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Rapid Physisorption of Cr(VI) Using Cassava Peel Biosorbents: Kinetics, Isotherm Analysis and Mechanistic Insights

Karthika Ayyar[1], Priyadharshini Senthilkumar[2], Karnika Sivavadivel[2], Janashruthi Karthikeyan[2], Sivaprakash Sivasamy[2], Vinetha Mayilesan[2], Rengesh Balakrishnan*[2]

[1]*Kamaraj College of Engineering and Technology, Department of Biotechnology, Tamil Nadu, India, karthikaayyar.128@gmail.com*
[2]*K.S.Rangasamy College of Technology, Department of Biotechnology, Tamil Nadu, India, pd7462942@gmail.com*
[3]*K.S.Rangasamy College of Technology, Department of Biotechnology, Tamil Nadu, India, karnikakaar@gmail.com*
[4]*K.S.Rangasamy College of Technology, Department of Biotechnology, Tamil Nadu, India, shruthikarthikeyan22@gmail.com*
[5]*K.S.Rangasamy College of Technology, Department of Biotechnology, Tamil Nadu, India, smileysiva2002@gmail.com*
[6]*K.S.Rangasamy College of Technology, Department of Biotechnology, Tamil Nadu, India, manivinitha185@gmail.com*
[7]*K.S.Rangasamy College of Technology, Department of Biotechnology, Tamil Nadu, India, rengeshb@gmail.com*

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Abstract

Increasing environmental concerns and strict discharge regulations have driven the need for efficient and low-cost treatment methods for industrial effluents. Chromium, particularly in its hexavalent form [Cr(VI)], is one of the most hazardous pollutants present in wastewater due to its high toxicity and carcinogenic nature. This study explores the potential of cassava peels (*Manihot esculenta*), an abundant agricultural byproduct, as a biosorbent for the rapid removal of Cr(VI) from aqueous solutions. Batch adsorption experiments were conducted to assess the influence of various parameters, including adsorbent dosage, initial Cr(VI) concentration, pH, and contact time. Optimal removal was observed at pH 2, with a contact time of just 5 min and an adsorbent dosage of 16 $g.L^{-1}$, achieving a maximum removal efficiency of 99.53 %. Adsorption equilibrium data were evaluated using Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models. Among these, the Langmuir model provided the best fit, indicating monolayer adsorption, with a maximum adsorption capacity of 5.076 $mg.g^{-1}$. The mean adsorption energy calculated from the Dubinin-Radushkevich model (E = 0.997 $kJ.mol^{-1}$) confirmed that the process was dominated by physisorption. Kinetic analysis showed a strong correlation with the pseudo-second-order model (R^2 = 1.0), suggesting that the rate-limiting step involves surface interaction between the Cr(VI) ions and functional groups on the cassava peel surface. These findings highlight cassava peels as a promising, renewable, and cost-effective material for the rapid removal of Cr(VI) from industrial wastewater, particularly under acidic conditions.

1. Introduction

Industrial wastewater from electroplating, textile, leather tanning, and mining operations contains high concentrations of toxic heavy metals such as cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), arsenic (As), lead (Pb), and zinc (Zn) [21]. These metals are non-biodegradable and persist in the environment, accumulating in water bodies and eventually entering the food chain [31]. Chronic exposure to heavy metals in humans leads to severe health disorders, including organ damage, neurological impairments, and cancer [47]. Therefore, effective wastewater treatment is crucial to mitigate environmental and public health risks. Among heavy metals, chromium (Cr) is a major pollutant in industrial effluents, with global production exceeding 107 tons annually [13]. Approximately 15 % of produced chromium is utilized in industries such as leather tanning, electroplating, textiles, pigments, and wood preservation, while 60–70 % is used in alloy manufacturing [13]. The permissible limit of chromium

in industrial wastewater is 0.5 $mg.L^{-1}$, as concentrations above this threshold are carcinogenic [55].

Chromium primarily exists in two stable oxidation states in aquatic environments: trivalent Cr(III) and hexavalent Cr(VI). While Cr(III) is an essential micronutrient involved in carbohydrate metabolism and insulin regulation in mammals [49], Cr(VI) is more toxic due to its high solubility (1680 $g.L^{-1}$) and mutagenic properties [26]. Prolonged exposure to Cr(VI) causes severe health effects, including nausea, lung carcinoma, and epigastric pain [41]. The Agency for Toxic Substances and Disease Registry (ATSDR) ranks Cr(VI) as the 16^{th} most hazardous substance [40]. Given its extreme toxicity, there is an urgent need to treat industrial effluents containing Cr(VI) concentrations exceeding permissible limits. Hexavalent chromium is not only carcinogenic but also mutagenic and teratogenic, meaning it can cause genetic mutations and developmental defects in addition to cancers. Even low-level exposure to Cr(VI) has been associated with DNA damage and embryo toxicity, highlighting the imperative to eliminate this contaminant from water sources [52].

Wastewater remediation poses significant challenges due to its complex and variable composition [3]. To meet regulatory discharge standards, industries employ multiple physicochemical treatment methods, including: Ion exchange, reverse osmosis, chemical precipitation, electrodialysis, membrane filtration [12]. While these methods are effective for heavy metal removal, they suffer from drawbacks such as high operational costs, sludge generation, and inefficiency at low metal concentrations [48]. Consequently, there is a growing demand for cost-effective and sustainable alternatives, particularly for chromium (Cr) removal. Biosorption is the use of biological materials to adsorb metal pollutants and has emerged as an eco-friendly and economical solution [50]. Studies have demonstrated the effectiveness of various low-cost adsorbents, including: eucalyptus bark [44], leechi fruit peel [43], sugarcane bagasse charcoal [16], oil palm fiber [30], yellow mustard seeds [45].

Cassava peels (*Manihot esculen*ta), an agro-industrial byproduct abundantly available in tropical and subtropical zones, form the core of this study [6]. Representing approximately 20–30% of the total tuber mass, these peels are produced in large volumes by starch and garri processing units and are often either discarded or utilized as livestock feed [28]. Rich in functional groups such as –OH, –COOH, and –CHO, cassava peels offer promising sites for heavy metal binding, both in their raw and modified states [28]. Their naturally high surface area, porosity, and consistent availability contribute to their appeal as an economical biosorbent [18]. Analogous to the role of rice husk ash in enhancing the consolidation behavior of cohesive soils through its interaction with soil particles and surface chemistry [33], the biosorptive effectiveness of cassava peel is significantly influenced by its textural and chemical characteristics. Moreover, considering the relevance of well-defined design parameters in optimizing wastewater treatment performance [32], cassava peel-based biosorbents hold great potential for integration into sustainable treatment frameworks, particularly targeting Cr(VI) removal under acidic conditions.

Adsorption capacity is the distinctive property of the adsorbent. Adsorption capacity is defined as the amount of adsorbate adsorbed per gram of the adsorbent. Langmuir and Freundlich adsorption isotherm are widely used to study the adsorption capacity of the adsorbent [22]. It is influenced by properties like pH, surface functional group, temperature, specific surface area, pore and particle size distribution [18].

Cassava peel (*Manihot esculenta*) has been explored as an economical biosorbent for heavy metal removal [23, 57], but no studies to date have examined its ability to achieve near-complete Cr(VI) uptake within minutes. To address this gap, the present work investigates the rapid adsorption of Cr(VI) using cassava peel, focusing on kinetics and mechanism. The novelty of this study lies in the exceptionally fast removal (approx. 99% in 5 mins) and analysis of the physisorption mechanism, which have not been reported previously. The aim of our research is to evaluate the efficacy of cassava peel in rapid Cr(VI) remediation, and our specific objectives are: to assess the effects of dosage, concentration, pH, and time on Cr(VI) removal; to model the adsorption kinetics and isotherms; and to elucidate the adsorption mechanism through isotherm modeling and supporting analyses.

2. Materials and Methods

2.1. Bio-sorbent

The cassava peels (*Manihot esculenta*) were collected from local market located near Thirupur, Tamil Nadu. The samples were washed with double distilled water and it was allowed to dry under sun light until it was fully dried. The samples were then milled using Ball mill to increase the surface area of the particles. The sample powder was retained between the mesh size of 600 μm and 300 μm in the multiple sieve analysis.

2.2. Preparation of reagents

2.2.1. Preparation of diphenylcarbazide

0.5 g of 1,5-diphenylcarbazide was prepared in 100 mL of acetone and the solution was made up to 200 mL with double distilled water. Prepared reagent was stored in brown bottle and it was stored in refrigerator.

2.2.2. Preparation of 1 N Sulphuric acid

36 N of concentrated sulphuric acid was used to prepare 1 N sulphuric acid. 150 mL of double distilled water was taken in a 250 mL measuring cylinder. 6.9 mL of concentrated H_2SO_4 was added to the measuring flask and the solution was made up to 250 mL with double distilled water. This acid serves only to modulate pH; the final sulfuric acid concentration in solution is low, and no change in chromium's oxidation state (Cr(VI) remains in the hexavalent form) was observed as a result of the pH adjustment.

2.2.3. Preparation of standard potassium dichromate solution

50 mg.L^{-1} potassium dichromate stock solution was prepared with double distilled water. Standard was plotted between the concentrations ranging from 0.75 mg.L^{-1} to 50 mg.L^{-1} by diluting the stock solution. 10 mL of standard solution of $K_2Cr_2O_7$ was transferred to a volumetric flask. 2 mL of 1, 5-diphenylcarbazide reagent was added to the standard solutions and it was mixed well. 5 mL of 1 N H_2SO_4 solution was added dropwise and the solution was made upto 25 mL with double distilled water. The solution was let to stand for 5 min for full colour development. The peak was observed at 544 nm and therefore the absorbance for all the solutions were measured at 544 nm.

2.3. Batch Sorption studies

2.3.1. Experimental Procedure

All the experiments were done with double distilled water. Experiments were carried out with 250 mL Erlenmeyer flask. These experiments were done by varying the various different parameters like absorbent concentration, initial chromium concentration, pH and time. The effect of adsorbent concentration was investigated by varying the concentration from 2 to 80 g.L^{-1} by keeping other parameters constant. The initial chromium concentration was varied from 10 to 100 mg.L^{-1}. The pH was varied from 2 to 11 and time from 5 min to 95 min. The samples were filtered using Whattman no1 filter paper after the batch sorption process. The filtrate was analyzed by UV-Visible spectrophotometer at 544 nm using 1,5-diphenylcarbazide assay.

2.3.2. Removal efficiency of Cr(VI)

The formula to calculate the removal percentage of Cr(VI) and the amount of Cr(VI) adsorbed per gram of the adsorbent reported by [38] is given as follows:

$$\%\ Removal\ of\ Cr(VI) = \frac{C_0 - C_e}{C_e} \times 100 \quad (1)$$

C_0 - Initial Cr(VI) concentration (mg.L^{-1}), C_e - Cr(VI) concentration after the batch sorption process (mg.L^{-1}).

$$q = \frac{C_0 - C_e}{W} \times V \quad (2)$$

Q - Amount of Cr(VI) taken up by the adsorbent (mg.g^{-1}), V - Volume of Cr(VI) solution (L) and W – mass of adsorbent (g).

3. Results and Discussion

3.1. Potassium dichromate standard

The linear relationship between potassium dichromate concentration and absorbance (Figure 1) confirms the validity of the colorimetric method for Cr(VI) quantification [7]. The high regression coefficient (R^2 > 0.9998) indicates excellent method precision.

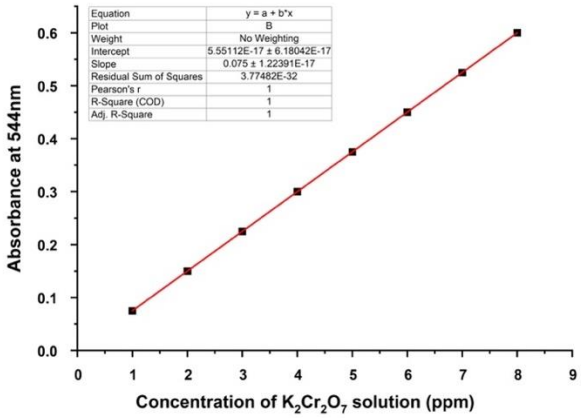

Figure 1. The relationship between the concentration of potassium dichromate and its corresponding absorbance by using colorimetric method.

3.2. Effect of adsorbent concentration

The effect of adsorbent concentration in the removal of Cr(VI) were investigated by varying the adsorbent concentration from 2 to 80 g.L^{-1} at a fixed Cr (VI) concentration 50 mg.L^{-1} with contact time allowed for 15 min at pH 2. Notably, 80 g.L^{-1} was tested to ensure observation of the saturation point; the optimal dose found was much lower, 16 g.L^{-1}, which is comparable to or less than dosages reported for other biosorbents achieving high Cr(VI) removal [42]. Also Cr(VI) removal efficiency (%) increased with cassava peel dosage from about 85% at 2 g.L^{-1} to 99.5% at 16 g.L^{-1}, and then leveled off. Beyond the optimal dose, the removal efficiency did not significantly improve (remaining 99%) – the slight dip observed at the highest dose was within experimental error and likely due to sorbent particle agglomeration at very high solids loading (Figure 2) [42]. Percent removal of Cr(VI) increased with increase in the adsorbent concentration. This trend aligns with the increased availability of binding sites at higher adsorbent loads [11]. i.e., At very high biosorbent concentrations, a phenomenon of 'overcrowding' can occur: particles can aggregate, effectively reducing the available surface area and creating diffusion barriers. Consequently, the removal efficiency may plateau or even exhibit a slight decline beyond the optimum dose [42]. In our system, once enough cassava peel was present to adsorb 99% of Cr(VI), additional biosorbent led to particle agglomeration and negligible further uptake, which explains the minor decrease in removal at 80 g·L^{-1}. Beyond 16 g.L^{-1}, efficiency plateaued due to site competition among Cr(VI) ions [56]. Notably, cassava peels outperformed maple sawdust (50 g.L^{-1} for 80 % removal) and coconut shell charcoal (24 g.L^{-1} for 80 ppm removal) [10], demonstrating superior cost-effectiveness.

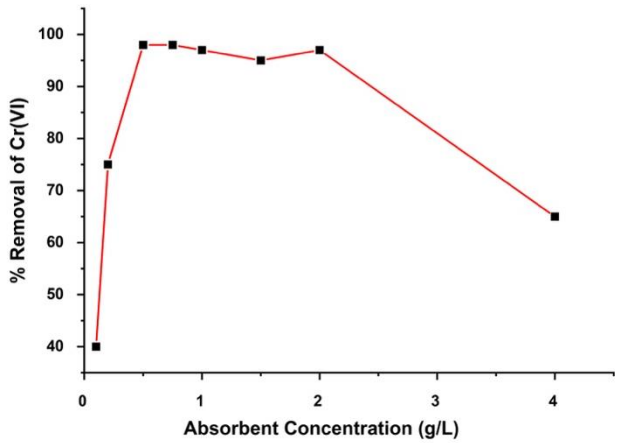

Figure 2. The effect of adsorbent concentration on the percentage removal of Cr(VI) from an aqueous solution.

3.3. Effect of initial Cr(VI) concentration

Figure 3 shows the order to establish the effect of initial chromium concentration in the removal of Cr(VI). Wherein the initial Cr(VI) concentration were varied from 10 to 100 mg.L^{-1} and the removal efficiency for Cr(VI) increased from 94.47 % to 99.93 %. It is noted that at 80 mg.L^{-1} Cr(VI), removal efficiency peaked at 99.93 %. This is because at higher concentrations (> 80 mg.L^{-1}) reduced uptake due to saturation of binding sites and interionic competition [34]. It was also witness that there was a decline in Cr(VI) concentration above 80 mg.L^{-1} as a result of increase in the number of ions competing for the available binding sites [28]. Also the charge distribution is altered due to the reduced distance between the Cr(VI) ions and thus affecting the binding to the sorbent [10]. In the present investigation, cassava peels achieved > 99 % removal at 80 mg.L^{-1}, surpassing coconut shell charcoal which in turn required 24 g to remove the Cr(VI) for 80 ppm solution [10].

3.4. Effect of pH

The pH of the aqueous solution critically influenced Cr(VI) adsorption onto cassava peels, with maximum removal efficiency (approx. 98 %) observed at pH 2 (Figure 4). This excellent removal at pH 2 is attributed to favorable Cr(VI) speciation and surface charge interactions. No further improvement in Cr(VI) removal was observed by lowering the pH below 2. In fact, pH 2 is typically optimal for Cr(VI) adsorption because the biosorbent surface is maximally protonated, attracting the dominant anionic species i.e. $HCrO_4^-$ (with some $Cr_2O_7^{2-}$). At pH < 2, the Cr(VI) exists increasingly as neutral H_2CrO_4 [57], which would diminish electrostatic adsorption, and thus practical removal efficiency would not increase beyond the 99% achieved at pH 2 [42]. Meanwhile, the cassava peel's functional groups are fully protonated, imparting a positive surface charge. This leads to strong electrostatic attraction between the biosorbent and the Cr(VI) anions [39]. As pH increased (3–11), removal efficiency sharply declined (45.71 % to 0.62 %) due to deprotonation of the adsorbent surface, leading to repulsion between negatively charged Cr(VI) ions (e.g., CrO_4^{2-}) and the adsorbent [1]. Thus, metal speciation under acidic conditions indeed plays a crucial role in the enhanced uptake observed. Comparative studies highlight cassava peels' superiority over other biosorbents: wool achieved only 70 % removal at pH 2 [15], while hazelnut shells required pH 3 for complete Cr(VI) removal [14]. The low optimal pH (2.0) for cassava peels aligns with typical industrial effluent conditions, underscoring their practicality for treating acidic wastewater contaminated with Cr(VI).

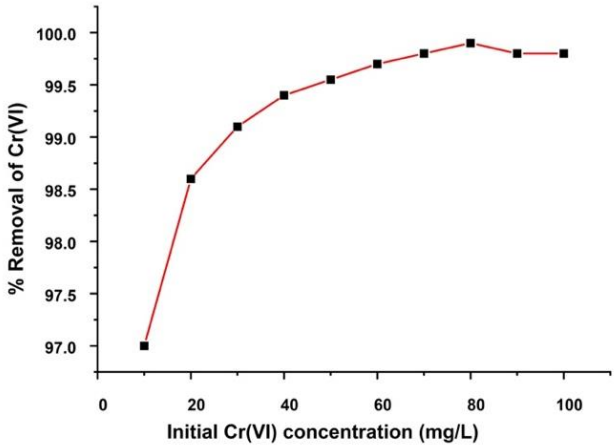

Figure 3. The effect of initial Cr(VI) concentration on the percentage removal of Cr(VI) from an aqueous solution.

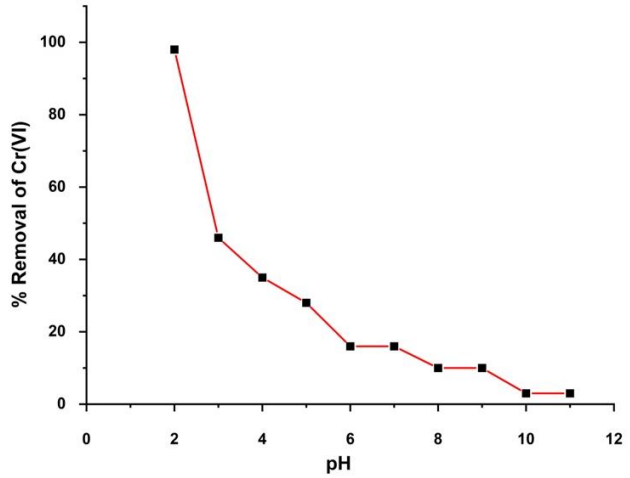

Figure 4. The effect of pH on the percentage removal of Cr(VI) from an aqueous solution.

3.5. Effect of Time

The adsorption kinetics of Cr(VI) onto cassava peels demonstrated remarkably fast removal, achieving 99.53 % efficiency within just 5 min of contact time (Figure 5). Beyond 5 min, the removal percentage remained essentially constant (within 0.5% of the 5 min value). The slight decrease in measured removal at 30 min is attributed to equilibrium desorption effects or experimental uncertainty, and does not imply a continuous decline in removal. This rapid adsorption can be attributed to the abundant availability of active binding sites on the fresh adsorbent surface [27]. As contact time increased beyond 5 min, the removal efficiency gradually decreased due to: saturation of active binding sites [2], developing repulsive forces between adsorbed Cr(VI) ions and remaining solution ions [46], possible desorption phenomena at prolonged

contact times [51]. Comparative analysis reveals cassava peels' superior performance: eucalyptus bark required 15-180 min for 87.4 % removal [44], maple sawdust needed 200 min for 80 % removal [56]. This demonstrates cassava peels' exceptional adsorption capacity and kinetic advantage, achieving near-complete removal in just 5 min with lower adsorbent dosage (i.e., 16 g.L^{-1} *vs* 50 g.L^{-1} for maple sawdust).

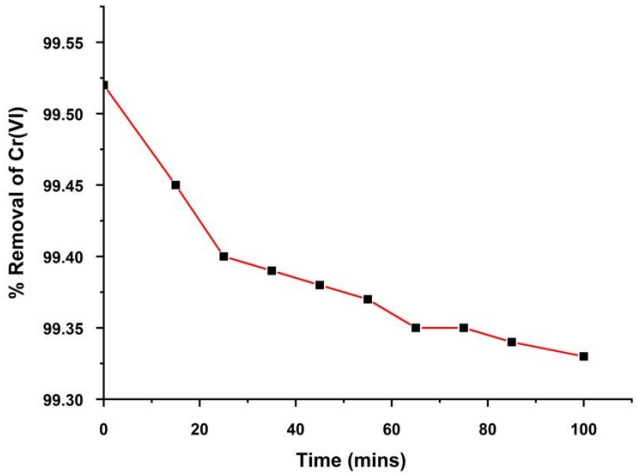

Figure 5. The effect of time on the percentage removal of Cr(VI) from an aqueous solution.

3.6. Adsorption Isotherm

The equilibrium isotherm analysis was conducted using four different initial Cr(VI) concentrations (in the range of 20–80 mg.L^{-1}) due to experimental limitations. These data points were used to fit the Langmuir, Freundlich, and D–R models. Although only four data points were employed for the isotherm (covering a Cr(VI) concentration range from 20 to 80 mg.L^{-1}), they were sufficient to achieve reliable model fits (e.g., Langmuir R^2 = 0.994) and to estimate the adsorption capacity. Additional data points would of course further refine the models, and we consider this a scope for future work.

3.6.1. Langmuir Isotherm

The Langmuir model (Figure 6) effectively described the adsorption process, indicating monolayer coverage of Cr(VI) on homogeneous cassava peel surfaces [36]. The linear form of the Langmuir adsorption isotherm equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (3)$$

C_e - Cr(VI) concentration after the batch sorption process (mg.L^{-1}), q_e - Amount of Cr(VI) taken up by the adsorbent (mg.g^{-1}), q_m - Maximum amount of Cr(VI) adsorbed per unit gram of the adsorbent (mg.g^{-1}) and b - Langmuir constant.

Langmuir isotherm is expressed using another dimensionless constant called separation factor or equilibrium factor, R_L which is defined as:

$$R_L = \frac{1}{1 + b\, C_o} \qquad (4)$$

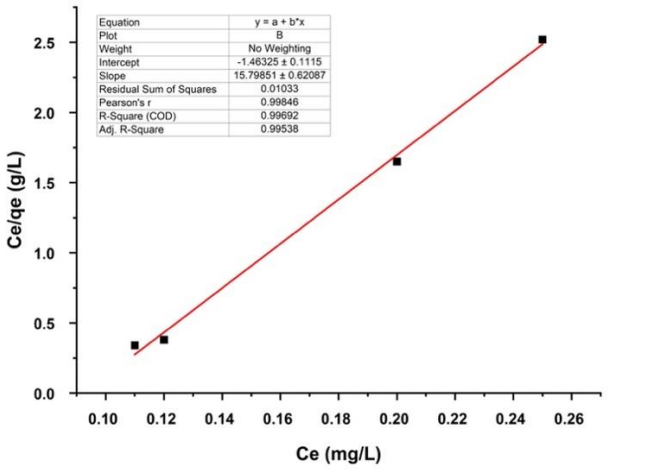

Figure 6. The Langmuir adsorption isotherm for varying initial Cr(VI) concentrations with a constant adsorbent concentration of 16 g.L^{-1}.

The Langmuir analysis yielded a maximum monolayer capacity q_m = 5.076 mg.g^{-1} and a Langmuir constant b = 0.21 L.mg^{-1}, with an excellent fit (R^2 = 0.994). The favorability of adsorption is further confirmed by the dimensionless separation factor R_L, which for initial Cr(VI) = 100 mg.L^{-1} is 0.045. As shown in Table 1, R_L values between 0 and 1 confirm favorable adsorption [53]. The decreasing R_L with increasing initial concentration suggests stronger driving force at higher concentrations [19]. This isotherm behavior indicates finite adsorption capacity corresponding to complete monolayer coverage, homogeneous distribution of active sites, and absence of intermolecular interactions between adsorbed ions [29].

Table 1. Significance of R_L value

R_L Value	Nature of adsorption process
$R_L > 1$	Unfavourable
$R_L < 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

3.6.2. Freundlich Isotherm

The Freundlich isotherm model (Figure 7) was employed to characterize the heterogeneous surface adsorption of Cr(VI) onto cassava peels [20]. i.e., for describing the adsorption of organic and inorganic chemicals onto the adsorbent including the biosorbent.

The linearized form of the equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (5)$$

K_f and $_n$ - Freundlich constants.

As shown in Table 2, the calculated n value of 2.3 ($1 < n < 10$) indicates favorable adsorption conditions [19]. The Freundlich model's lower regression coefficient (R^2 = 0.818) compared to Langmuir suggests the surface, while heterogeneous, predominantly exhibits monolayer coverage characteristics. This dual behavior may result from non-uniform distribution of active sites [5], variable adsorption energies across the surface [9], multilayer formation at higher concentrations [25].

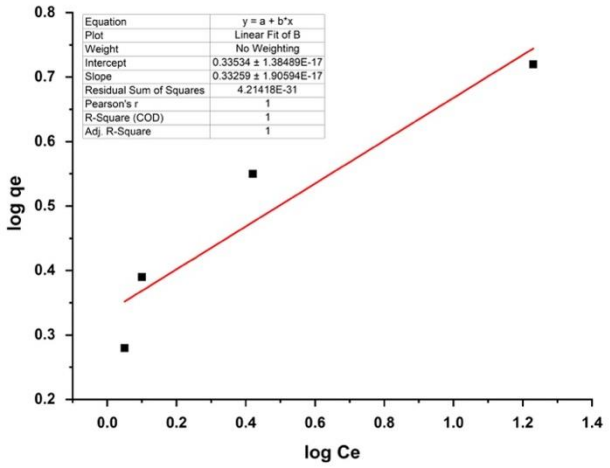

Figure 7. The Freundlich adsorption isotherm for varying Cr(VI) concentrations with a constant adsorbent concentration of 16 g.L^{-1}.

Table 2. Significance of n value

n Value	Nature of adsorption process
n = 1 to 10	Favourable adsorption
n > 10	Stronger interaction between adsorbent and metal ions
$1/n$ = 1	Linear adsorption

3.6.3. Dubinin-Radushkeyich Isotherm

The Dubinin-Radushkevich (D-R) isotherm (Figure 8) was applied to determine the adsorption mechanism through the equation:

$$\ln q_e = \ln X_m^{'} - K^{'} \varepsilon^2 \qquad (6)$$

q_e - Amount of Cr(VI) adsorbed per unit weight of the adsorbent (mg.g^{-1}), $X_m^{'}$ - Adsorption capacity of the sorbent (mg.g^{-1}), $K^{'}$- Constant related to adsorption energy (mol^2.kJ^{-2}) and ε - Polanyi potential.

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad (7)$$

C_e - Equilibrium concentration of Cr(VI) in solution (mg.L^{-1}), R - Gas constant (kJ.K^{-1}.mol^{-1}), T - Temperature (K).

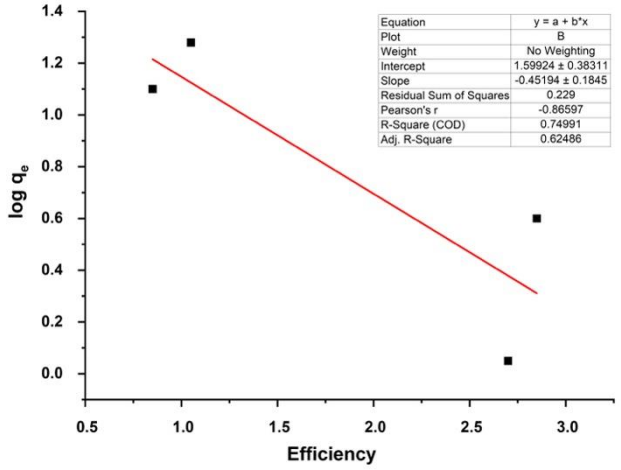

Figure 8. The Dubinin-Radushkevich (D-R) adsorption isotherm for varying Cr(VI) concentrations.

The mean adsorption energy is obtained from the $K^{'}$ values of the D-R isotherm using the following equation:

$$E = \left(-2K^{'}\right)^{-\frac{1}{2}} \qquad (8)$$

E - Mean adsorption energy (kJ.mol^{-1}).

The Dubinin-Radushkevich (D-R) isotherm analysis revealed key insights about the Cr(VI) adsorption mechanism onto cassava peels (Figure 8). Dubinin–Radushkevich (D–R) isotherm analysis was applied to the 30°C equilibrium data. (Note: All batch experiments were conducted at 303 K; no separate temperature-dependent study was performed.) The model yielded an adsorption capacity ($X_m^{'}$) of 5.027 mg.g^{-1}, closely matching the Langmuir qm value (5.076 mg.g^{-1}), confirming consistency between both models. The calculated mean adsorption energy (E) of 0.997 kJ.mol^{-1}, determined from the D-R constant $K^{'}$ using Equation 8, falls within the range characteristic of physisorption processes (E < 8 kJ.mol^{-1}) as outlined in Table 3. This low energy value suggests the adsorption occurs primarily through weak van der Waals forces rather than chemical bonding [17]. The moderate regression coefficient (R^2 = 0.854) indicates the D-R model provides a reasonable but not perfect fit to the experimental data, complementing the superior Langmuir isotherm fit [8]. The physisorption dominance implied by the E value aligns with the observed reversibility of adsorption at longer contact times (Figure 5). These findings collectively suggest that the Cr(VI) removal process involves physical attraction mechanisms rather than strong chemisorption, which has important implications for potential adsorbent regeneration and reuse strategies.

Table 3. Significance of mean adsorption energy (E)

E value	Nature of adsorption
E < 8 kJ.mol^{-1}	Physisorption dominates
E between 8 and 16 kJ.mol^{-1}	Ion exchange dominates
E > 8 kJ.mol^{-1}	Particle diffusion dominates

3.6.4. Comparative Isotherm Analysis

The experimental data showed significantly better fit with the Langmuir isotherm model (R^2 = 0.993) than with the Freundlich model (R^2 = 0.818), revealing three fundamental aspects of the adsorption process. First, the Cr(VI) ions formed primarily a monolayer on the cassava peel surface, as predicted by Langmuir's original adsorption theory [36]. Second, the uniform R_L values suggested energetically homogeneous binding sites across the adsorbent surface [53]. Third, the system exhibited finite adsorption capacity behavior, indicating a limited number of equivalent active sites [29]. The consistently favorable separation factors (0 < R_L < 1) across all tested concentrations (10-100 mg.L^{-1}) provided additional evidence for three important characteristics. The adsorption process demonstrated: strong electrostatic attraction between Cr(VI) anions and protonated functional groups on the biosorbent [27], highly efficient occupation of available binding sites at optimal conditions [37], and promising potential for real-world wastewater treatment applications [4]. These isotherm analysis results collectively establish cassava peels as a homogeneous, effective adsorbent for Cr(VI) removal with immediate practical utility.

3.7. Kinetics Study

The adsorption kinetics of Cr(VI) onto cassava peels were analyzed using pseudo-first-order and pseudo-second-order models to elucidate the removal mechanism. For comparison, the pseudo-first-order model (Equation 9) was also evaluated; however, it yielded a poor fit (e.g., R^2 = 0.85) and significantly underestimated the experimental adsorption capacity. This indicates that the pseudo-first-order kinetics do not adequately describe the Cr(VI) uptake in our system, consistent with many reports that biosorption of heavy metals is better captured by the pseudo-second-order model [57]. Therefore, the pseudo-first-order plot is not shown here, and we focus on the superior pseudo-second-order model [35]:

$$\log(q_e - q_t) = log q_e - \frac{k_1}{2.303} \qquad (9)$$

q_e, q_t - Amount of Cr(VI) adsorbed at equilibrium and at time t, (mg.g^{-1}), t - time (min) and k_1 - rate constant of adsorption (min^{-1}).

In contrast, the pseudo-second-order model (Equation10) exhibited excellent agreement with experimental data (R^2 = 0.999, Figure 9), confirming its adsorption rate is controlled by surface interations [27]. The high R^2 is indicative of a very strong correlation; similar near-unity R^2 values for pseudo-second-order kinetics have been reported in literature for heavy metal adsorption experiments [24].

The integrated and linearized pseudo second order rate expression is given by the following equation:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \qquad (10)$$

k_2 - rate constant of second order adsorption (g.mg.min^{-1}).

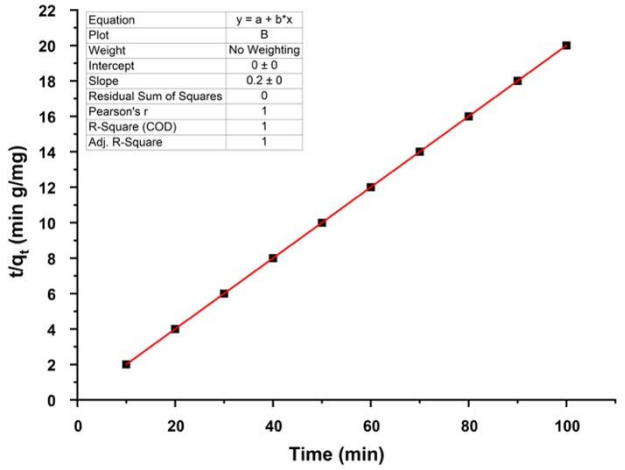

Figure 9. The Pseudo-second-order kinetics model for Cr(VI) removal, the sharing (or) exchange of electrons between the adsorbent and adsorbate.

The linear plot of t/q_t *vs* t yielded q_e and k_2 values from the slope and intercept, respectively. This strong fit suggests that chemisorption involving valence forces through electron sharing or exchange between Cr(VI) and cassava peel functional groups dominates the adsorption process [54].

4. Conclusion

The experimental results establish cassava peels (*Manihot esculenta*) as a highly efficient biosorbent for hexavalent chromium removal from aqueous solutions. The study revealed several critical findings that includes optimal removal efficiency occurred at an adsorbent dosage of 16 g.L^{-1} and initial Cr(VI) concentration of 80 mg.L^{-1}, maximum adsorption capacity reached 2.699 mg.g^{-1} under these conditions, and solution pH significantly influenced removal efficiency, with peak performance (97.88 %) observed at pH 2. Remarkably, the adsorption process achieved 99.53 % Cr(VI) removal within just 5 min, following pseudo-second-order kinetics. The mean adsorption energy (E < 8 kJ.mol^{-1}) confirmed physisorption as the dominant mechanism, likely involving weak van der Waals forces and electrostatic interactions. These findings position cassava peels as a sustainable, low-cost alternative for treating chromium-contaminated industrial effluents, particularly in acidic wastewater streams common in electroplating and tannery operations. The agricultural origin of this adsorbent offers additional advantages of renewability and waste valorization, supporting circular economy principles in water treatment.

Nomenclature

Cr	:	Chromium
ATSDR	:	Agency for Toxic Substances and Disease Registry
C_o	:	Initial Cr(VI) concentration (mg.L^{-1})
C_e	:	Cr(VI) concentration after the batch sorption process (mg.L^{-1})
Q	:	Amount of Cr(VI) taken up by the adsorbent (mg.g^{-1})
V	:	Volume of Cr(VI) solution (L)
W	:	mass of adsorbent (g)
q_e	:	Amount of Cr(VI) taken up by the adsorbent (mg.g^{-1})
q_m	:	Maximum amount of Cr(VI) adsorbed per unit gram of the adsorbent (mg.g^{-1})
b	:	Langmuir constant
R_L	:	Value indicates the nature of adsorption process
K_f, n	:	Freundlich constants
q_e	:	Amount of Cr(VI) adsorbed per unit weight of the adsorbent (mg.g^{-1})
$X_m^{'}$	:	Adsorption capacity of the sorbent (mg.g^{-1})
$K^{'}$	:	Constant related to adsorption energy (mol^2.kJ^{-2})
C_e	:	Equilibrium concentration of Cr(VI) in solution (mg.L^{-1})
R	:	Gas constant (kJ.K^{-1}.mol^{-1})
T	:	Temperature (K)
E	:	Mean adsorption energy (kJ.mol^{-1})
q_e,q_t	:	Amount of Cr(VI) adsorbed at equilibrium and at time t, (mg.g^{-1})
t	:	time (min)
k_1	:	rate constant of adsorption (min^{-1})
k_2	:	rate constant of second order adsorption (g.mg.min^{-1})

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Author contributions

Karthika Ayyar: Conceptualization, Methodology, Investigation and Original draft preparation. **Priyadharshini Senthilkumar, Karnika Sivavadivel, Janashruthi Karthikeyan, Sivaprakash Sivasamy, Vinetha Mayilesan:** Data curation, Writing-Reviewing, Editing, Software/data processing, Validation. **Rengesh Balakrishnan:** Conceptualization, Supervision, Proofreading and Technical validation.

Conflicts of interest

The authors declare no conflicts of interest.

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