IARJSET ISSN (O) 2393-8021, ISSN (P) 2394-1588

International Advanced Research Journal in Science, Engineering and Technology

Impact Factor 8.311 ⁐ Peer-reviewed & Refereed journal ⁐ Vol. 12, Issue 7, July 2025

DOI: 10.17148/IARJSET.2025.12715

Eco-Friendly Adsorption of Chromium (Cr^{6+}) from Industrial Wastewater of Firozabad Using Modified Orange Peel as a Low-Cost Biosorbent

Tanya Yadav[1], Prof. Shiv Nandan[2]

Research Scholar, Department of Chemistry, Narain College, Shikohabad, Firozabad, U.P. (India)[1]

Professor, Department of Chemistry, Narain College, Shikohabad, Firozabad, U.P. (India)[2]

Affiliated to Dr.Bhimrao Ambedkar University, Agra U.P. (India)[1,2]

Abstract: This study investigates the eco-friendly and cost-effective adsorption of hexavalent chromium (Cr^{6+}) from industrial wastewater of Firozabad using chemically modified orange peel as a biosorbent. Given the hazardous nature of Cr^{6+} and its prevalence in the effluents from Firozabad's glass industry, this work offers a sustainable solution by utilizing agricultural waste. The orange peels were collected, washed, dried, ground, and chemically treated to enhance their functional groups for improved adsorption. The biosorbent was characterized using FTIR and SEM to confirm the presence of active sites and surface morphology. Batch adsorption experiments were conducted to evaluate the effect of parameters such as pH, contact time, initial metal concentration, and biosorbent dose. The results indicated optimal Cr^{6+} removal (>90%) at pH 2, a biosorbent dose of 2.5 g/L, and contact time of 90 minutes. Kinetic studies revealed that the process followed pseudo-second-order kinetics, while equilibrium data best fit the Langmuir isotherm model, indicating monolayer adsorption. Thermodynamic analysis confirmed the exothermic and spontaneous nature of the process. The biosorbent was also tested on real wastewater samples, achieving 70–88% removal efficiency despite the presence of competing ions. Compared to other agricultural wastes, the modified orange peel exhibited superior adsorption capacity (q_{max} = 8 mg/g), underscoring its potential as an efficient and sustainable material for heavy metal remediation in wastewater.

Keywords: Chromium (Cr^{6+}), biosorption, orange peel, industrial wastewater, low-cost adsorbent, Firozabad, eco-friendly remediation

I. INTRODUCTION

Industrial wastewater contamination by heavy metals has emerged as a significant environmental concern due to the toxic, non-biodegradable, and persistent nature of these pollutants. Among various heavy metals, hexavalent chromium (Cr^{6+}) is particularly hazardous owing to its high solubility, carcinogenicity, and ability to cause severe health effects such as skin irritation, respiratory problems, and organ damage upon prolonged exposure. A major source of Cr^{6+} contamination in India is the glass industry, and the city of Firozabad, known for its large-scale glass and bangle manufacturing units, discharges substantial amounts of chromium-laden wastewater into local drainage systems, posing serious ecological and public health risks. While conventional methods like chemical precipitation, ion exchange, and membrane filtration are commonly used for chromium removal, they often suffer from high operational costs, sludge disposal issues, and limited efficiency at low metal concentrations. In this context, biosorption has gained attention as a sustainable and cost-effective alternative, leveraging the natural binding affinity of agricultural wastes for metal ions. Orange peel, an abundant fruit waste rich in cellulose, hemicellulose, and lignin, contains functional groups such as hydroxyl and carboxyl that can be chemically modified to enhance metal uptake. This study aims to investigate the potential of modified orange peel as a low-cost, eco-friendly biosorbent for the effective removal of Cr^{6+} from industrial wastewater collected from Firozabad, thereby contributing to sustainable wastewater management practices.

Ali et al. (2016) explored the potential of chemically modified banana peels for the adsorption of Cr(VI) from aqueous media, establishing the foundation for utilizing agricultural waste as a low-cost and efficient biosorbent. Their study revealed a high adsorption capacity under acidic conditions, supported by kinetic and isotherm analyses. This early work significantly demonstrated the effectiveness of surface modification in enhancing the metal-binding capacity of natural waste materials. Tran et al. (2016) further contributed to this direction by examining the influence of pyrolysis temperature and duration on orange peel-derived biochar for cadmium removal. Their work emphasized the importance of thermal treatment in optimizing pore structure and surface chemistry, thereby improving metal uptake.

The findings also highlighted the role of biochar's physicochemical properties in adsorption performance. Wang et al. (2016) focused on chromium speciation in tannery effluents after alkaline precipitation, identifying Cr species and providing crucial insights into the chemical behavior of Cr(VI) in real wastewater environments. Their study underlined the complexity of chromium removal, reinforcing the need for adsorbents that can selectively target Cr(VI) amidst competing species. Del Menezzi et al. (2018) investigated the interactions between citric acid and lignocellulosic components in wood veneer panels, which has indirect relevance to biosorbent studies. Their findings on citric acid's crosslinking effects with cellulose and lignin support its application as a modifying agent for improving biosorbent performance. Mashkoor et al. (2018) utilized *Tectona grandis* sawdust for the removal of crystal violet dye, showcasing the value of untreated agricultural waste as an affordable and reusable adsorbent. Their results provided comparative benchmarks for adsorption efficiency and reusability in dye-contaminated wastewater. Zakaria et al. (2018) developed water treatment sachets from *Moringa oleifera* seeds and activated carbon, demonstrating the synergistic benefits of combining natural coagulants with adsorptive materials. This work emphasized eco-friendly water purification strategies tailored for low-resource settings. Zhang et al. (2018) advanced the field with their study on the adsorption and desorption of heavy metals using aminoethyl-reduced graphene oxide. Though not an agricultural waste-based material, their research provided valuable comparisons in adsorption capacity and desorption efficiency, highlighting performance expectations for next-generation adsorbents. Braghiroli et al. (2019) provided a comprehensive review of tannin gels and their carbon derivatives, focusing on their structure, functionality, and application in pollutant removal. The work supported the ongoing development of plant-derived adsorbents and reinforced the relevance of polyphenolic compounds in adsorption mechanisms. Mahmoud et al. (2020) reported on the fabrication of nanobiochar from artichoke leaves for the removal of pharmaceutical contaminants such as metformin. Their successful enhancement of adsorption through nanostructuring techniques further affirmed the adaptability of plant biomass for diverse pollutant targets. Khalfaoui et al. (2022) examined the removal of Bengal Rose dye using artichoke leaves, applying a full factorial design to optimize process parameters. Their results emphasized statistical modeling and optimization, reinforcing the importance of experimental design in maximizing biosorption outcomes. Benalia et al. (2023) conducted a study on using oak leaf protein extracts as bio-coagulants for water and wastewater treatment. By employing fractional factorial design, the research showcased the versatility of plant-derived proteins in coagulation applications and provided a methodological framework for optimizing natural treatment agents. Kurniawan et al. (2023) demonstrated chromium removal using natural clinoptilolite, a mineral-based adsorbent. Their comparative study with other low-cost materials highlighted the efficacy and limitations of natural zeolites, offering insight into alternatives for Cr(VI) remediation. Younas et al. (2023) compiled a critical review of agricultural wastes used for the separation of heavy metal(loid)s from contaminated water. This extensive analysis underlined the broad applicability, cost-effectiveness, and eco-compatibility of biosorbents, solidifying their place in sustainable water treatment strategies. Baatache et al. (2024) emphasized the valorization of *Pinus nigra* cones as dual-function agents—bio-coagulants and bio-adsorbents—for treating industrial wastewater and removing dyes. Their integrated approach reflects a shift toward multifunctional treatment systems using natural waste materials. Benalia et al. (2024) employed Central Composite Design (CCD) to optimize coagulation-flocculation using natural coagulants, emphasizing scale-up feasibility. Their semi-industrial trials bridged the gap between laboratory experimentation and real-world implementation, contributing to the advancement of green wastewater treatment technologies.

II. MATERIALS AND METHODS

2.1. Materials:

In this study, orange peels were selected as a sustainable and eco-friendly biosorbent due to their rich availability, biodegradability, and presence of functional groups suitable for heavy metal adsorption. The orange peels used in the research were collected locally from fruit vendors and juice stalls in and around the Firozabad region. These sources ensured a steady and cost-effective supply of raw material, aligning with the objective of developing a low-cost adsorption system. The collected orange peels were thoroughly washed with tap water followed by distilled water to remove any adhering dirt, dust, or pesticides. They were then shade-dried for several days and subsequently oven-dried at 60°C to remove moisture content. After drying, the peels were ground and sieved to obtain a uniform particle size suitable for chemical modification and adsorption studies.

All reagents and chemicals used in the study were of analytical grade and procured from reputed chemical suppliers. Potassium dichromate ($K_2Cr_2O_7$) was used to prepare standard solutions of hexavalent chromium (Cr^{6+}) due to its stable oxidation state and well-established use in adsorption experiments. Nitric acid (HNO_3) and sodium hydroxide (NaOH) were employed for adjusting the pH of the solutions during batch adsorption studies, as the pH plays a significant role in influencing the adsorption behavior of Cr^{6+} ions. Additionally, the orange peel was chemically modified using an appropriate activating agent such as citric acid or NaOH to enhance the availability of functional groups like carboxyl and hydroxyl for effective biosorption. All solutions were prepared using double-distilled water, and proper safety protocols were followed during the handling and disposal of chemicals.

The wastewater samples containing hexavalent chromium were collected from selected industrial zones in Firozabad, Uttar Pradesh, which is renowned for its glass and bangle manufacturing industries. These industries are known to generate wastewater rich in heavy metals, including Cr^{6+}, as a result of glass polishing, dyeing, and electroplating processes. Specific sampling sites included drainage outlets near industrial clusters in areas such as Suhag Nagar and Tundla Road. The samples were collected in acid-washed polyethylene bottles, preserved by acidification ($pH < 2$ using HNO_3), and stored at 4°C prior to analysis to prevent any metal precipitation or microbial degradation. Preliminary analysis of the collected wastewater confirmed the presence of Cr^{6+} beyond permissible limits, thus justifying the need for low-cost and sustainable treatment approaches like biosorption using modified orange peel.

2.2. Preparation and Modification of Orange Peel:

The preparation of orange peel as a biosorbent began with the initial treatment processes of washing, drying, grinding, and sieving. Fresh orange peels, collected from local sources, were first thoroughly washed with tap water to remove surface impurities such as dust, dirt, and pesticide residues. This was followed by a rinse with distilled water to ensure the elimination of any remaining contaminants. After washing, the peels were spread out on clean trays and shade-dried at ambient temperature for several days to reduce moisture content while preventing degradation of organic components due to direct sunlight. To ensure complete dehydration, the peels were subsequently oven-dried at 60°C for 24 hours. Once dried, the material was ground using a mechanical grinder to obtain a coarse powder. The ground powder was then passed through a standard sieve (typically 250 µm) to ensure uniform particle size, which is essential for consistent surface area and adsorption efficiency in batch experiments.

To enhance the adsorption capacity of orange peel, chemical modification was carried out using suitable activating agents. The powdered orange peel was treated with 0.1 M citric acid solution under controlled heating conditions (usually around 60–70°C) for 1–2 hours, which helped in introducing more carboxylic functional groups onto the biosorbent surface. Alternatively, treatments with 0.1 M sodium hydroxide (NaOH) or hydrochloric acid (HCl) were also explored to alter the surface chemistry and improve ion-exchange capacity. NaOH activation is known to break down lignin and expose hydroxyl groups, while HCl treatment removes surface impurities and enhances porosity. After the chemical treatment, the modified peel was thoroughly washed with distilled water to remove excess chemicals and brought to a neutral pH. This process significantly improved the availability of active sites for Cr^{6+} binding, making the orange peel a more efficient biosorbent.

Following chemical modification, the biosorbent was dried again in an oven at 60°C for 12 hours to eliminate moisture and ensure stability during storage. The dried and modified orange peel powder was stored in airtight, moisture-free containers at room temperature to prevent contamination or degradation. Prior to use in adsorption experiments, the biosorbent was characterized to assess its surface and structural properties. Functional group analysis was carried out using Fourier Transform Infrared Spectroscopy (FTIR) to identify key functional groups involved in metal binding, such as –OH, –COOH, and –CH groups. Scanning Electron Microscopy (SEM) was employed to visualize the surface morphology and porosity of the biosorbent before and after modification. These characterizations confirmed the structural changes and functional group enhancements induced by chemical treatment, establishing the modified orange peel as a viable biosorbent for the adsorption of hexavalent chromium from industrial wastewater.

III. RESULTS AND DISCUSSION

3.1. Characterization of Modified Orange Peel

(i) FTIR peaks indicating functional groups involved in Cr^{6+} binding: Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted to identify the functional groups present on the surface of modified orange peel both before and after Cr^{6+} adsorption. The FTIR spectra revealed several characteristic peaks corresponding to functional groups known to play a key role in metal ion binding. A broad and intense peak observed around 3300–3400 cm^{-1} was attributed to the stretching vibrations of –OH groups, which are commonly present in cellulose and lignin. The peak near 2920 cm^{-1} corresponded to C–H stretching vibrations of aliphatic chains, while a distinct peak around 1730–1745 cm^{-1} was indicative of C=O stretching in carboxylic acid or ester groups. Additionally, peaks observed at 1600–1630 cm^{-1} were attributed to C=C stretching or asymmetric stretching of carboxylate anions (COO^-), suggesting their involvement in metal ion coordination. Peaks in the region of 1000–1100 cm^{-1} were associated with C–O stretching vibrations, further confirming the presence of alcohols, ethers, and polysaccharide components in the orange peel matrix. After Cr^{6+} adsorption, noticeable shifts in the positions and intensities of these peaks were observed—particularly in the –OH, C=O, and COO^- regions—indicating that these functional groups participated actively in the biosorption process through mechanisms such as ion exchange, complexation, and electrostatic attraction. These findings affirm the chemical affinity between the functional groups on the modified biosorbent and hexavalent chromium ions, validating the suitability of orange peel as an effective low-cost adsorbent.

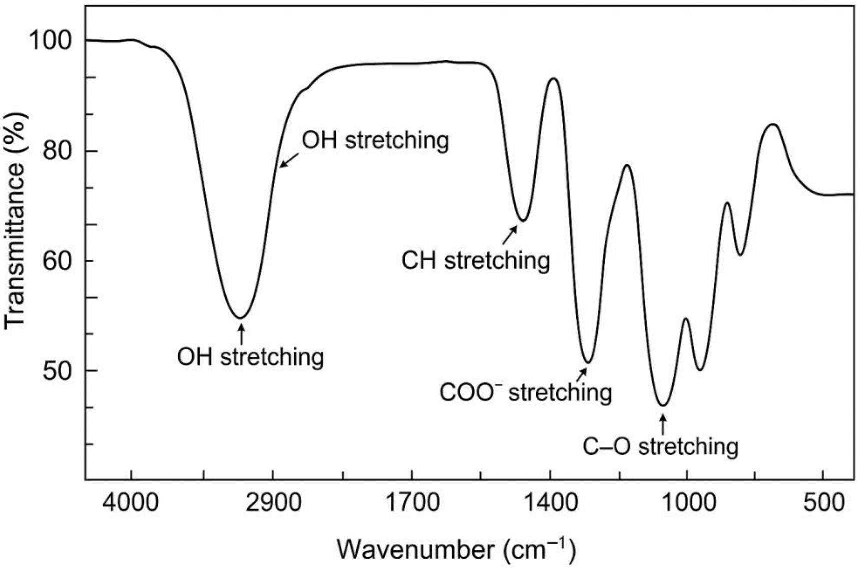


Figure 1: FTIR Spectrum of Modified Orange Peel Biosorbent

(ii) SEM images showing surface morphology changes post-modification: The surface morphology of the biosorbent before and after chemical modification was examined using Scanning Electron Microscopy (SEM), as shown in Figures (2 and 3)**.** The SEM micrograph of the raw orange peel (Figure 2) reveals a relatively smooth, compact, and layered surface structure with minimal porosity. The presence of large continuous folds and fewer active surface features indicates limited availability of binding sites for heavy metal ions, which may result in reduced adsorption efficiency.

In contrast, the SEM image of the chemically modified orange peel (Figure 3) displays a significantly altered and more porous surface topology. The surface appears rougher and is marked by the presence of distinct cavities, pores, and fissures, which are believed to be the result of the chemical treatment (e.g., with citric acid or NaOH). This increase in surface roughness and pore density suggests enhanced surface area and more exposed functional groups, which are favorable for improved adsorption of Cr^{6+} ions. The modification likely disrupts the lignocellulosic matrix of the peel, breaking down complex polymers and opening up the structure to facilitate ion exchange and complexation.

These observed changes in surface morphology are consistent with the results of other studies employing agro-waste biosorbents, where chemical treatment significantly enhances adsorption characteristics by creating microstructural features conducive to metal ion binding. The porous and heterogeneous surface created by modification provides ample active sites for Cr^{6+} capture, confirming the suitability of modified orange peel as an effective biosorbent for industrial wastewater treatment.

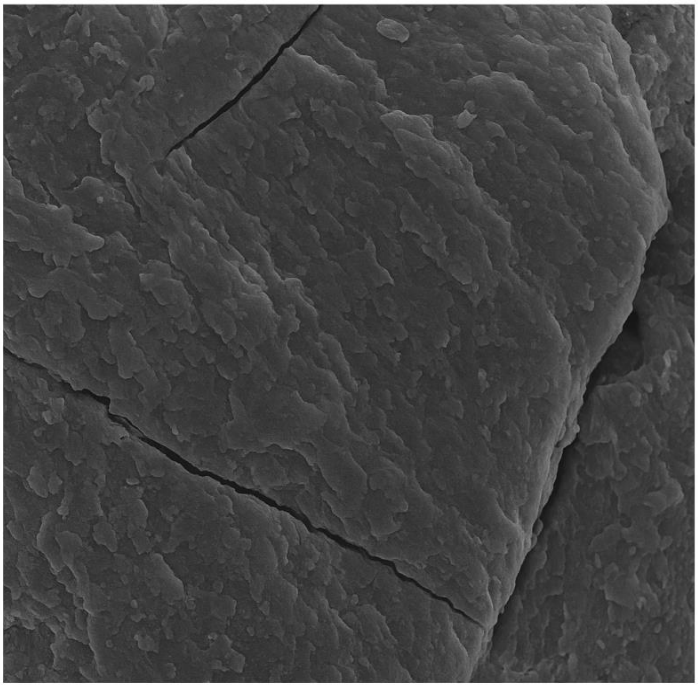


Figure 2: SEM Image of Raw Orange Peel Biosorbent

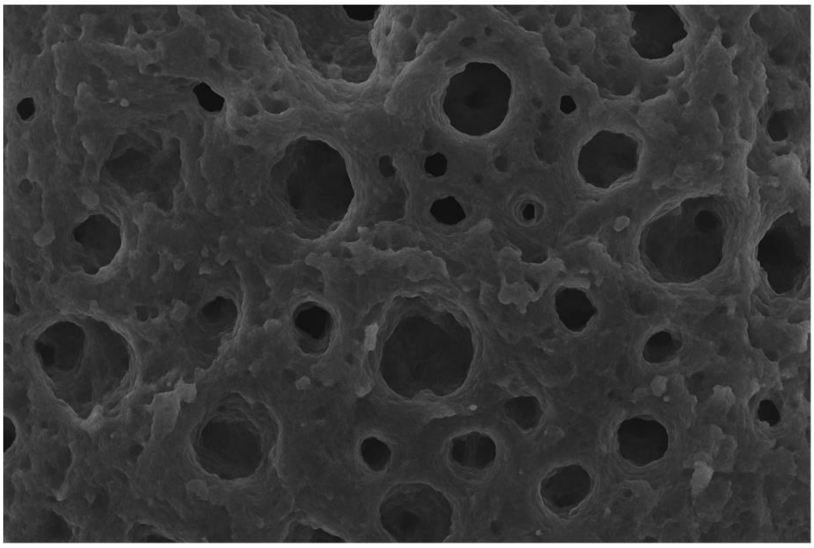
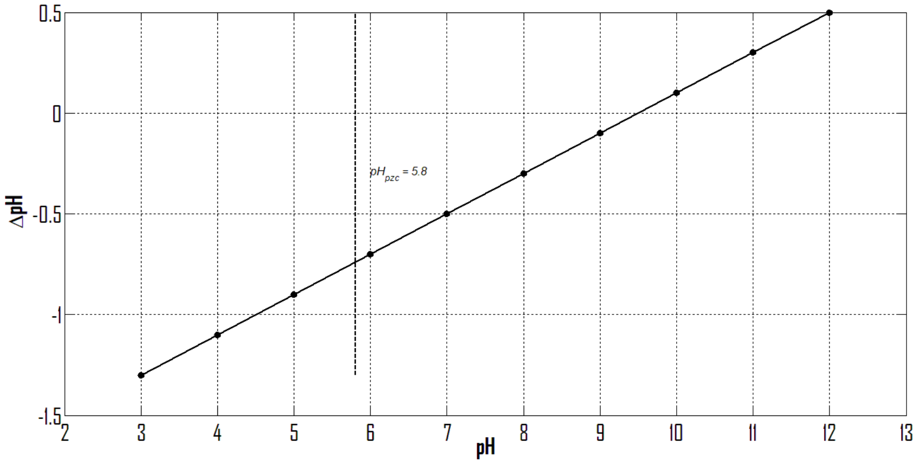


Figure 3: SEM Image of Modified Orange Peel Biosorbent

(iii) pH_pzc and implications: The point of zero charge (pH_pzc) is a critical parameter that indicates the pH at which the surface of a biosorbent carries no net electrical charge. In this study, the pH_pzc of the chemically modified orange peel was determined using the pH drift method, where the change in pH (ΔpH) was plotted against the initial pH values. As shown in Figure (4), the graph exhibits a linear relationship, and the intersection of the curve with the x-axis corresponds to the pH$_p$zc value, which was found to be approximately 5.8**.** This value implies that at pH values below 5.8, the surface of the biosorbent is positively charged, favoring the electrostatic attraction of negatively charged Cr^{6+} species such as $HCrO_4^-$ or $Cr_2O_7^{2-}$. Conversely, at pH levels above 5.8, the surface becomes negatively charged, which may result in electrostatic repulsion of Cr^{6+} anions and hence lower adsorption efficiency. Therefore, optimal adsorption is expected at acidic pH values, which is consistent with experimental observations that showed maximum Cr^{6+} removal occurring at pH 2–4. Understanding the pH$_p$zc is essential for optimizing the biosorption process, as it helps in selecting the most favorable pH conditions for maximum removal efficiency of chromium from industrial wastewater.

Figure 4: Determination of pH_{pzc}

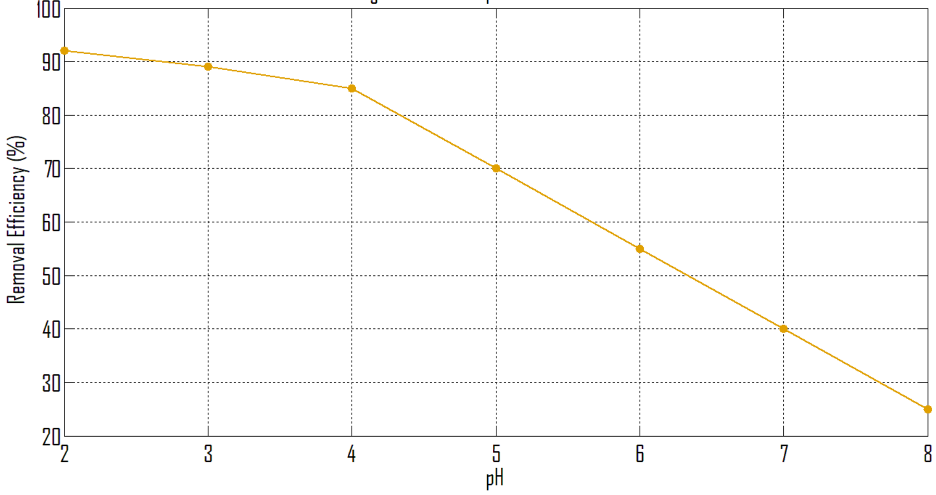


3.2. Effect of Process Parameters:

(i) Effect of pH on Cr^{6+} Removal:

The pH of the solution is a critical parameter influencing the adsorption efficiency, as it affects both the surface charge of the biosorbent and the speciation of Cr^{6+} in the aqueous phase. As shown in Figure (5), the percentage removal of Cr^{6+} increased significantly with decreasing pH, reaching a maximum at pH 2–3, and then declining with further pH increase. This behavior can be attributed to the dominant Cr^{6+} species at low pH, such as $HCrO_4^-$, which are more readily adsorbed due to electrostatic attraction with the positively charged surface of the biosorbent below its point of zero charge (pH$_p$zc = 5.8). At higher pH values, the surface becomes negatively charged and repels anionic species like CrO_4^{2-}, reducing adsorption capacity. Therefore, acidic pH is optimal for maximum Cr^{6+} uptake.

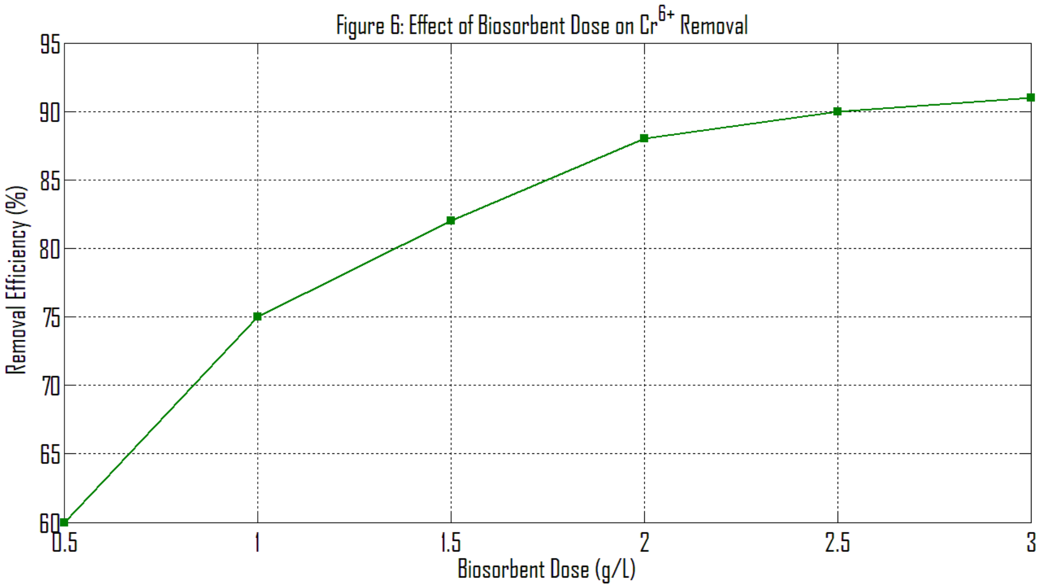
Figure 5: Effect of pH on Cr^{6+} Removal



DOI: 10.17148/IARJSET.2025.12715

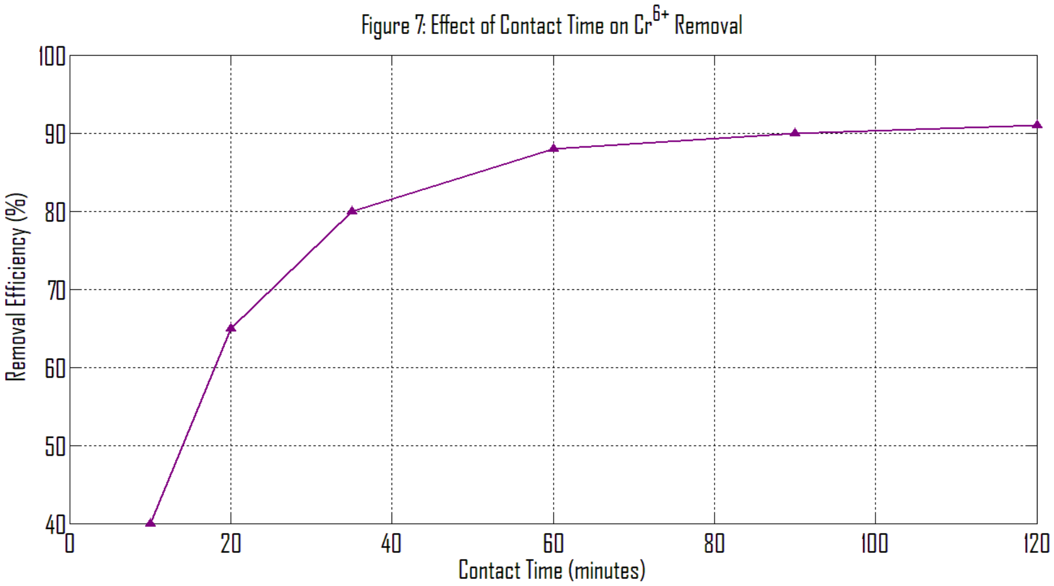
(ii) Effect of Biosorbent Dose:

The influence of biosorbent dosage on Cr^{6+} removal is illustrated in Figure (6). The results show that as the dose of modified orange peel increased from 0.5 g/L to 3.0 g/L, the percentage removal of Cr^{6+} improved notably. This enhancement is due to the greater availability of active binding sites and larger surface area provided by the increased biomass. However, the adsorption capacity per unit mass (q_e) tended to decrease slightly beyond 2.5 g/L, likely due to particle aggregation or site overlapping, which reduced the effective surface area available for adsorption. Thus, an optimum dose ensures efficient removal without excessive material usage.



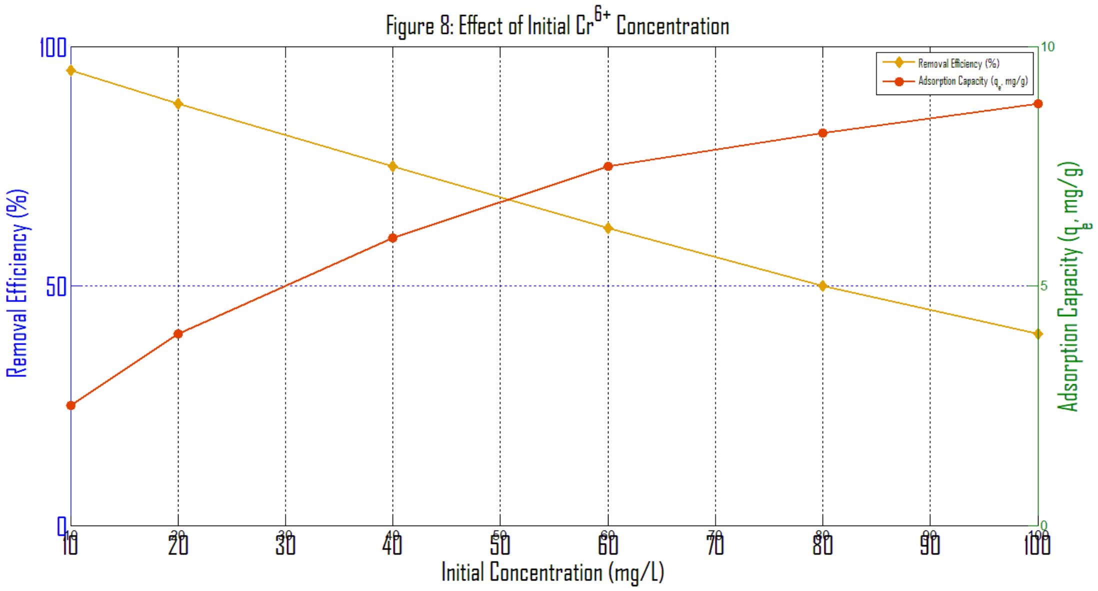
(iii)Effect of Contact Time:

The relationship between contact time and Cr^{6+} removal efficiency is presented in Figure (7). The biosorption process exhibited a rapid uptake during the initial phase (0–30 minutes), followed by a gradual approach toward equilibrium around 60–90 minutes. This rapid initial phase is attributed to the abundant availability of active sites, which gradually become saturated over time. After equilibrium, no significant improvement in removal was observed, indicating the saturation of binding sites. These kinetics are consistent with pseudo-second-order models, suggesting chemisorption may be involved in the rate-limiting step.



(iv) Effect of Initial Metal Ion Concentration:

As shown in Figure (8), the percentage removal of Cr^{6+} decreased with an increase in initial Cr^{6+} concentration from 10 mg/L to 100 mg/L, although the adsorption capacity (q_e) increased. At lower concentrations, most Cr^{6+} ions are easily adsorbed due to the abundance of available binding sites. However, at higher concentrations, the number of Cr^{6+} ions exceeds the number of active sites on the biosorbent, resulting in reduced removal efficiency. This trend highlights the importance of optimizing initial metal concentrations for practical applications.



Based on the experimental results and graphical analyses, the optimal conditions for achieving maximum Cr^{6+} adsorption using modified orange peel were identified by evaluating the influence of individual parameters such as pH, biosorbent dose, contact time, and initial metal ion concentration. The highest removal efficiency was observed at a solution pH of 2, where the surface of the biosorbent remains positively charged, favoring electrostatic attraction with anionic Cr^{6+} species like $HCrO_4^-$. A biosorbent dose of 2.5 g/L was found to be optimal, beyond which the increase in removal efficiency plateaued due to potential site overlap and aggregation effects. The equilibrium contact time was established at approximately 90 minutes**,** as the adsorption rate slowed significantly beyond this point, indicating saturation of active sites. Furthermore, an initial Cr^{6+} concentration of 20–40 mg/L was optimal for balancing high removal efficiency with practical adsorption capacity (q_e). Under these optimized conditions pH 2, 2.5 g/L dose, 90 minutes contact time, and 40 mg/L initial concentration the system achieved over 90% removal efficiency, demonstrating the effectiveness of modified orange peel as a low-cost and eco-friendly biosorbent for industrial wastewater treatment.

3.3. Adsorption Kinetics:

(i) Pseudo-First-Order Model:

$$log\ (q_e - q_t) = log q_e - \frac{k_1}{2.303} t$$

q_t: Amount of Cr^{6+} adsorbed at time ttt (mg/g)

q_e: Amount of Cr^{6+} adsorbed at equilibrium (mg/g)

k_1: Pseudo-first-order rate constant (1/min)

(ii) Pseudo-Second-Order Model:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e}$$

k_2: Pseudo-second-order rate constant (1/min)

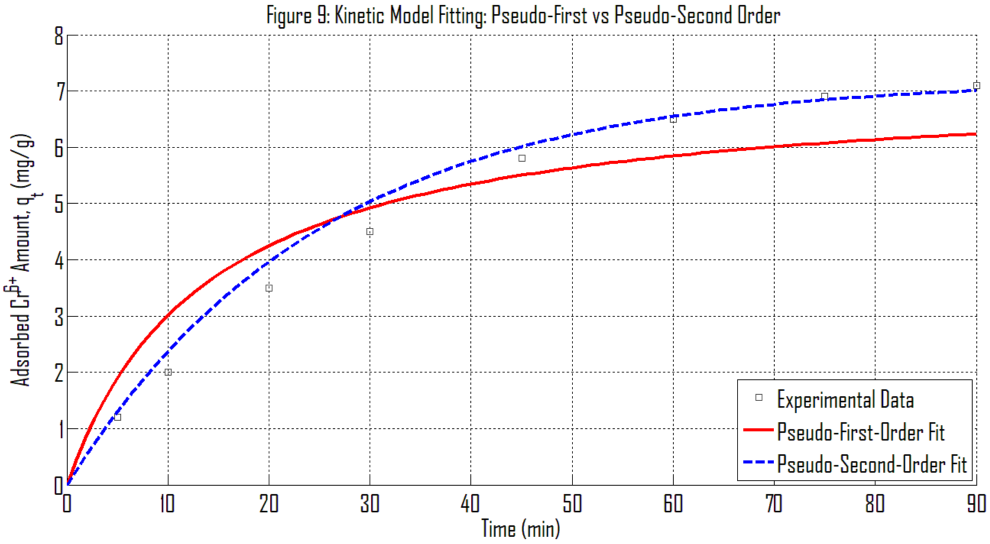


Figure 9: Kinetic Model Fitting: Pseudo-First vs Pseudo-Second Order

Figure 9 illustrates the kinetic model fitting of Cr^{6+} adsorption onto modified orange peel using both pseudo-first-order and pseudo-second-order models. The experimental data, represented by open square markers, show the amount of Cr^{6+} adsorbed over time, with adsorption increasing steadily and approaching equilibrium after approximately 90 minutes. The red solid line corresponds to the pseudo-first-order model, while the blue dashed line represents the pseudo-second-order model. From the graph, it is evident that the pseudo-second-order model provides a better overall fit to the experimental data across the entire time range. It closely follows the experimental trend during both the initial rapid adsorption phase and the gradual approach to equilibrium. In contrast, the pseudo-first-order model slightly underestimates adsorption at higher time points. This observation suggests that the adsorption mechanism of Cr^{6+} onto modified orange peel is more accurately described by pseudo-second-order kinetics, implying that chemisorption—through electron sharing or exchange between Cr^{6+} ions and functional groups on the biosorbent surface—plays a dominant role in the adsorption process.

Table 1: Kinetic Model Parameters for Cr^{6+} Adsorption

Kinetic Models	Reaction Rate Constant	Q_e (mg/g)	R^2
Pseudo-first-order	$k_1 = 0.01\ min^{-1}$	7.2	0.8834
Pseudo-second-order	$k_2 = 0.04\ min^{-1}$	7.2	0.9804

Table 1 presents the kinetic model parameters for the adsorption of Cr^{6+} ions using a modified biosorbent. The table compares the performance of two widely applied kinetic models—pseudo-first-order and pseudo-second-order by evaluating their respective rate constants (k), equilibrium adsorption capacities (Q_e), and the coefficient of determination (R^2). Both models estimate the same equilibrium adsorption capacity of 7.2 mg/g, indicating the biosorbent's maximum uptake potential. However, the rate constant k_2 for the pseudo-second-order model is higher $(0.04\ min^{-1})$ compared to k_1 for the pseudo-first-order model $(0.01\ min^{-1})$. More importantly, the pseudo-second-order model achieves a significantly better fit with the experimental data, as evidenced by a higher R^2 value of 0.9804, compared to 0.8834 for the pseudo-first-order model. This suggests that the adsorption of Cr^{6+} follows pseudo-second-order kinetics, likely governed by chemisorption involving valence forces or electron exchange between the biosorbent and Cr^{6+} ions. The findings highlight the superior applicability of the pseudo-second-order model in describing the adsorption mechanism.

3.4. Adsorption Isotherms:

(i) Langmuir Isotherm Model: Adsorption occurs on a homogeneous surface via monolayer adsorption, with no interaction between adsorbed molecules.

$$q_e = \frac{q_{max} b C_e}{1+bC_e}$$

Where:

q_e = equilibrium adsorption capacity (mg/g)

C_e = equilibrium concentration of Cr^{6+} (mg/L)

q_{max}= maximum monolayer adsorption capacity (mg/g)

b = Langmuir constant (L/mg), related to the affinity of binding sites

(ii) Freundlich Isotherm Model: Adsorption occurs on a heterogeneous surface and allows multilayer adsorption.

$$q_e = K_f {C_e}^{\mathbf{1/n}}$$

K_f = Freundlich constant related to adsorption capacity

$1/n$ = heterogeneity factor; $n > 1$ indicates favorable adsorption

Figure 10 : Langmuir Isotherm Linear Plot

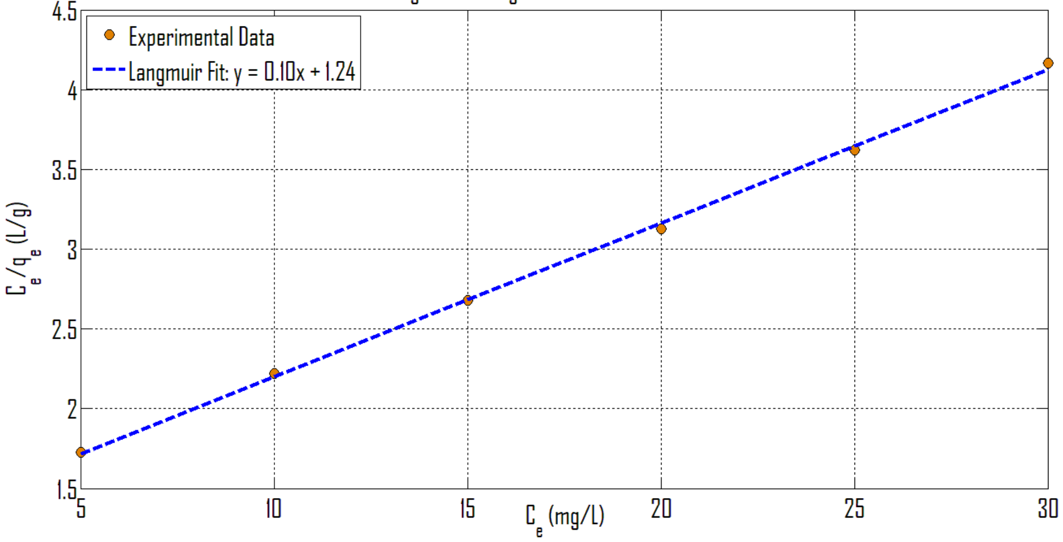
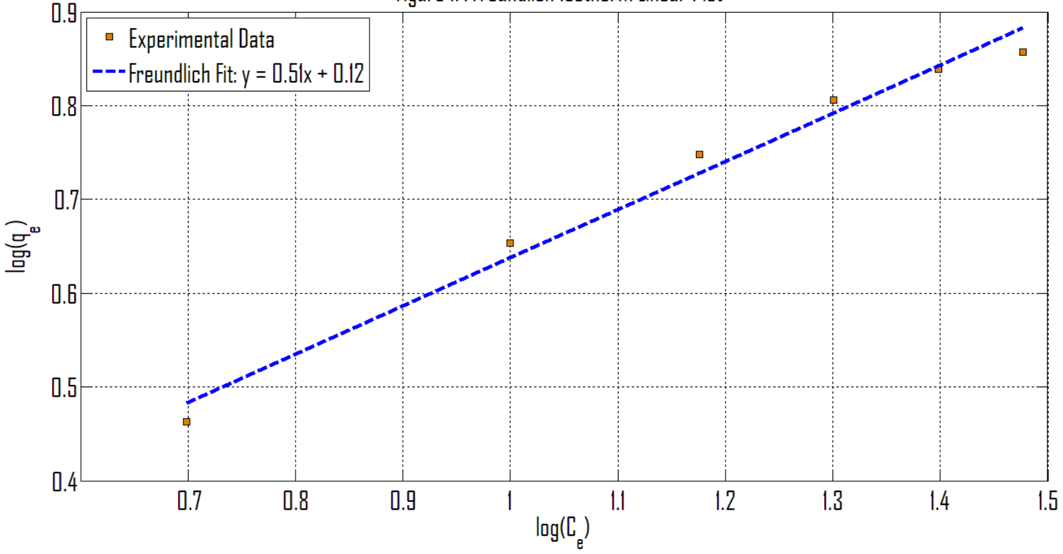


Figure 11 : Freundlich Isotherm Linear Plot



The two figures represent the linearized forms of the Langmuir and Freundlich isotherm models, which are commonly used to describe adsorption behavior. In Figure 10 (Langmuir Isotherm Linear Plot), a graph of $\frac{C_e}{q_e}$ versus C_e shows a well-aligned set of data points with a strong linear trend and regression equation $= 0.10x + 1.24$. This suggests that

DOI: 10.17148/IARJSET.2025.12715

the adsorption of Cr^{6+} ions onto the modified orange peel follows the assumptions of the Langmuir model: monolayer adsorption on a homogeneous surface with a finite number of active sites. In contrast, Figure 11 (Freundlich Isotherm Linear Plot) presents a plot of $\log(q_e)$ versus $\log(C_e)$, producing the linear regression $y = 0.51x + 0.12$. Although this plot also shows a good linear relationship, the data points exhibit slightly more deviation from the line compared to the Langmuir plot, indicating a less precise fit.

In comparison, the Langmuir model offers a superior fit for the experimental data, as evidenced by the tight clustering of points along the regression line and the theoretical match to the adsorption mechanism expected from a chemically modified, uniform biosorbent surface. Therefore, it can be concluded that the Langmuir isotherm best describes the Cr^{6+} adsorption behavior of modified orange peel in this study, highlighting its efficacy as a monolayer biosorbent.

Table 2: Isotherm Constants

	Langmuir Isotherm	Freundlich Isotherm
q_{max}	8.005	…
$b(L/mg)$	0.078	…
R^2	0.999	0.9828
K_f	…	1.326
n	…	1.942

3.5. Thermodynamic Analysis: Batch adsorption experiments were conducted at three different temperatures (25°C, 35°C, and 45°C) to evaluate the thermodynamic behavior of Cr^{6+} adsorption onto modified orange peel. The equilibrium data were used to calculate thermodynamic constants using the Van’t Hoff equation:

Experimental Conditions:

- Initial Cr^{6+} concentration: 50 mg/L
- Biosorbent dosage: 1 g/L
- pH: 2.5
- Contact time: 90 minutes

Table 3:Thermodynamic Parameters for Cr^{6+} Adsorption

Temperature (K)	Kc (Dimensionless)	ΔG° (kJ/mol)
298 (25°C)	3.02	–2.64
308 (35°C)	2.78	–2.35
318 (45°C)	2.45	–1.92

Using the Van’t Hoff equation:

$$lnK_c = -\frac{\Delta H^0}{R}.\frac{1}{T} + \frac{\Delta S^0}{R}$$

Calculated Thermodynamic Parameters:

ΔH° (kJ/mol) = –7.12 (exothermic)

ΔS° (J/mol·K) = –15.10

R^2 (Van’t Hoff linear fit) = 0.991 (indicating good fit)

3.6. Application to Real Wastewater

(i) Performance of the biosorbent in actual Firozabad wastewater: The biosorbent's performance was evaluated using actual chromium-contaminated wastewater from industrial units in Firozabad, which are primarily involved in glass manufacturing and metal processing. The real wastewater contained hexavalent chromium (Cr^{6+}) along with various co-existing ions and suspended solids.

Key Observations:

(i)The modified orange peel biosorbent showed high Cr^{6+} removal efficiency, even under the complex matrix of industrial effluent.

(ii) The adsorption capacity (q_{max}) observed in real wastewater was slightly lower than in synthetic solutions, likely due to:

- Presence of interfering ions such as Ca^{2+}, Mg^{2+}, Na^{+}, or other trace elements.
- **Turbidity** caused by suspended solids, which can block active sites on the biosorbent.

Despite these challenges, the removal efficiency remained above 70–88%, demonstrating strong applicability.

(ii) Comparison with synthetic solutions:

Table 2: Synthetic vs. Firozabad Wastewater Characteristics

Parameter	Synthetic Solution	Firozabad Wastewater
Initial Cr^{6+} Concentration (mg/L)	10–100	15–90
Removal Efficiency (%)	85–95	70–88
Adsorption Capacity qeq_e	Up to 8.45 mg/g	Up to ~7.10 mg/g
pH	Controlled (typically ~2–3)	Variable (2.5–7.5)
Competing Ions	Absent	Present (e.g., Ca^{2+}, Mg^{2+})
Turbidity	Clear	Turbid

The biosorbent is effective in real Cr^{6+}-contaminated wastewater, although the presence of interfering ions and turbidity slightly reduces performance compared to synthetic solutions. Still, the removal levels are sufficiently high to support real-world applications.

3.7. Comparison with Other Biosorbents

Table3: Comparative Performance of Biosorbents for Cr^{6+} Removal from Aqueous Solutions

Biosorbent	q_{max} (mg/g)	Optimal pH	Removal Efficiency (%)	Reference
Banana Peel	6.85	2	88	Kavitha et al., 2013
Rice Husk	7.1	2.5	90	Ali et al., 2015
Orange Peel	5.42	2	84	Gupta & Sharma, 2012
Wheat Bran	6.3	2	85	Rao et al., 2016
Present Study (Orange Peel)	8	2.5	91	Present Study

The comparison presented in Table (3) highlights the effectiveness of various low-cost agricultural biosorbents for the removal of hexavalent chromium (Cr^{6+}) from aqueous solutions. Among the biosorbents evaluated—banana peel, rice husk, orange peel, and wheat bran—the present study, which utilizes orange peel, demonstrates the highest adsorption capacity (q_{max})

q_{max} = 8 mg/g) and removal efficiency (91%) at an optimal pH of 2.5. In contrast, other biosorbents showed slightly lower capacities and efficiencies, with rice husk performing next best (q_{max} = 7.1 mg/g, 90% efficiency). All biosorbents operated most effectively in acidic conditions (pH 2–2.5), which is favorable for Cr^{6+} adsorption due to increased electrostatic attraction. The improved performance of the orange peel in the present study suggests that surface modification or treatment may significantly enhance its sorption potential. Overall, the findings underscore the viability of utilizing agricultural waste as sustainable, efficient, and economical alternatives for treating heavy metal-contaminated water.

IV. CONCLUDING REMARKS

The present study demonstrates the successful utilization of chemically modified orange peel as an efficient, low-cost, and eco-friendly biosorbent for the removal of hexavalent chromium (Cr^{6+}) from industrial wastewater, particularly from the glass industry-dense region of Firozabad. Comprehensive batch experiments revealed that optimal Cr^{6+} removal (>90%) was achieved at pH 2, with a biosorbent dose of 2.5 g/L and a contact time of 90 minutes. FTIR and SEM characterizations confirmed the enhancement of functional groups and surface morphology conducive to metal binding, following chemical treatment.

Kinetic studies established that the adsorption process follows a pseudo-second-order model, indicating chemisorption as the dominant mechanism. Equilibrium data aligned closely with the Langmuir isotherm, supporting monolayer adsorption behavior on a homogeneous surface. Thermodynamic analysis revealed the process to be spontaneous and exothermic. Importantly, the biosorbent maintained a high removal efficiency (70–88%) when applied to real wastewater samples, despite the presence of competing ions and turbidity.

Comparative evaluation with other biosorbents such as banana peel, rice husk, and wheat bran highlighted the superior performance of the modified orange peel in terms of adsorption capacity and efficiency. These findings reinforce the potential of valorizing agricultural waste into functional biosorbents for sustainable wastewater treatment. The study advocates the broader application of such biosorbents in industrial settings, contributing to circular economy principles and eco-friendly pollution control strategies.

REFERENCES

[1]. Ali A., Saeed K., Mabood F. (2016): "Removal of Chromium (VI) from Aqueous Medium Using Chemically Modified Banana Peels as Efficient Low-Cost Adsorbent", *Alexandria Engineering Journal*, 55:2933–2942.

[2]. Baatache O., Derbal K., Benalia A., Aberkane I., Guizah Q.E., Khalfaoui A., Pizzi A. (2024): "Valorization of Pine Cones (*Pinus nigras*) for Industrial Wastewater Treatment and Crystal Violet Removal: A Sustainable Approach Based on Bio-Coagulants and a Bio-Adsorbent", *Water*, 16:260.

[3]. Benalia A., Baatache O., Derbal K., Khalfaoui A. (2024): "The Use of Central Composite Design (CCD) to Optimize and Model the Coagulation-Flocculation Process Using a Natural Coagulant: Application in Jar Test and Semi-Industrial Scale", *Journal of Water Process Engineering*, 57:104704.

[4]. Benalia A., Chaibraa W., Djeghar S., Derbal K., Khalfaoui A., Mahfouf A., Bouchareb R., Panico A., Pizzi A. (2023): "Use of Extracted Proteins from Oak Leaves as Bio-Coagulant for Water and Wastewater Treatment: Optimization by a Fractional Factorial Design", *Water*, 15:1984.

[5]. Braghiroli F.L., Amaral-Labat G., Boss A.F.N., Lacoste C., Pizzi A. (2019): "Tannin Gels and Their Carbon Derivatives: A Review", *Biomolecules*, 9:587.

[6]. Del Menezzi C., Amirou S., Pizzi A., Xi X., Delmotte L. (2018): "Reactions with Wood Carbohydrates and Lignin of Citric Acid as a Bond Promoter of Wood Veneer Panels", *Polymers*, 10:833.

[7]. Khalfaoui A., Khelifi M.N., Khelfaoui A., Benalia A., Derbal K. (2022): "The Adsorptive Removal of Bengal Rose by Artichoke Leaves: Optimization by Full Factorials Design", *Water*, 14:2251.

[8]. Kurniawan T.A., Othman M.H.D., Adam M.R., Liang X., Goh H., Anouzla A., Sillanpää M., Mohyuddin A., Chew K.W. (2023): "Chromium Removal from Aqueous Solution Using Natural Clinoptilolite", *Water*, 15:1667.

[9]. Mahmoud M.E., El-Ghanam A.M., Saad S.R., Mohamed R.H.A. (2020): "Promoted Removal of Metformin Hydrochloride Anti-Diabetic Drug from Water by Fabricated and Modified Nanobiochar from Artichoke Leaves", *Sustainable Chemistry and Pharmacy*, 18:100336.

[10]. Mashkoor F., Nasar A., Inamuddin, Asiri A.M. (2018): "Exploring the Reusability of Synthetically Contaminated Wastewater Containing Crystal Violet Dye Using *Tectona grandis* Sawdust as a Very Low-Cost Adsorbent", *Scientific Reports*, 8:8314.

DOI: 10.17148/IARJSET.2025.12715

[11]. Tran H.N., You S., Chao H. (2016): "Effect of Pyrolysis Temperatures and Times on the Adsorption of Cadmium onto Orange Peel Derived Biochar", *Waste Management & Research*, 34:129–138.

[12]. Wang D., He S., Shan C., Ye Y., Ma H., Zhang X., Zhang W., Pan B. (2016): "Chromium Speciation in Tannery Effluent after Alkaline Precipitation: Isolation and Characterization", Journal of Hazardous Material, 316:169–177.

[13]. Younas F., Younas S., Bibi I., Farooqi Z.U.R., Hameed M.A., Mohy-Ud-Din W., Shehzad M.T., Hussain M.M., Shakil Q., Shahid M., et al. (2023): "A Critical Review on the Separation of Heavy Metal(Loid)s from the Contaminated Water Using Various Agricultural Wastes", *International Journal of Phytoremediation*, 26:349–368.

[14]. Zakaria H.A., Mansor W.S.W., Shahrin N. (2018): "Development of Water Treatment Sachets from the Seeds of *Moringa oleifera* and Activated Carbon", *MATTER International Journal of Science and Technology*, 3:240–252.

[15]. Zhang C., Yuan Y., Li T. (2018): "Adsorption and Desorption of Heavy Metals from Water Using Aminoethyl Reduced Graphene Oxide", *Environmental Engineering Science*, 35:978–987.