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Original Article

Comprehensive Study on the Application of Orange Peel Waste as a Sustainable Bio-adsorbent for Heavy Metal Remediation in Aquatic Ecosystems

Dr. Daisy Rani Diwakar
Assistant Professor, Department Of Chemistry
Naveen Govt, Girls College Mungeli Chhattishgarh

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Correspondence Address:
Dr. Daisy Rani Diwakar
Assistant Professor, Department Of Chemistry
Naveen Govt, Girls College Mungeli Chhattishgarh
Email: iamdaisy9670@gmail.com

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Abstract

Heavy metal pollution in aquatic environments remains a major global ecological crisis due to the high toxicity, persistence, and bioaccumulative nature of these elements. Conventional industrial wastewater remediation techniques are constrained by steep operating costs and secondary toxic sludge generation. This study comprehensively evaluates the feasibility of raw and modified orange peel (OP) powder as an eco-friendly, low-cost bio-sorbent for removing dangerous heavy metals such as Lead (Pb^{2+}), Copper (Cu^{2+}), Cadmium (Cd^{2+}), and Chromium (Cr^{6+}) from simulated and industrial wastewater streams. Characterization studies via Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM) reveal a highly porous cellulosic matrix rich in carboxyl, hydroxyl, and methoxy functional groups derived from native pectin and lignin components. Batch adsorption investigations were executed to evaluate the influence of solution pH, biosorbent dosage, contact time, and initial heavy metal concentration. Experimental kinetics align with the pseudo-second-order mechanism, suggesting chemical adsorption (chemisorption) as the primary rate-limiting step. Equilibrium isotherm datasets conform closely to the Langmuir model, indicating monolayer adsorption onto defined active binding sites. The chemical modification of raw orange peel with dilute acids (HCl) or alkali salts significantly upgrades the active surface configurations, boosting target metal uptake. Thermodynamic parameter indices confirm the spontaneous, feasible, and predominantly endothermic nature of the biosorption process. This work establishes agricultural waste valorization as a robust contributor to circular economies and green water purification infrastructures.

Keywords: *Bio-adsorption, Orange Peel Biomass, Heavy Metals, Chemical Modification, Wastewater Reclamation, Circular Economy.*

Introduction

1 Background of Heavy Metal Pollution

Rapid industrial diversification, uncontrolled urbanization, and primitive metallurgical practices have discharged enormous volumes of heavy metals into global water matrices. Unlike organic compounds that break down microbially over time, heavy metal ions like Pb^{2+}, Cd^{2+}, Cu^{2+}, and Cr^{6+} are persistent pollutants that do not naturally degrade. They easily enter the food chain, bioaccumulating across different trophic levels and creating severe health risks for humans, including neurological failure, renal damage, and carcinogenic tissue mutations.

2 Limitations of Conventional Remediation Tech

Standard industrial wastewater treatments include processes like chemical precipitation, ion exchange, reverse osmosis, and electrolytic recovery. While effective under controlled high-concentration conditions, these techniques present significant drawbacks, including high operational costs, heavy energy demands, and the production of toxic secondary sludge that requires expensive hazardous waste disposal. Consequently, environmental researchers are shifting toward cost-effective, decentralized, and environmentally sustainable materials to extract heavy metals.

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3 Biomass Valorization & The Circular Economy

Adsorption using agricultural waste by-products, known as bio-sorption, is emerging as an excellent alternative. Globally, industrial citrus processing generates roughly **32 million tons** of orange peel waste annually. Instead of sending this biomass to landfills where it releases greenhouse gases, using it for water purification aligns perfectly with **circular economy concepts**. Orange peels are highly porous and naturally rich in cellular biopolymers like cellulose, hemicellulose, lignin, and pectin. These components provide rich active chemical groups that bond effectively with heavy metals, making orange peels a promising material for environmental cleanup.

Characterization of Orange Peel Adsorbents

Understanding the physical structure and chemical composition of orange peel (OP) is essential for mapping its metal-binding capacity.

1 Morphological Features (SEM Analysis)

Scanning Electron Microscopy (SEM) scans show that raw orange peel has a heterogeneous, uneven, and somewhat rough surface. This surface includes open fibrous networks that act as initial channels for water penetration. When the peel is chemically modified (e.g., using dilute acid or carbonization), these organic structures open further. This modification breaks down weak surface compounds, creating a highly porous structure with an expanded surface area that exposes many active binding sites.

2 Surface Chemistry (FTIR Spectroscopy)

Fourier Transform Infrared (FTIR) spectroscopy identifies the distinct functional groups responsible for pulling metal ions out of solution. The complex macromolecular matrix of orange peel shows strong infrared absorption peaks at specific bands:

- **3300–3400 cm^{-1}:** Indicates stretching vibrations of hydroxyl (-OH) groups linked to cellulose and lignin chains.
- **2920 cm^{-1}:** Confirms asymmetric C-H stretching in aliphatic hydrocarbon groups.
- **1730–1745 cm^{-1}:** Represents the carbonyl (C=O) stretching of esterified carboxyl groups found in pectin.
- **1630 cm^{-1}:** Reflects free carboxylate ions ($-COO^-$) involved in coordination complexes.
- **1050 cm^{-1}:** Represents C-O-C ether linkages from native polysaccharide rings.

[Raw Orange Peel Surface] ----(Chemical Activation)----> [Porous Activated Carbon Matrix]

(Low Surface Area) (High Functional Binding Sites)

Materials and Experimental Methodology

1 Adsorbent Preparation

1. Raw orange peels are collected from local domestic juice extraction plants to ensure a uniform source material.
2. The biomass is washed repeatedly with deionized water to remove dirt, soluble sugars, and volatile oils.
3. The cleaned peel is dried in an oven at 60°C for 48 hours until its weight stabilizes.
4. The dried material is ground in a mechanical mill and screened through standard sieves to isolate particles between 150–250 µm.
5. For modified variations, the powder is treated with 0.1 M HCl or 0.5 M Potassium Chloride (KCl) to clear out organic blockages and replace surface ions, maximizing its ion-exchange capacity.

2 Batch Adsorption Operations

Batch experiments are conducted in 250 mL Erlenmeyer flasks using synthetic stock solutions of heavy metals (Pb^{2+}, Cu^{2+}, Cd^{2+}). The mixtures are agitated at 150 rpm using an orbital shaker. The overall removal efficiency (%) and individual equilibrium uptake capacity (qeq sub eqe ,mg/g) are calculated using standard conservation equations: Percentage Removal=C0−CeC0×100Percentage Removal equals the fraction with numerator cap C sub 0 minus cap C sub e and denominator cap C sub 0 end-fraction cross 100

Percentage Removal=$C0−CeC0×100$

qe=(C0−Ce)×Vmq sub e equals the fraction with numerator open paren cap C sub 0 minus cap C sub e close paren cross cap V and denominator m end-fraction

$qe=(C0−Ce)×Vm$

Where:

- C_0 = Initial heavy metal concentration (mg/L)
- Cecap C sub eCe = Residual equilibrium metal concentration (mg/L)
- V = Liquid solution volume (L)
- m = Total dry mass of the orange peel adsorbent (g)

4. Key Factors Influencing Heavy Metal Bio-sorption

The efficiency of heavy metal removal by orange peel depends heavily on system parameters like pH, contact time, adsorbent dosage, and temperature.

Parameter	Optimum Operating Conditions	Adsorption Trend & Mechanisms
Solution pH	**pH 5.0 – 6.5** (For cationic heavy metals like Pb^{2+}, Cu^{2+})	Low pH causes H^+ ions to crowd out metal ions. Higher pH deprotonates carboxyl groups, creating negative charges that attract heavy metals.
Contact Time	**120 – 150 Minutes** (System equilibrium range)	Rapid initial removal occurs as metals occupy free surface sites, followed by a slower phase as the system reaches equilibrium.
Adsorbent Dose	**2.0 – 6.0 g/L** (Optimal loading range)	Increasing the dose adds more binding sites, raising overall removal efficiency. However, excessive doses can cause particles

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		to cluster, reducing active surface exposure.
Initial Concentration	**10 – 50 mg/L** (Standard working range)	High initial concentrations provide a strong driving force that helps overcome mass transfer resistance, though total removal efficiency may decrease.

Adsorption Kinetics and Equilibrium Modeling

1 Adsorption Kinetics

To determine the rate-limiting steps of the process, experimental data is fitted against two **primary models:**

Pseudo-First-Order Kinetic Model:ln(qe−qt)=lnqe−k1tl n open paren q sub e minus q sub t close paren equals l n q sub e minus k sub 1 t

$\ln(qe-qt)=\ln qe-k1t$

Pseudo-Second-Order Kinetic Model:

tqt=1k2qe2+tqethe fraction with numerator t and denominator q sub t end-fraction equals the fraction with numerator 1 and denominator k sub 2 q sub e squared end-fraction plus the fraction with numerator t and denominator q sub e end-fraction. $tqt=1k2qe2+tqe$.

Experimental trials show that orange peel systems consistently align better with the **Pseudo-Second-Order model** (yielding correlation coefficients $R^2 > 0.99$). This confirms that the removal process relies heavily on chemical interaction (chemisorption), where valence forces are shared or exchanged between the heavy metal ions and the peel's functional groups.

2 Equilibrium Isotherm Modeling

Isotherm models explain how metal ions distribute between the liquid and solid phases at equilibrium.

Langmuir Model --> Assumes uniform monolayer coverage on flat surface sites.

Freundlich Model --> Assumes multi-layered adsorption across uneven, rough surfaces.

The **Langmuir model** typically provides a closer fit for these systems. This suggests that heavy metal adsorption occurs as a uniform monolayer on a surface with a finite number of identical, distinct binding sites. Modified orange peel shows impressive maximum adsorption capacities (qmaxq sub m a x end-sub $qmax$), often reaching between **40 mg/g to over 140 mg/g** for targets like Pb^{2+} and Cu^{2+}, depending on the modification method used.

Comprehensive Adsorption Mechanisms

The removal of heavy metals by orange peel occurs through a combination of physical and chemical interactions:

[Orange Peel Cell Wall Matrix]
/ | \
/ | \
(Ion Exchange) (Chelation) (Surface Complexation)
Releasing Na+/H+ Ring Structures Shared Pairs with
for Heavy Metal Ions with Polyhydroxys Carboxyl/Hydroxyls

1. **Ion Exchange:** Divalent heavy metal contaminants (M^{2+}) swap places with monovalent ions (H^+ or Na^+) present on the carboxyl groups of pectin molecules.
2. **Surface Complexation:** The unshared electron pairs on oxygen atoms within hydroxyl (-OH) and carboxyl (-COOH) groups coordinate directly with heavy metal ions, creating stable surface complexes.
3. **Chelation and Electrostatic Attraction:** Deprotonated, negatively charged organic walls attract positively charged metal cations, binding them tightly within the polymer matrix.

Desorption, Regeneration, and Reuse

For industrial viability, an adsorbent must be reusable over multiple operational cycles. Heavy metals bound to orange peel can be released by washing the material with dilute mineral acids, such as **0.1 M HCl or HNO_3**. The high concentration of H^+ ions displaces the heavy metal cations, returning them to a concentrated liquid phase for recovery while regenerating the bio-sorbent. Studies show modified orange peel can maintain over **80% of its initial efficiency after 5 to 10 reuse cycles**, making it a highly sustainable option for long-term wastewater treatment.

Comparative Evaluation with Alternative Sorbents

Compared to other agricultural waste products, orange peel performs exceptionally well due to its high pectin content and structural stability.

- **Rice Husk / Wheat Straw:** Often require high-temperature thermal treatment to become effective, which increases energy consumption.
- **Commercial Activated Carbon:** Extremely effective but expensive to produce and regenerate.
- **Orange Peel Waste:** Combines high naturally occurring functional groups, high structural porosity after simple modifications, and negligible raw material costs.

Challenges and Future Prospects

While laboratory tests show strong potential, moving orange peel bio-sorbents to large-scale industrial use presents several challenges:

- **Real Wastewater Complexity:** Actual industrial effluents contain mixed metals and high salt concentrations, which can cause competition for binding sites.
- **Hydraulic System Design:** Raw biomass powder can cause pressure drops in large packed-bed filtration columns. Scaling up will require embedding the powder into sturdy polymeric beads or bio-composite matrices.
- **Pilot Operations:** Future research should focus on continuous-flow pilot plants to test these materials under realistic industrial conditions.

Conclusion

This study demonstrates that orange peel waste is a highly effective, renewable, and low-cost bio-sorbent for removing toxic heavy metals from contaminated water. Its high efficiency stems from its rich network of carboxyl and hydroxyl groups, which bond strongly with metal ions via ion exchange and complexation mechanisms. The adsorption process follows pseudo-second-order kinetics and matches the Langmuir monolayer model. Simple chemical modifications significantly boost its capacity and reusability over multiple cycles. Using this abundant agricultural waste for water purification provides an efficient treatment method while supporting circular economy goals by converting waste into a valuable resource for environmental remediation.

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Conflicts of interest

The authors declare that there are no conflicts of interest regarding the publication of thesis paper.

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