygenated functional groups on the surface. The strengths of acidic and basic groups are as follows: Carbonyl > lactone > phenol (Wan Ngah and Hanafiah, 2008).

2.3. Point of zero charge

The electric charges on the surfaces of particles are highly significant characteristics of solid-liquid systems, influencing the adsorption behavior of contaminants. A critical parameter in this context is the Point of Zero Charge (PZC), which refers to the pH at which the surface of the adsorbent carries no net electrical charge. The surface is similarly likely to attract cations and anions at this pH, meaning its surface charge is neutral. This parameter is particularly critical in adsorption studies, as it helps predict the surface behavior under different pH conditions. To determine the samples' PZC, three different initial pH solutions containing HNO_3 and NaOH were prepared.

The initial pH of 3, 6, or 11 was employed as the background electrolyte. For each, six containers were filled with 100 mL of the solution, followed by adding different amounts of samples (0.05, 0.l, 0.5, l, 5, and 10 wt%), and the equilibrium pH was measured after 24 h.

2.4. Batch adsorption study of Cd^{2+} ions onto treated pistachio green hulls

The research utilized batch adsorption experiments to investigate the adsorption of Cd^{2+} from solutions. Experiments were conducted in a 200-mL vessel surrounded by a glass cylindrical jacket that facilitated water circulation to cool the reactor while maintaining a controlled temperature. In a typical experiment, a specific amount of treated or untreated pistachio green hulls was added to 50 mL of Cd^{2+} solution (20 mg/L) and stirred at a fixed agitation speed of 800 rpm for a predetermined time.

The solution was filtered and the Cd^{2+} ion concentration was determined by a flame atomic absorption spectrometer (Shimadzu, AA-6200, Japan). A deuterium background correction was employed to correct non-specific absorbance, and a Cd hollow cathode lamp was used as a radiation source (Hamamatsu Photonics, Japan) for measurement. The equilibrium Cd^{2+} ion uptake capacity (qe, mg/g) was calculated using the following equation:

$$q_e = V(C_0 - C_e)/m \quad (1)$$

where C_0 and C_e represent the initial and equilibrium concentrations of Cd^{2+} ions (mg/L), V is volume (l), and m is the adsorbent dose (g). The effects of adsorbent dose, initial concentrations, pH, time, and temperature on the efficacy of chemically treated pistachio green hulls in removing Cd^{2+} ions were investigated through experiments.

Equilibrium isotherms were evaluated using the aforementioned procedure by adding 0.2 g of chemically treated pistachio green hulls to 50 mL of Cd^{2+} solutions (20 mg/L) at 25, 45, and 65 °C in the concentration ranges of 200 to 800 mg/L. The mixture was then agitated at a constant speed of 800 rpm. After equilibrium, the solutions were analyzed for the remaining Cd^{2+} concentration with flame atomic absorption spectrometry.

3. Results and Discussion

3.1. Effect of chemical treatment

The chemical treatment was carried out to improve the efficiency of the chelating process and to extract soluble organic compounds (Sarangi and Mishra, 2023). It affects the adsorption capacity of pistachio green hulls toward Cd^{2+} ions, caused by the formation of functional groups on the solid surface. The effect of various chemical treatments on the pistachio green hull adsorbent is depicted in Fig. 2, demonstrating the significant influence of chemical treatment on its adsorption performance. The adsorbent demonstrated a diminished capacity for adsorbing Cd^{2+} ions in the absence of any pretreatment

Our observation indicated that the amounts of adsorbed Cd^{2+} were rapidly increased during the short contact period using all chemically treated sorbents, and then the process reached equilibrium. Specifically, for 0.6 g of adsorbent and after 1 min, the removal efficiencies of sorbent for the untreated, HNO_3-treated, NH_3/H_2O_2-treated, and acetone/H_2O_2-treated samples were 68%, 55%, 88%, and 95%, respectively.

The differences in adsorption capacities among the chemical treatments can be attributed to variations in the types and densities of functional groups introduced onto the hull surface and potential competitive interactions or complexation effects between cadmium ions and the treated hulls. Chemical treatments usually attach functional groups on the adsorbent surfaces with different affinities toward metal ions in the aqueous solution. However, HNO_3 treatment can introduce carboxyl and hydroxyl functional groups onto the surface of the hulls through acid hydrolysis, creating more active sites for cadmium adsorption, but it showed lower adsorption behavior compared to an untreated one. It can be attributed to the excessive etching or degradation of the hull surface, of the available adsorption sites. Amino and hydroxyl groups can be introduced onto the hull surface by treating with H_2O_2/NH_3, which also may create more active sites for Cd^{2+} ions, increasing hulls' adsorption behaviour.

Furthermore, the results imply that the pistachio green hull treated with H_2O_2 (2 vol%)/acetone (2 vol%) has higher Cd^{2+} removal efficiency than other chemical treatments. It can be attributed to a more significant modification of the hull structure, potentially breaking the cellulosic components and increasing surface roughness. This treatment could introduce more oxygen-containing functional groups onto the hull surface, such as carbonyl and hydroxyl groups, which enhance the adsorption capacity for Cd^{2+} ions. Additionally, acetone might aid in dissolving certain organic compounds, further exposing adsorption sites and increasing the overall adsorption capacity. Accordingly, the subsequent experiments have employed the H_2O_2/acetone chemically treated pistachio green hull as adsorbent.

Acetone is a common organic solvent, while hydrogen peroxide is a potent oxidizing agent (Oxley et al., 2012). Their mixing can induce various chemical reactions and modifications in the structure and composition of the pistachio green hulls. They can react with organic compounds present in the hulls, leading to the breakdown of complex organic molecules, such as cellulose, hemicellulose, lignin, and pectin, which are abundant in fruit peels. The reaction of H_2O_2 and acetone with functional groups on the hull surface can lead to the formation of new chemical bonds or the modification of existing ones. This can result in changes in the polarity, charge, reactivity, the surface properties, such as roughness, hydrophobicity, and surface energy, of green hulls. Their combination can also effectively remove surface impurities (T. Ahmad and Danish, 2018; Jamkar et al., 2023; Rahman et al., 2023; Yeow et al., 2021).

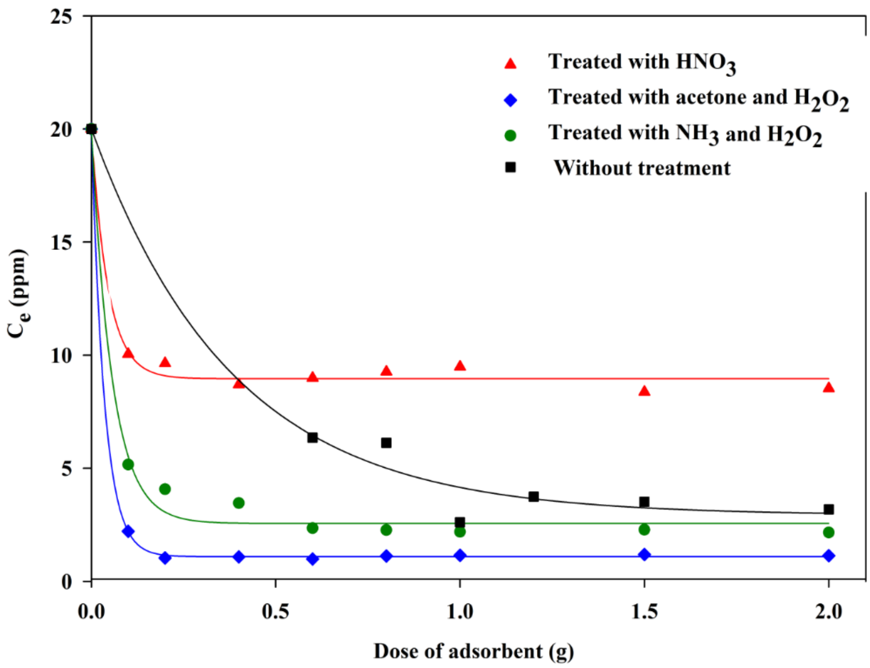

Fig. 2. Effect of different chemical treatments on the Cd^{2+} adsorption from aqueous solution (Cd^{2+} initial concentration = 20 mg/L; 25 °C, 10 min)

3.2. Sorbent characteristics

The structural characteristics of the acetone/H_2O_2-treated pistachio green hull with particle size <63μm were explored, and the quantities of surface functional groups on the treated pistachio green hull adsorbent were calculated by Boehm's technique. Results obtained from Boehm's method are given in Table 1. As seen, the amounts of acidic and basic groups on the solid surface are obtained in the order of carboxylic > phenolic > basic > lactonic.

Table 1. Surface acidity and basicity of pistachio green hull treated with acetone/H_2O_2 obtained from Boehm's method.

Phenolic groups (mmol/g)	Lactonic groups (mmol/g)	Carboxylic groups (mmol/g)	Surface basicity (mmol/g)
0.4	0.0	1.5	0.15

The isoelectric point of the acetone/H_2O_2-treated sorbent was measured, and the mass titration curves presented for the treated pistachio green hull sorbent are shown in Fig. 3. It shows pH values as a function of the mass fraction of the treated sorbent in the solution. As observed in the figure, the asymptotic isoelectric point (pH_{pzc}) is about 4.5, verifying the results of Boehm's tests about the functional groups. According to Boehm's results, the most functional groups on the surface of the treated sorbent were carboxylic, phenolic, and basic groups. Consequently, these functional groups play an important role in the removal of Cd^{2+} ions from aqueous solutions.

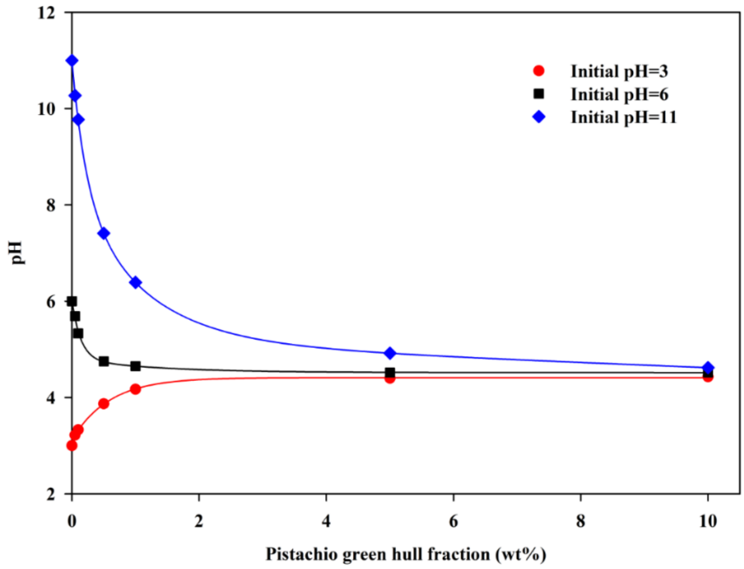

Fig. 3. Mass titration results for pistachio green hull treated with acetone/H_2O_2

3.3. Effect of initial concentration and adsorbent dose

The effect of the initial Cd^{2+} ion concentration was assessed at three different concentrations of 20, 80, and 150 mg/L and different sorbent dosages in the range of 0.1–1.5 g. The equilibrium times (~10 min) were kept the same for all experiments. The obtained results are demonstrated in Fig. 4a. It shows that the Cd^{2+} removal efficiency was increased at a higher adsorbent/adsorbate ratio, which can be attributed to the presence of more active sites. It indicates that the dosage of the adsorbent has a greater impact on the removal efficiency and is more significant for higher metal concentrations. The ratio of existing adsorption sites for Cd^{2+} ions is lower, and binding sites saturate more quickly at higher initial concentrations.

3.4. Effect of pH

This study investigated the effect of pH on the adsorption process of Cd^{2+} ions using acetone/H_2O_2-treated pistachio green hull adsorbent in the pH range of 2–9, considering its crucial function in this process (Osman et al., 2024). The pH of the solution was fixed using NaOH and HCl solutions (0.1 M), and the obtained results are shown in Fig. 4b. The chemical activation resulted in an increase in the number of carboxylic groups at the surface of pistachio hulls. As seen, the adsorbent showed high adsorption capability within the pH range of 4–9, which corresponded to the adsorbent's estimated pH_{pzc} of 4.5. Acetone/H_2O_2-treated pistachio green hull has a net positively charged surface at a pH below 4.5 and is negatively charged at higher pHs. Assuming the electrostatic interaction-based mechanism as the main responsible interaction involved in this adsorption process, the cationic Cd^{2+} ions were easier to adsorbed at pH > 4.5. Based on pH_{zpc}, acidic groups dominate the surface of the active site (Sudrajat et al., 2021). Besides, due to the positive charge of the adsorbent surface at a low pH value, H^+ ions efficiently competed with metal ions, reducing the adsorptive uptake.

3.5. Effect of contact time and temperature

Figure 3c depicts the effect of time on the adsorption of Cd^{2+} ions onto acetone/H_2O_2-treated pistachio green hull at 25 °C and a fixed dose of 0.2 g treated adsorbent. The findings indicate that the adsorption of Cd^{2+} ions increase significantly in the initial contact times, below 4 min, and followed a plateau trend, achieving roughly 94% removal efficiency. The rapid adsorption to the equilibrium state may be attributed to the adsorbent surface's readily accessible functional groups and high adsorption efficiency.

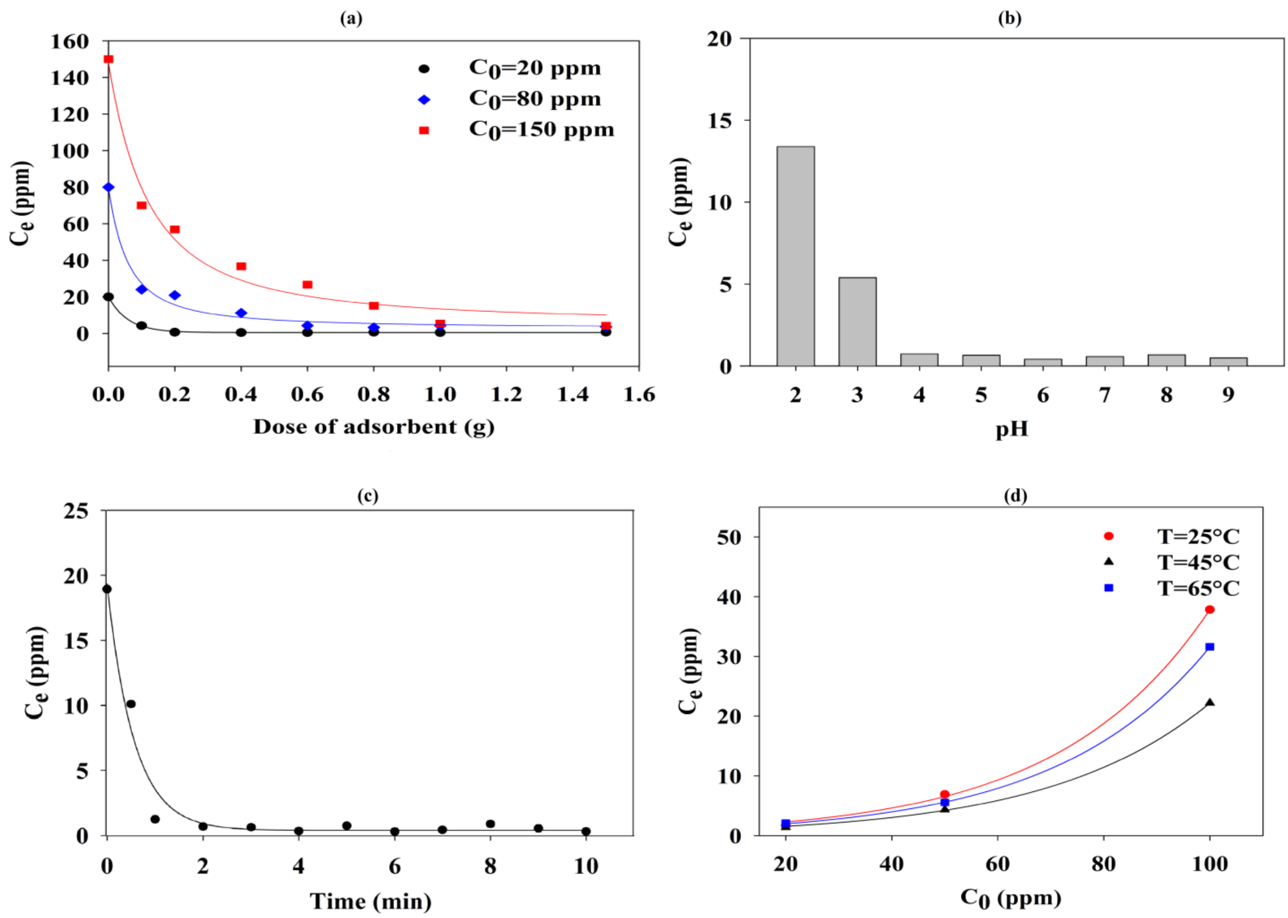

Fig. 4. (a) Effect of initial concentration at different sorbent dosages (T =25 °C and 10 min), (b) Effect of pH on Cd^{2+} removal (initial Cd^{2+} concentration = 20 mg/L, T=25 °C, and 10 min), (c) Effect of contact time (initial Cd^{2+} concentration = 20 mg/L, T= 25 °C, and pH = 7.0), and (d) Effect of temperature on the Cd^{2+} adsorption (initial Cd^{2+} concentration = 20 mg/L, pH = 7.0)

The effect of temperature was assessed at three distinct temperatures of 25, 45, and 65 °C and three doses of acetone/H_2O_2-treated pistachio green hull (20, 50, and 100 mg/L) in the fixed 0.2 g of treated adsorbent, and the results are shown in Fig. 3d. It is observed that there is a slight difference in the amounts of adsorbed Cd^{2+} ions at different temperatures at low initial concentrations, while it increases with raising concentration. By increasing the temperature, the diffusion rate of metal ions improves, resulting in stronger adsorption; however, at higher temperatures, the attraction interactions between the adsorbent surface and metal ions weaken, and sorption decreases. Additionally, Horsfall and Spiff (Horsfall and Spiff, 2005) stated in their investigation on the impact of temperature on Cd^{2+} sorption that the thickness of the boundary layer decreases due to the increased tendency of the metal ion to escape from the adsorbent surface to the solution phase, resulting in a decrease in adsorption as temperature increases.

3.6. Kinetic study

The adsorption kinetic study was carried out by evaluating the experimental data of Cd^{2+} adsorption onto acetone/H_2O_2-treated pistachio green hulls with the pseudo-first-order and pseudo-second-order models using the following equations, respectively:

$$log(q_e - q_t) = logq_e - k_1 t/2.303 \qquad (2)$$

$$t/q_t = 1/(k_2.q_e^2) + t/q_e \qquad (3)$$

where k_1 is the first-order rate constant (1/min), calculated from the slope of the plot of log ($q_e - q_t$) vs. t, as shown in Fig. 5a. The rate constant for pseudo-second-order adsorption is k_2 (g/mg.min), that can be calculated by plotting t/q_t vs. t (see Fig. 5b). The initial adsorption rate (h, mg/g.min) was also determined using the second-order rate constants as follow:

$$h = k_2 q_e^2 \quad (4)$$

The values of different determined parameters are listed in Table 2. Higher correlation coefficients obtained from the pseudo-second-order model (> 0.99), well agreeing with the calculated q_e values from this model with the experimental value, demonstrate that the Cd^{2+} adsorption onto acetone/H_2O_2-treated pistachio green hulls follow the second-order kinetic model. The evidence suggests that the process is a chemisorption process. Also, to evaluate the adsorption mechanism, the adsorption experimental data were analyzed in terms of an intra-particle diffusion model, as follows (Najafi et al., 2022):

$$q_t = K_{id} t^{0.5} \quad (5)$$

where k_{id} is the rate constant for intra-particle diffusion adsorption (mg/g.min$^{0.5}$), which can be determined by plotting q_t vs. $t^{0.5}$, as shown in Fig. 5 (c). In solid-liquid adsorption processes, the sorbate transfer typically occurs through intra-particle diffusion, external mass transfer (boundary layer diffusion), or both.

Table 2. Calculated parameters in the adsorption kinetics of Cd^{2+} removal using acetone/H_2O_2-treated pistachio green hulls (C_0=20 mg/L).

Pseudo-first-order model		Pseudo-second-order model	
k_1 (1/min)	0.5576	k_2 (g/mg.min)	3.708
q_e (mg/g)	0.5429	h, mg/g.min	89.29
R^2	0.2522	q_e (mg/g)	4.907
		R^2	0.9995

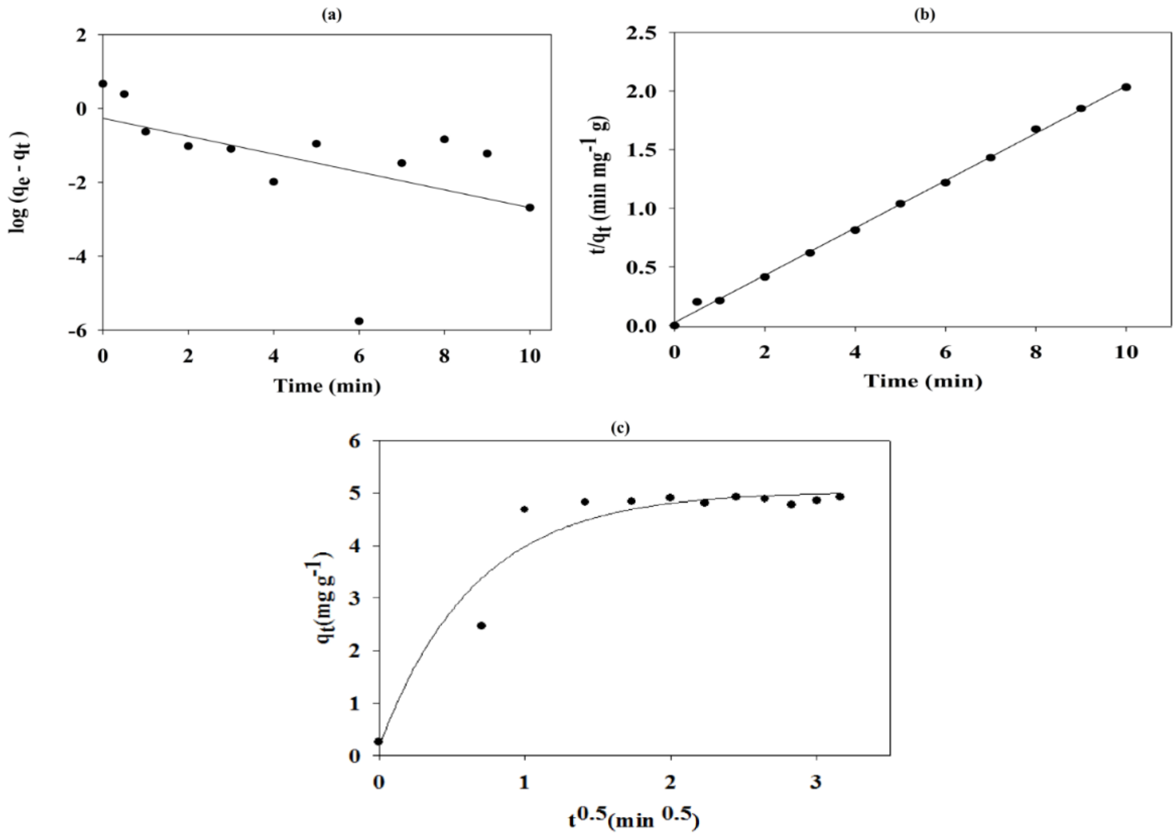

Fig. 5. Fitting the experimental data of Cd^{2+} adsorption onto acetone/H_2O_2-treated pistachio green hulls (sorbent dosage = 0.2 g, pH = 7.0, and T = 25 °C) by (a) pseudo-first-order kinetics model, (b) pseudo-second-order kinetics model, and (c) intra-particle diffusion model

The adsorption mechanisms may consist of the subsequent three stages: i) transport from the bulk solution to the external surface of the sorbent through liquid film (film diffusion), ii) transport of the adsorbate within the adsorbent pores (particle diffusion), and iii) adsorption of on the exterior surface of the adsorbent (pore diffusion) (Tanhaei et al., 2019).

The adsorption of Cd2+ onto pistachio green hulls treated with acetone/H2O2 proceeds in two distinct stages, as illustrated in Fig. 5c. The first step is a linear portion that signifies intra-particle diffusion, while the second is a plateau portion that represents the equilibrium state.

3.6. Isotherm study

Three distinct and widely used isotherm models, Freundlich, Langmuir, and Temkin models, were utilized to explain adsorption equilibrium. The Langmuir isotherm was proposed based on monolayer adsorption on the active sites, whereas the adsorption heat remains constant across all sites (Doshi et al., 2018). This model was used in linear form as follows:

$$1/q_e = 1/q_m + 1/(bq_mC_e) \quad (6)$$

where q_e and q_m represent the equilibrium sorption uptake (mg/g) and theoretical maximal adsorption capacity (mg/g), respectively, C_e is the equilibrium concentration (mg/L), and b denotes the Langmuir constant (mL/mg). The separation factor (R_L), as a dimensionless constant, expresses the fundamental properties of the Langmuir isotherm as follows (Tanhaei et al., 2015):

$$R_L = 1/\,(1 + bC_0) \quad (7)$$

The R_L values classify adsorption as favorable ($0 < R_L < 1$), irreversible ($R_L = 0$), linear ($R_L = 1$), and unfavorable ($R_L > 1$). The empirical Freundlich isotherm describes multilayer adsorption on heterogeneous surfaces. It was also used in the following linear form:

$$log\, q_e = log\, k_f + (1/n)(logC_e) \quad (8)$$

The Freundlich constants are denoted as K_f and n, expressing the adsorbent's adsorption capacity and intensity, respectively, so that n>1 indicates the adsorption process's favorability. The Temkin isotherm, which characterizes the reaction of an adsorption system on heterogeneous surfaces, was also applied to the equilibrium experimental data using the following linear form:

$$q_e = A + BlnC_e \quad (9)$$

$$A = (RT/b_T)lnK_{Te} \quad (10)$$

$$B = (RT/b_T) \quad (11)$$

where A and B denote isotherm constants, while R signifies the gas constant (8.341 J/mol K) and T represents the absolute temperature (K). The heat of adsorption (J/mol) and equilibrium binding constant (L/g) are respectively associated with b_T and K_{Te}. The calculated parameters for the Langmuir, Freundlich, and Temkin isotherm models at 25, 45, and 65 °C for the adsorption of Cd^{2+} ions onto acetone/H_2O_2-treated pistachio green hulls over a concentration range of 200-800 mg/L are detailed in Table 3. The corresponding plots are shown in Fig. 6. As seen, the correlation coefficients show that the adsorption of Cd^{2+} ions onto treated pistachio green hull correlated well with the Langmuir isotherm model, suggesting the monolayer adsorption of metal ions onto the adsorbent. The values of R_L are in the range of $0 < R_L < 1$, suggesting the favorability of Cd^{2+} ion adsorption onto treated pistachio green hull.

Table 3. Calculated isotherms' parameters for the adsorption of Cd^{2+} onto acetone/H_2O_2-treated pistachio green hulls at different temperatures.

T (°C)	Langmuir			Freundlich			Temkin		
	q_m (mg/g)	b	R^2	n	K_f	R^2	b_T	K_t	R^2
25	140.8	0.0014	0.983	1.436	0.886	0.958	97.75	0.018	0.975
35	151.5	0.0045	0.975	1.887	1.852	0.914	69.71	0.025	0.981
45	107.5	0.0011	0.988	1.432	0.735	0.929	184.99	0.020	0.971

3.8. Thermodynamic study

To conduct the thermodynamic investigation, the standard Gibbs free energy (ΔG°, J/kmol), standard enthalpy change (ΔH°, J/kmol), and standard entropy change (ΔS°, J/kmol.K) were assessed, using the following equations, respectively:

$$\Delta G^o = -RTlnK_0 \quad (12)$$

$$lnK_0 = \Delta S^0/R - \Delta H^0/RT \quad (13)$$

$$K_0 = q_e/C_e \quad (14)$$

where R, T and K_0 are gas constant (8.314 J/mol K), temperature (K), and Langmuir constant (L/mol). The calculated thermodynamic parameters are summarized in Table 4. Increased magnitudes of negative values for ΔG° indicate a more potent drive force during the adsorption process. The absolute value of ΔG° exhibited an upward trend as the temperature rose from 25 to 45 °C, signifying an increase in driving force and consequently, a greater adsorption capacity. The negative values of ΔH° indicate the process's exothermic nature, and the negative values of ΔS° clarified the less randomness of Cd^{2+} adsorption onto acetone/H_2O_2-treated pistachio green hulls.

Table 4. Thermodynamic parameters of Cd^{2+} ions adsorption onto acetone/H_2O_2-treated pistachio green hulls.

T (°C)	ΔG°, J/kmol	(ΔH°, J/kmol	ΔS°, J/kmol.K
25	-2492		
45	-3160	-53.25	-18902
65	-2053		

3.9. Comparison with other natural adsorbents

To contextualize the adsorption performance of the acetone/H_2O_2-treated pistachio green hulls evaluated in this study, several natural and agricultural waste-based adsorbents previously reported in the literature were compared (Table 5).

Key parameters such as optimal pH, contact time, and maximum adsorption capacity (q_m) were compared across different adsorbents. Moreover, the equilibrium time required for pistachio green hulls to reach maximum adsorption (less than 4 minutes) was significantly shorter than most previously studied materials, indicating a faster adsorption process.

Table 5. Comparison of Cd^{2+} adsorption performance of various natural and agricultural waste-based adsorbents.

Adsorbent	pH	Time (min)	q_m (mg/g)	Reference
Apple peels	5.5	300	0.8	(Abdolali et al., 2016)
Coffee grounds	5.0	30	16.2	(Dutta et al., 2016)
Orange peel	7.0	210	40.0	(Gupta and Nayak, 2012)
Walnut shell	4-6	60	11.6	(Almasi et al., 2012)
Compost derived from fruits and	6.0	1140	7.14	(I. Ahmad et al., 2017)
Acetone/H_2O_2-treated pistachio green hulls	7.0	<4	151.5	This work

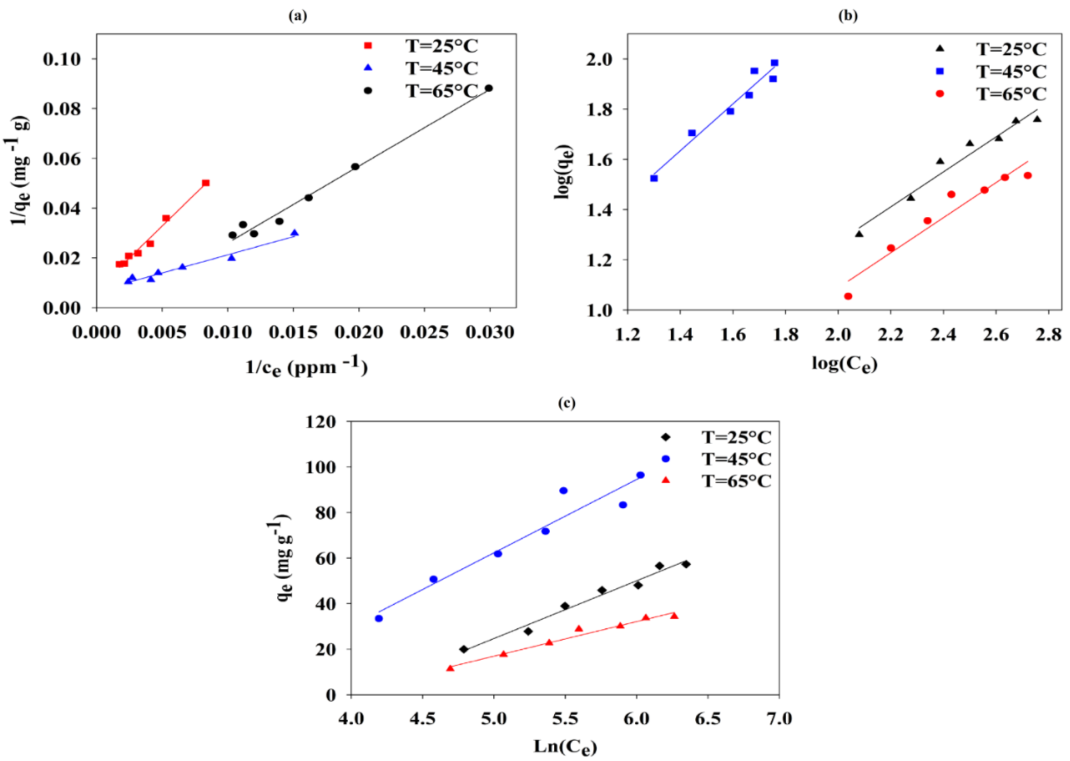

Fig. 6. Fitting the equilibrium experimental data of Cd^{2+} adsorption onto acetone/H_2O_2-treated pistachio green hulls at different temperatures with a) Langmuir model, b) Freundlich model, and c) Temkin model

As shown in Table 5, pistachio green hulls treated with acetone/ H_2O_2 demonstrated a remarkably higher adsorption capacity (151.5 mg/g) compared to many other adsorbents, including apple peels (0.8 mg/g), coffee grounds (16.2 mg/g), orange peels (40.0 mg/g), walnut shells (11.6 mg/g), and fruit-derived compost (7.14 mg/g).

This superior performance can be attributed to the enhanced surface functionality resulting from the acetone/H_2O_2 treatment, which increased the availability of active adsorption sites. Furthermore, the optimal adsorption pH of 7.0 observed for pistachio green hulls is close to neutral pH, which is advantageous for practical applications in real water treatment scenarios.

Overall, this comparison highlights the high potential of chemically modified pistachio green hulls as an efficient, sustainable, and low-cost adsorbent for cadmium removal, outperforming many conventional bioadsorbents reported in the literature.

4. Conclusion

Herein, the feasibility of utilizing a new adsorbent produced from pistachio green hull to remove Cd^{2+} ions from aqueous solutions was studied. Acetone/H_2O_2 treatment was an efficient chemical procedure to improve the adsorption behavior of used biowaste. Adsorption occurred fast and efficiently within only 1 minute of contact time, and the maximum adsorption capacity was found to be 151 mg/g. It showed high adsorption performance in a wide pH range of 4–9. The kinetics and isotherm studies revealed that the Cd^{2+} adsorption onto acetone/H_2O_2-treated pistachio green hulls follows the pseudo-second-order and Langmuir models, respectively. The adsorption mechanism suggests electrostatic interaction as the primary interaction in the process.

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6. Conflict of Interest

No potential conflict of interest was reported by the authors.

7. References

Abdolali, A., Ngo, H. H., Guo, W., Lu, S., Chen, S.-S., Nguyen, N. C., Zhang, X., Wang, J. & Wu, Y. (2016). A breakthrough biosorbent in removing heavy metals: Equilibrium, kinetic, thermodynamic and mechanism analyses in a lab-scale study. *Science of The Total Environment*, *542*, 603–611.

Ahmad, I., Akhtar, M. J., Jadoon, I. B. K., Imran, M., Imran, M. & Ali, S. (2017). Equilibrium modeling of cadmium biosorption from aqueous solution by compost. *Environmental Science and Pollution Research*, *24*(6), 5277–5284.

Ahmad, T. & Danish, M. (2018). Prospects of banana waste utilization in wastewater treatment: A review. *Journal of Environmental Management*, *206*, 330–348.

Almasi, A., Omidi, M., Khodadadian, M., Khamutian, R. & Gholivand, M. B. (2012). Lead(II) and cadmium(II) removal from aqueous solution using processed walnut shell: kinetic and equilibrium study. *Toxicological & Environmental Chemistry*, *94*(4), 660–671.

Alsulaili, A., Elsayed, K. & Refaie, A. (2024). Utilization of agriculture waste materials as sustainable adsorbents for heavy metal removal: A comprehensive review. *Journal of Engineering Research*, *12*(4), 691–703.

Armagan, B. & Toprak, F. (2015). Using pistachio shell for Remazol Red removal from aqueous solutions: equilibrium, kinetics and thermodynamics. *Desalination and Water Treatment*, *56*(1), 136–145.

Bhattacharyya, K., Sen, D., Banik, A. K. & Ganguly, S. (2024). Adsorptive removal of cadmium from aqueous medium-a critical review. Physics and Chemistry of the Earth, Parts A/B/C, 134, 103538-103555.

Deniz, F. & Kepekci, R. A. (2016). Dye biosorption onto pistachio by-product: A green environmental engineering approach. *Journal of Molecular Liquids*, *219*, 194–200.

Dorri, H., Zeraatkar Moghaddam, A., Ghiamati, E. & Barikbin, B. (2022). A comprehensive study on the adsorption-photocatalytic processes using CoFe2O4/SiO2/MnO2 magnetic nanocomposite as a novel photo-catalyst for removal of Cr (VI) under simulated sunlight: Isotherm, kinetic and thermodynamic studies. *Journal of Environmental Health Science and Engineering*, 1–19.

Doshi, B., Ayati, A., Tanhaei, B., Repo, E. & Sillanpää, M. (2018). Partially carboxymethylated and partially cross-linked surface of chitosan versus the adsorptive removal of dyes and divalent metal ions. *Carbohydrate Polymers*, *197*, 586–597.

Dutta, A., Diao, Y., Jain, R., Rene, E. R. & Dutta, S. (2016). Adsorption of Cadmium from Aqueous Solutions onto Coffee Grounds and Wheat Straw: Equilibrium and Kinetic Study. *Journal of Environmental Engineering*, *142*(9), 1–6.

Fiyadh, S. S., Alardhi, S. M., Al Omar, M., Aljumaily, M. M., Al Saadi, M. A., Fayaed, S. S., Ahmed, S. N., Salman, A. D., Abdalsalm, A. H., Jabbar, N. M. & El-Shafi, A. (2023). A comprehensive review on modelling the adsorption process for heavy metal removal from waste water using artificial neural network technique. *Heliyon*, *9*(4), e15455–e15468.

Foo, K. Y. & Hameed, B. H. (2011). Preparation and characterization of activated carbon from pistachio nut shells via microwave-induced chemical activation. *Biomass and Bioenergy*, *35*(7), 3257–3261.

Gogoi, B., Acharjee, S. A., Bharali, P., Sorhie, V., Walling, B. & Alemtoshi. (2024). A critical review on the ecotoxicity of heavy metal on multispecies in global context: A bibliometric analysis. *Environmental Research*, *248*, 118280–118304.

Gupta, V. K. & Nayak, A. (2012). Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe2O3 nanoparticles. *Chemical Engineering Journal*, *180*, 81–90.

Hamdaoui, O. (2009). Removal of cadmium from aqueous medium under ultrasound assistance using olive leaves as sorbent. *Chemical Engineering and Processing: Process Intensification*, *48*(6), 1157–1166.

Horsfall, M. & Spiff, A. I. (2005). Effects of temperature on the sorption of Pb2+ and Cd 2+ from aqueous solution by Caladium bicolor (Wild Cocoyam) biomass. *Electronic Journal of Biotechnology*, *8*(2), 162–169.

Jamkar, S., Tripathy, A., Mallik, S. & Pal, D. (2023). Methodologies of Removal of Heavy Metals from Contaminated Water Using Various Waste Materials: A Comprehensive Review. *ChemBioEng Reviews*, *10*(6), 959–992.

Joshi, H. K., Vishwakarma, M. C., Kumar, R., Sharma, H., Bhandari, N. S. & Joshi, S. K. (2023). The biosorption of Zn2+ by various biomasses from wastewater: A review. *Journal of Water Process Engineering*, *56*, 104389–104414.

Karić, N., Maia, A. S., Teodorović, A., Atanasova, N., Langergraber, G., Crini, G., Ribeiro, A. R. L. & Đolić, M. (2022). Bio-waste valorisation: Agricultural wastes as biosorbents for removal of (in)organic pollutants in wastewater treatment. *Chemical Engineering Journal Advances*, *9*, 100239–100256.

Karimi, F., Ayati, A., Tanhaei, B., Sanati, A. L., Afshar, S., Kardan, A., Dabirifar, Z. & Karaman, C. (2022). Removal of metal ions using a new magnetic chitosan nano-bio-adsorbent; A powerful approach in water treatment. *Environmental Research*, *203*, 111753–111761.

Khan, M. A., Al Othman, Z. A., Kumar, M., Ola, M. S. & Siddique, M. R. (2015). Biosorption potential assessment of modified pistachio shell waste for methylene blue: thermodynamics and kinetics study. *Desalination and Water Treatment*, *56*(1), 146–160.

Najafi, M., Bastami, T. R., Binesh, N., Ayati, A. & Emamverdi, S. (2022). Sono-sorption versus adsorption for the removal of congo red from aqueous solution using NiFeLDH/Au nanocomposite: Kinetics, thermodynamics, isotherm studies, and optimization of process parameters. *Journal of Industrial and Engineering Chemistry*, *116*, 489–503.

Nguyen, T. A. H., Ngo, H. H., Guo, W. S., Zhang, J., Liang, S., Yue, Q. Y., Li, Q. & Nguyen, T. V. (2013). Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. *Bioresource Technology*, *148*, 574–585.

Osman, A. I., Ayati, A., Farghali, M., Krivoshapkin, P., Tanhaei, B., Karimi-Maleh, H., Krivoshapkina, E., Taheri, P., Tracey, C., Al-Fatesh, A., Ihara, I., Rooney, D. W. & Sillanpaä, M. (2024). Advanced adsorbents for ibuprofen removal from aquatic environments: a review. *Environmental Chemistry Letters*, *22*(1), 373–418.

Oxley, J. C., Brady, J., Wilson, S. A. & Smith, J. L. (2012). The risk of mixing dilute hydrogen peroxide and acetone solutions. *Journal of Chemical Health and Safety*, *19*(2), 27–33.

Rahman, D. Z., Vijayaraghavan, J. & Thivya, J. (2023). A comprehensive review on zinc(II) sequestration from wastewater using various natural/modified low-cost agro-waste sorbents. *Biomass Conversion and Biorefinery*, *13*(7), 5469–5499.

Ramesh, B., Saravanan, A., Senthil Kumar, P., Yaashikaa, P. R., Thamarai, P., Shaji, A. & Rangasamy, G. (2023). A review on algae biosorption for the removal of hazardous pollutants from wastewater: Limiting factors, prospects and recommendations. *Environmental Pollution*, *327*, 121572–121585.

Sadeghi, S., Rad, F. A. & Moghaddam, A. Z. (2014). A highly selective sorbent for removal of Cr(VI) from aqueous solutions based on Fe3O4/poly(methyl methacrylate) grafted Tragacanth gum nanocomposite: Optimization by experimental design. *Materials Science and Engineering C*, *45*, 136–145.

Santhosh, K., Kamala, K., Ramasamy, P., Musthafa, M. S., Almujri, S. S., Asdaq, S. M. B. & Sivaperumal, P. (2024). Unveiling the silent threat: Heavy metal toxicity devastating impact on aquatic organisms and DNA damage. *Marine Pollution Bulletin*, *200*, 116139–116148.

Sarangi, B. & Mishra, S. P. (2023). A glance at the potential of Artocarpus genus fruit peels and its derivatives as adsorbent. *Bioresource Technology Reports*, *21*, 101363–101374.

Saravanan, A., Karishma, S., Kumar, P. S., Thamarai, P. & Yaashikaa, P. R. (2023). Recent insights into mechanism of modified bio-adsorbents for the remediation of environmental pollutants. *Environmental Pollution*, *339*, 122720–122738.

Solangi, N. H., Kumar, J., Mazari, S. A., Ahmed, S., Fatima, N. & Mubarak, N. M. (2021). Development of fruit waste derived bio-adsorbents for wastewater treatment: A review. *Journal of Hazardous Materials*, *416*, 125848–125879.

Sudrajat, H., Susanti, A., Putri, D. K. Y. & Hartuti, S. (2021). Mechanistic insights into the adsorption of methylene blue by particulate durian peel waste in water. *Water Science and Technology*, *84*(7), 1774–1792.

Tanhaei, B., Ayati, A., Lahtinen, M. & Sillanpää, M. (2015). Preparation and characterization of a novel chitosan/Al2O3/magnetite nanoparticles composite adsorbent for kinetic, thermodynamic and isotherm studies of Methyl Orange adsorption. *Chemical Engineering Journal*, *259*, 1–10.

Tanhaei, B., Ayati, A. & Sillanpää, M. (2019). Magnetic xanthate modified chitosan as an emerging adsorbent for cationic azo dyes removal: Kinetic, thermodynamic and isothermal studies. *International Journal of Biological Macromolecules*, *121*, 1126–1134.

Teğin, İ., Öc, S. & Saka, C. (2025). Adsorption of copper (II) from aqueous solutions using adsorbent obtained with sodium hydroxide activation of biochar prepared by microwave pyrolysis. *Biomass Conversion and Biorefinery*, *15*, 6805–6816.

Wan Ngah, W. S. & Hanafiah, M. A. K. M. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresource Technology*, *99*(10), 3935–3948.

Xue, X., Han, Y., Wu, X., Wang, H., Wang, S., Zheng, J., Ran, R. & Zhang, C. (2023). Review: Phytate modification serves as a novel adsorption strategy for the removal of heavy metal pollution in aqueous environments. *Journal of Environmental Chemical Engineering*, *11*(6), 111440–111465.

Yeow, P. K., Wong, S. W. & Hadibarata, T. (2021). Removal of azo and anthraquinone dye by plant biomass as adsorbent – a review. *Biointerface Research in Applied Chemistry*, *11*(1), 8218–8232.

Zeraatkar Moghaddam, A., Esmaeilkhanian, E. & Shakourian-Fard, M. (2019). Immobilizing magnetic glutaraldehyde cross-linked chitosan on graphene oxide and nitrogen-doped graphene oxide as well-dispersible adsorbents for chromate removal from aqueous solutions. *International Journal of Biological Macromolecules*, *128*, 61–73.