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"Sustainable Detoxification of Electroplating Wastewater Using Cow Dung-Enriched Microbial Consortia and Kitchen Waste Biosorbents"

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Abstract
The electroplating industry generates wastewater laden with a complex matrix of hazardous pollutants, notably high concentrations of toxic heavy metals (such as zinc, chromium, and cadmium), free and complexed cyanides, and a broad spectrum of suspended and dissolved solids. These pollutants contribute to significant physicochemical variability and environmental risk. In India, the majority of electroplating units operate in decentralized and unregulated clusters, often lacking advanced technologies, process automation, and adequate effluent management systems. Consequently, the wastewater discharged from such units exhibits erratic and elevated levels of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), total dissolved solids (TDS), turbidity, and color—ultimately leading to severe oxygen depletion and aquatic toxicity in receiving water bodies.
To address these environmental challenges, the present study investigates a sustainable and low-cost treatment strategy utilizing biosorption. Biosorption, a passive physicochemical process, involves the selective binding of metal ions to functional groups on the surface of biological materials, particularly those present in microbial cell walls. This research explores the potential of employing organic biosorbents derived from cow dung and decomposed vegetable waste—both abundantly available agricultural byproducts as effective adsorbents for the removal of heavy metals from synthetic electroplating wastewater.
A series of controlled batch adsorption experiments were conducted to evaluate the removal efficiency of these organic substrates under varying operating conditions. The results indicate that both cow dung and vegetable waste exhibit significant sorption capacities, attributable to their porous structure, high surface area, and the presence of active functional groups such as carboxyl, hydroxyl, and amine groups. These findings suggest that such organic waste materials can serve as cost-effective and environmentally benign alternatives to conventional physico-chemical treatments.
The study contributes to the growing body of knowledge on green remediation technologies and highlights the viability of organic biosorbents in industrial wastewater management, especially for applications in resource-constrained settings. This eco-centric approach not only enhances the sustainability of wastewater treatment but also promotes the valorization of organic solid waste, aligning with circular economic principles.
Keywords: *Electroplating wastewater, Heavy metal removal, Biosorption, Organic biosorbents*

INTRODUCTION

1.1 Overview of Environmental Pollution and Industrial Contributions

Rapid industrialization and urban development, coupled with unsustainable practices across sectors such as transportation, agriculture, and manufacturing, have severely disrupted the balance of natural ecosystems.

Among the myriad environmental challenges, water pollution from industrial effluents stands as a critical concern, particularly in regions where regulatory frameworks are weak and technological implementation is limited. Electroplating industries, primarily operating in fragmented clusters with inadequate waste treatment infrastructure, are among the leading contributors to heavy metal pollution. Their effluents are characterized by high variability and contain complex mixtures of toxic substances including cyanides, acidic compounds, and heavy metals like cadmium (Cd), chromium (Cr), and zinc (Zn). These pollutants not only elevate parameters such as Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), and Total Dissolved Solids (TDS), but also pose severe risks to aquatic and human health by altering biochemical cycles and bioaccumulating through food chains.

1.2 Impact and Persistence of Heavy Metals in the Environment

Heavy metals, defined as elements with a density greater than 5 g/cm^3, are notorious for their toxicity, persistence, and bioaccumulation. While trace quantities of metals like zinc, copper, and manganese are essential for enzymatic functions in living organisms, their elevated concentrations especially of non-essential metals such as lead (Pb), mercury (Hg), and cadmium (Cd) are detrimental to ecological and human health. Once released, these metals infiltrate surface and subsurface water bodies and can persist for decades due to their non-biodegradable nature.

Exposure to heavy metals can lead to numerous chronic disorders, including neurological damage, renal dysfunction, respiratory issues, and carcinogenic effects. The cumulative toxicity of these metals, especially through continuous industrial discharge, underscores the necessity for innovative, cost-effective, and sustainable remediation techniques.

1.3 Limitations of Conventional Treatment and Scope for Biosorption

Conventional treatment techniques such as precipitation, membrane filtration, electrochemical methods, and ion exchange are often capital-intensive, require skilled operation, and generate toxic sludge or secondary pollutants. Consequently, biological and biosorption-based methods have emerged as sustainable alternatives. These techniques harness the natural metal-binding capacity of biological materials—including microbial biomass, agricultural residues, and animal waste—to sequester heavy metals from aqueous environments.

This study investigates the biosorptive potential of cow dung and vegetable waste organic, cost-effective, and abundantly available materials—as promising biosorbents for the removal of cadmium, chromium, and zinc from electroplating wastewater. These materials not only serve the dual purpose of waste valorization and pollution remediation but also align with the principles of circular economy and sustainable development.

2. Heavy Metals: Properties, Toxicity, and Treatment Challenges

2.1 Chemical Behavior and Toxicological Impact

Heavy metals pose a unique threat due to their ability to form stable complexes with biological ligands. They interfere with enzyme activity, disrupt DNA replication, and impair vital physiological processes. For instance:

- Cadmium (Cd): Replaces calcium in bones, leading to skeletal demineralization (e.g., Itai-Itai disease).
- Chromium (Cr^{6+}): Highly oxidative, causes nephrotoxicity and gastrointestinal cancers.
- Zinc (Zn): Though essential, excess levels disrupt enzyme function and immunity.
- Lead (Pb): Causes neurological damage and developmental delays in children.
- Mercury (Hg): Affects the central nervous system and bioaccumulates in aquatic food chains.

2.2 Conventional Removal Techniques

Traditional methods for heavy metal removal include:

- Chemical methods: Precipitation, redox reactions, neutralization.
- Physical methods: Filtration, membrane separation, ion exchange, and reverse osmosis.
- Biological methods: Phytoremediation, microbial biosorption, and bioaccumulation.

While effective to a degree, conventional methods are hindered by high costs, sludge production, limited selectivity, and maintenance needs. Hence, biosorption has gained momentum as a feasible alternative.

3. Biosorbents: Cow Dung and Vegetable Waste

3.1 Cow Dung as a Biosorbent

Cow dung is a multifunctional organic waste material traditionally used as fertilizer, fuel, and biogas feedstock. Its composition—rich in calcium oxide, silica, iron oxide, and alumina—enables strong metal-binding capabilities. The high silica content provides numerous active sites for metal ion adsorption.

Activated cow dung, when carbonized and processed, has shown significant potential for removing heavy metals due to its porous structure, ion-exchange capacity, and cost-efficiency. It also contains diverse microbial flora that could enhance the biodegradation of organic pollutants.

3.2 Vegetable Waste as an Adsorptive Biomass

Vegetable waste comprises biodegradable components like cellulose, hemicellulose, lignin, and starch. When composted or thermochemically treated, it exhibits favorable surface characteristics for heavy metal sorption. Additionally, vegetable peels and trimmings are rich in functional groups that interact with metal ions via complexation, ion exchange, or physical adsorption.

Using these materials not only diverts biodegradable waste from landfills but also contributes to sustainable environmental management by offering low-cost treatment media for wastewater remediation.

4. Environmental and Economic Feasibility

Developing nations face economic constraints in adopting sophisticated wastewater treatment technologies. Biosorption using cow dung and vegetable waste provides a low-cost, eco-friendly alternative with high adsorption capacity, minimal secondary pollution, and potential for resource recovery.

By transforming organic waste into value-added biosorbents, this approach contributes to the circular economy, promotes waste valorization, and offers scalability for rural and industrial applications. Furthermore, it aligns with sustainable development goals (SDGs), particularly SDG 6 (Clean Water and Sanitation) and SDG 12 (Responsible Consumption and Production).

Fig 1: Major Anthropogenic and Natural Sources of Heavy Metal Contamination

Objectives

This study is structured around the following key objectives:

1. To evaluate the effectiveness of organic biosorbents—specifically cow dung and vegetable-based biomass—for the removal of cadmium, chromium, and zinc from electroplating wastewater.
2. To determine the optimal dosage and contact time of the biosorbents through batch adsorption studies under varying concentrations.
3. To assess the potential for heavy metal recovery and reuse of the treated effluent for non-potable purposes, ensuring minimal environmental impact and promoting industrial water circularity.

2.1 Overview of Biosorption in Heavy Metal Remediation

The rapid industrialization of the 20th and 21st centuries has led to an alarming accumulation of heavy metals in aquatic ecosystems. These metals are non-biodegradable and capable of bioaccumulating in food chains, posing serious health and ecological risks. Conventional chemical and physical treatment methods, while effective, are often cost-intensive and generate secondary pollutants. This has directed research towards biosorption, a biologically mediated physicochemical process in which heavy metal ions are sequestered through interactions with functional groups present on the surface of biomass materials.

Biosorption can occur via living or dead microbial cells, including bacteria, algae, fungi, and yeast, or through non-living agricultural and industrial by-products such as plant husks, peels, stalks, and even animal-derived wastes. The effectiveness of biosorption depends on numerous parameters, such as pH, temperature, biosorbent dosage, initial metal ion concentration, and surface functional group availability. Isotherm models such as Langmuir and Freundlich are typically employed to characterize the adsorption process, while desorption and recovery of bound metals may be achieved using eluents like mineral acids or organic solvents.

2.2 Critical Review of Related Studies

2.2.1 Sugarcane Waste for Metal Extraction from Sewage Sludge

Okareh and Enesi evaluated the potential of fermented sugarcane waste extracts—both crude (CFE) and fungus-specific (FFE)—for the removal of Cu, Zn, Cr, Ni, Cd, and Pb from sewage sludge. At low pH (3–4), optimal removal was achieved within five days, outperforming commercial citric acid in most cases. CFE showed superior efficiency in removing Cr, Ni, and Pb, suggesting its suitability as an eco-friendly chelating agent for agricultural sludge detoxification.

2.2.2 Synergistic Solvent Extraction of Metals

Li et al. proposed a synergistic solvent extraction system incorporating Versatic 10 and Mextral 984H to selectively remove Cu, Ni, Zn, and Cd from zinc-hydrometallurgical effluents. Their staged pH-dependent extraction yielded removal rates exceeding 98%, providing an effective mechanism for sequential metal recovery in industrial-scale treatment systems.

2.2.3 Organic Acids for Metal Extraction from Sludge

Veeken and Hamelers investigated the use of biodegradable organic acids, particularly citric acid, to extract Cu and Zn from sewage sludge under mildly acidic conditions (pH 3–4). The study reported 60–70% Cu and 90–100% Zn recovery. The process proved economically viable and environmentally superior to traditional incineration or landfill methods, promoting nutrient recycling through composting.

2.2.4 Agricultural Byproducts as Adsorbents

Alalwan et al. demonstrated the effectiveness of various plant-based wastes such as coconut shells, wheat bran, and oak bark in adsorbing Pb, Cd, Hg, and Cr from aqueous solutions. Adsorption capacities ranged from 263–400 mg/g depending on the material and metal. The study emphasized chemisorption, ion exchange, and pore diffusion as primary mechanisms, and employed kinetic models like Lagergren and BET to validate adsorption behavior.

2.2.5 Phytoremediation via Water Hyacinth

Rezania et al. provided a comprehensive review on water hyacinth (Eichhornia crassipes), a notorious aquatic weed, highlighting its potential in removing organic and inorganic pollutants, including heavy metals. While its uncontrolled proliferation is a challenge, its high uptake capacity and ease of cultivation make it viable for phytoremediation. Ancillary benefits include by-products such as animal feed, biofuel, and compost.

2.2.6 Magnetic Biopolymer Nanocomposites

Raouf and Raheim explored biopolymer-functionalized magnetic nanomaterials, including starch-modified Fe_3O_4 particles, for heavy metal adsorption. These nanocomposites offer high surface area and magnetically assisted separation. Modified starch composites showed strong adsorption for Pb^{2+}, Cu^{2+}, and Ni^{2+}, validated by Langmuir isotherms and pseudo-second-order kinetics.

2.2.7 Waste Tea Leaves as a Biosorbent

Ahluwalia and Goyal employed waste tea leaves to remove Pb, Fe, Zn, and Ni, achieving removal efficiencies up to 96%. FTIR analysis revealed the involvement of carboxyl and amine groups in metal binding. Sorption was rapid (within 60 minutes) and conformed to Langmuir and Freundlich models, suggesting multilayer and heterogeneous adsorption behavior.

2.2.8 Coffee Husk for Metal Removal

Oliveira et al. assessed untreated coffee husk for adsorption of Cu(II), Cd(II), Zn(II), and Cr(VI). With up to 98% Cu removal, the material demonstrated strong biosorption capacity and was best described by Langmuir isotherms and pseudo-second-order kinetics. The study highlights the potential of agro-waste valorization for water treatment applications.

2.2.9 Papaya Wood as a Novel Biosorbent

Saeed et al. introduced papaya wood, an underutilized agricultural residue, as a biosorbent for Cu, Cd, and Zn. At pH 5 and short contact time (60 min), it achieved removal efficiencies of 97.8%, 94.9%, and 66.8%, respectively. The process was reproducible over multiple sorption–desorption cycles, showing promise for sustainable metal recovery.

2.2.10 Rice Husk for Multimetal Remediation

Tarley and Arruda investigated rice husk for the removal of Cd, Pb, Cu, and Zn from synthetic and laboratory effluents. Optimization at pH 4 and particle size <355 µm showed excellent adsorption under continuous flow. The material's high surface area and chemical composition (silica, lignin) were responsible for its superior performance.

2.2.11 Cow Dung as a Low-Cost Adsorbent

Bello and Ojedokun reviewed the use of cow dung in batch biosorption studies. Cow dung was found to be an effective, economical, and biodegradable adsorbent for heavy metal ions. Biosorption followed Langmuir and Freundlich isotherms and was influenced by initial metal concentration and dosage. The study advocated its application in decentralized water treatment settings.

2.2.12 Mustard Husk for Pb and Cd Adsorption

Meena and Kadirvelu studied mustard husk as an adsorbent for Pb(II) and Cd(II). Adsorption occurred via ion exchange and surface complexation and conformed to both Langmuir and Freundlich models. Thermodynamic analysis suggested that the process was spontaneous and exothermic, validating its practical applicability.

2.2.13 Chemically Modified Plant Wastes

Ngah and Hanafiah examined chemically treated plant wastes, such as rice husk and sugarcane bagasse, for enhanced heavy metal adsorption. Modifications using acids, bases, and oxidizing agents increased surface reactivity, leading to improved Cd, Cu, Pb, Zn, and Ni removal. The review advocates for low-cost modifications to optimize biosorption efficiency.

2.2.14 Poultry Manure-Based Activated Carbon

Lima and Marshall transformed poultry manure into granular activated carbon. Upon activation at 800°C, the material showed exceptional adsorption for Cu, Cd, and Zn, outperforming commercial carbons. The carbon's structure allowed for effective metal uptake in both single and multi-metal systems.

2.2.15 Agricultural Waste-Based Biosorbents

Nguyen and Ngo provided a critical analysis of agricultural waste biosorbents (AWBs) for heavy metal removal. While AWBs demonstrated adsorption capabilities comparable to traditional sorbents, the authors highlighted the need for:

- Multifunctional biosorbents
- Improved surface modification techniques
- Validation in real wastewater conditions

The study concluded that AWBs hold significant promise for replacing conventional materials in future wastewater treatment systems.

2.3 Synthesis of Findings and Research Gap

The literature establishes that a wide variety of **organic waste materials**—including crop residues, animal waste, and food processing by-products—have significant potential for heavy metal remediation. These materials are:

- Economically viable
- Environmentally sustainable

- Structurally rich in functional groups conducive to metal ion binding

However, despite promising laboratory-scale results, **gaps remain** in the translation of these technologies to industrial-scale settings. Key challenges include:

- Regeneration and reuse of biosorbents
- Consistency in performance across varying wastewater compositions
- Limited studies on combined metal systems (multi-metal biosorption)
- Lack of integration with existing industrial effluent treatment plants

3. Experimental Programme

The primary objective of this experimental programme is to evaluate the efficiency of low-cost, organic adsorbents specifically cow dung and vegetable waste in removing heavy metals from electroplating industry wastewater through biologically enhanced biosorption. The experimental approach emphasizes both physical and biological mechanisms by fostering microbial activity in a controlled environment to support enhanced heavy metal uptake.

The study involves culturing aerobic bacteria in prepared tanks containing wastewater mixed with the adsorbents, followed by analysis of the adsorption potential and heavy metal reduction percentage. In addition to assessing heavy metal concentrations, auxiliary water quality parameters such as pH, dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), and acidity were monitored throughout the experiment.

3.2 Materials and Methodology

3.2.1 Experimental Setup

Two transparent glass tanks, each with a capacity of 10 liters, were constructed to facilitate observation and aeration. The tanks were rectangular in shape, providing a large surface area-to-volume ratio, which enhances contact between the adsorbents and the contaminated water, and promotes efficient bacterial colonization on the substrate.

The adsorbents—cow dung and mixed vegetable/fruit waste—were placed at the bottom of the tanks in separate batches. The tanks were fitted with air diffusers to provide continuous aeration, a critical component in sustaining aerobic microbial activity that facilitates the degradation of organic compounds and supports metal adsorption through biofilm formation.

Figure 2: Aerated Glass Tank Setup for Biosorption Experiments Using Organic Adsorbents

The effectiveness of biosorption is enhanced when microbial colonies are established on the adsorbent surface. The microbial cultivation strategy involved:

- **Use of aerobic conditions**: Oxygen diffusion was facilitated using aerators, and the physical tank configuration was optimized by maintaining an appropriate liquid depth and horizontal surface area.
- **Bio-seeding**: Filter media previously colonized with beneficial bacteria from mature aquaculture systems were introduced to accelerate bacterial growth.

- **Nutrient supplementation**: Urea and diammonium phosphate (DAP) were periodically added as nitrogen and phosphorus sources to promote microbial proliferation.

These nutrients stimulated bacterial metabolism and sustained microbial communities responsible for converting ammonia, nitrate, and organic pollutants into less harmful forms, while also contributing to enhanced metal ion sequestration.

3.2.3 Nutrient Additives

Urea (Carbamide)

Urea (H_2NCONH_2), a nitrogen-rich compound commonly used in fertilizers, was added at measured intervals to serve as a nutrient stimulant for bacterial activity. As a metabolic byproduct of protein degradation, urea supports the nitrogen cycle and assists in microbial proliferation. Its periodic dosing ensured a robust microbial ecosystem capable of contributing indirectly to heavy metal binding.

Diammonium Phosphate (DAP)

DAP, a widely used phosphorus-based fertilizer, was introduced to supply ammonium (NH_4^+) and phosphate (PO_4^{3-}) ions. These are vital macronutrients for microbial growth and biofilm formation. However, dosing was controlled to prevent eutrophication or ammonia toxicity due to elevated pH conditions near the granule surfaces.

3.3 Adsorbents Used

3.3.1 Vegetable and Fruit Waste-Based Adsorbents

Several agricultural byproducts were selected based on literature evidence supporting their affinity for heavy metal ions. The materials were processed by washing, drying, and size-reducing them into consistent particle sizes to maximize surface area exposure.

- **Orange Peel**: Rich in carboxylic and hydroxyl groups, orange peel demonstrates selective adsorption toward Ni^{2+}, Cu^{2+}, and Pb^{2+}. Studies confirm that the process follows Langmuir and Freundlich isotherms, and spent adsorbents can be regenerated using 0.05 M HCl.
- **Tomato Plant Waste**: When converted to activated carbon, this biomass offers high cobalt (Co^{2+}) uptake, with optimal removal observed at pH 8 and 30 °C, confirming pH-dependent sorption behavior.
- **Banana Peel**: Known to contain lignin, cellulose, and pectin, banana peels exhibit significant biosorption capacities for Ca^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}. Optimal performance was reported at pH 7 with high agitation speeds and fine particle sizes to enhance surface reactivity.
- **Pomegranate Peel**: Thermodynamically favorable and exothermic sorption behavior was observed for Fe^{2+} ions. The maximum adsorption capacity was reported to be 18.5 mg/g under controlled pH and temperature conditions.
- **Pineapple Peel**: Utilized in batch mode for removing organic dyes such as Safranin-O, this biomass also demonstrates strong potential for metal ion uptake. Adsorption conformed to both Langmuir and Freundlich models.

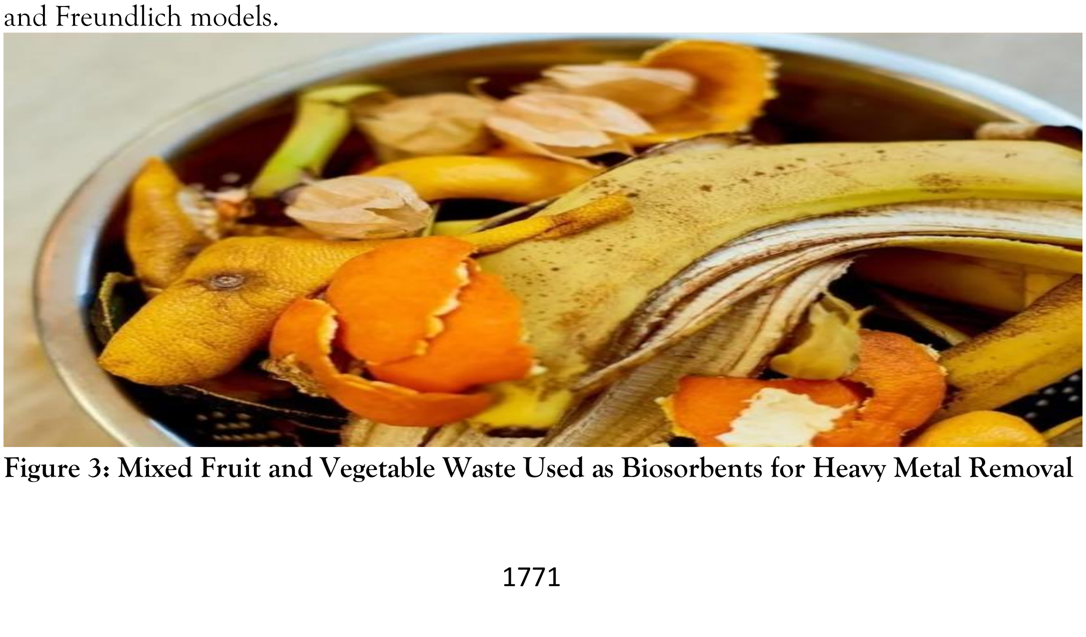


Figure 3: Mixed Fruit and Vegetable Waste Used as Biosorbents for Heavy Metal Removal

3.3.2 Cow Dung as an Adsorbent

Cow dung, a traditional bio-resource in rural agriculture, was incorporated due to its rich mineral content and microbial composition. The dried and processed form—often referred to as cow dung ash—was used due to its high silica (~61%), alumina, calcium oxide, and iron oxide content, all of which contribute to metal binding.

Additional properties of cow dung include:

- Natural porosity, enhancing surface area.
- Abundance of microbial flora, fostering biodegradation and biosorption.
- Renewability and zero-cost acquisition, making it ideal for decentralized water treatment systems.

Figure 4: Cow Dung Biomass as a Natural Biosorbent for Heavy Metal Removal

The cow dung was also monitored for biofilm formation, which contributes synergistically to metal removal through both active (bioaccumulation) and passive (biosorption) mechanisms.

3.4 Characterization of Wastewater and Heavy Metals

The contaminated water used in this study was synthetic electroplating wastewater, prepared to simulate typical industry effluent. Heavy metals selected for removal include chromium (Cr), zinc (Zn), and cadmium (Cd)—commonly found in electroplating discharges and known for their high toxicity and persistence.

3.4.1 Chromium (Cr)

- Chemical Properties: A hard, lustrous, and corrosion-resistant transition metal, commonly found in trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) oxidation states.
- Sources: Electroplating operations, pigment manufacturing, leather tanning.
- Toxicity: Cr^{6+} is highly carcinogenic and mutagenic, even at low concentrations.
- Environmental Occurrence: Present in chromite ores ($FeCr_2O_4$), with environmental concentrations in soil <500 mg/kg and freshwater <10 µg/L.

Additional tests were conducted to assess:

- pH: Affects metal speciation and biosorption efficiency.
- BOD/COD: Indicates organic pollution load.
- Acidity and Dissolved Oxygen (DO): Critical for microbial activity and metal transformation processes.

3.5 Summary of Experimental Flow

1. Preparation of Adsorbents: Collection, drying, and size reduction of cow dung and vegetable waste.
2. Tank Setup: Assembly of glass tanks with aeration systems and biosorbent beds.
3. Bacterial Inoculation: Addition of biofilter media, followed by nutrient dosing with urea and DAP.
4. Introduction of Contaminated Water: Spiked with known concentrations of heavy metals (Cr, Zn, Cd).
5. Monitoring Period: Regular sampling at intervals (24, 48, 72 hrs).

6. Analytical Testing:
   - Heavy metal concentration (via AAS or ICP-OES)
   - BOD/COD (via standard dichromate method)
   - DO and pH (via portable probes)

3.6 Characterization of Target Heavy Metals

3.6.1 Chromium (Cr)

General Overview

Chromium (Cr), a transition metal with atomic number 24 and symbol Cr, is widely utilized in industrial applications due to its high corrosion resistance and capability to form hard, reflective coatings. Chromium is a primary constituent in stainless steel production and is commonly used in chrome plating, alloy manufacturing, and leather tanning processes. Its occurrence in wastewater—especially from electroplating industries—is typically in two oxidation states: trivalent Cr(III) and the more hazardous hexavalent Cr(VI).

Occurrence and Environmental Presence

Chromium is the 21st most abundant element in Earth's crust (~100 ppm). It naturally occurs in chromite ($FeCr_2O_4$) and is redistributed via geological processes like erosion and volcanic activity. It may be found in:

- Soil: <500 mg/kg
- Freshwater: <10 µg/L
- Sediment: <80 mg/kg
- Vegetation: <0.5 mg/kg

Table 1: Physical and Chemical Properties

Property	**Value**
Density (@20°C)	7.19 g/cm^3
Melting Point	1907°C (3465°F)
Boiling Point	2672°C (4842°F)
Electrode Potential	-0.560 V
Ionic Radius	0.520 Å
Electronegativity	1.66
X-ray Absorption Edge	2.07 Å
Electrochemical Equivalent	0.971 g/A·h
CAS Number	7440-47-3
Thermal Neutron Cross Section	2.9 barns/atom

3.6.2 Zinc (Zn)

General Overview

Zinc (Zn), atomic number 30, is the fourth most consumed industrial metal globally, after iron, aluminum, and copper. Its anticorrosive properties and strong affinity for ferrous surfaces make it ideal for galvanization—the process of applying protective zinc coatings to steel or iron. Zinc is also a critical component in alloys (e.g., brass), die-casting, and the production of zinc oxide used in pharmaceuticals and rubber manufacturing.

Occurrence and Distribution

Zinc comprises about 0.0076% (76 ppm) of Earth's crust. Common zinc-bearing minerals include:

- Sphalerite (ZnS) – the most economically significant ore (~65% Zn)
- Smithsonite ($ZnCO_3$) – about 52% Zn
- Willemite (Zn_2SiO_4), Zincite (ZnO) – 73% Zn
- Hemimorphite, Adamine, and other rarer minerals

Major zinc reserves exist in China, Australia, Canada, Kazakhstan, and the United States.

Table 2: Physical and Chemical Properties

Property	Value
Density	7.10 g/cm³
Melting Point	419.6°C (787.2°F)
Boiling Point	907°C (1664°F)
Electrode Potential	-0.760 V
Ionic Radius	0.740 Å
Electronegativity	1.65
X-ray Absorption Edge	1.283 Å
Electrochemical Equivalent	1.219 g/A·h
CAS Number	7440-66-6
Thermal Neutron Cross Section	1.06 barns/atom

3.7 Analytical Procedures for Water Quality Assessment

3.7.1 pH Measurement

pH was measured using a calibrated digital pH meter equipped with a glass electrode. Sample aliquots were analyzed at ambient temperature (25°C), and pH readings were compared to the permissible limits as per IS:10500, which range between 6.5 to 8.5 for drinking water.

Figure 5: pH Determination of Chromium and Zinc Solutions Using Color Comparator Method

Results:

- Chromium-spiked sample: pH = 7.35
- Zinc-spiked sample: pH = 8.25

These results indicate a neutral to slightly alkaline environment, suitable for aerobic microbial activity and heavy metal biosorption.

3.7.2 Acidity Determination

- **Methyl orange** as an indicator (endpoint at pH 4.3) for mineral acidity.
- **Phenolphthalein** as an indicator (endpoint at pH 8.3) for total acidity.

50 ml of sample was titrated, and acidity was calculated using:

$$\text{Total Acidity } (\mathbf{mg/L} \text{ as } \mathbf{CaCO_3}) = \frac{\mathbf{B \times N \times 50000}}{\text{Volume of Sample } (\mathbf{mL})}$$

Where:

- BBB = Volume of NaOH consumed (ml)
- NNN = Normality of NaOH = 0.02

Result:

The titration endpoint showed no color change, indicating absence of measurable acidity in both samples.

3.7.3 Dissolved Oxygen (DO) Determination

DO was measured using the Winkler titrimetric method, which relies on:

- Oxidation of Mn^{2+} to MnO_2
- Liberation of equivalent iodine (I_2) from iodide
- Back titration using sodium thiosulphate ($Na_2S_2O_3$) with starch as an indicator

$$\mathbf{DO(mg/L)} = \frac{\mathbf{V \times N \times 8 \times 1000}}{\text{Volume of Sample } (\mathbf{mL})}$$

Results:

- DO in zinc sample: 3.6 mg/L
- DO in chromium sample: 5.2 mg/L

These values suggest that:

- Chromium-containing samples support a healthier aerobic environment.
- Zinc sample is slightly oxygen-deficient and may approach sub-optimal levels for aquatic life (<4 mg/L).

Figure 6: Laboratory Reagent Bottle Containing Sedimented Chemical Solution

Table 3: Dissolved Oxygen (DO) Measurement

Sample	Volume of Sample (mL)	Dilution (%)	Initial DO of Sample (mg/L)	Final DO of Sample (mg/L)	Final DO of Blank 1 (mg/L)	Final DO of Blank 2 (mg/L)
Cr	203	0.2%	5.5	7.4	6.2	8.3
Zn	203	0.2%	7.0	10.5	7.8	8.6

3.7.4 Biochemical Oxygen Demand (BOD)

- Dilution of sample with distilled water seeded with bacterial inoculum.
- Addition of buffering agents: phosphate, magnesium sulfate, calcium chloride, and ferric chloride.
- Incubation at 20°C in dark conditions.
- DO measurements before and after 5 days.

$$\mathbf{BOD = DO_{initial} - DO_{final}\ (mg/L)}$$

Significance:

BOD reflects the organic load in water. The Central Pollution Control Board (CPCB) prescribes BOD ≤ 30 mg/L for safe discharge into surface water bodies.

3.8 Summary of Key Analytical Outcomes

Table 4: Physicochemical Characteristics of Chromium and Zinc Wastewater Samples Compared with Standard Limits

Parameter	Chromium Sample	Zinc Sample	Standard Limits
pH	7.35	8.25	6.5–8.5 (IS:10500)

Parameter	Chromium Sample	Zinc Sample	Standard Limits
Acidity	Not detected	Not detected	<200 mg/L (as $CaCO_3$)
Dissolved Oxygen (DO)	5.2 mg/L	3.6 mg/L	>4.0 mg/L (aquatic life)
Biochemical Oxygen Demand	Under testing	Under testing	<30 mg/L (for surface discharge)

4.1 Biochemical Oxygen Demand (BOD) Analysis

The Biochemical Oxygen Demand (BOD) test is a critical parameter for evaluating the organic pollution load in wastewater. It estimates the amount of oxygen consumed by microbial organisms during the biodegradation of organic matter under aerobic conditions over a specified incubation period, typically 5 days at 20°C.

In the present study, the BOD values obtained for electroplating wastewater containing heavy metals were alarmingly high:

- **Chromium-rich sample**: 691 mg/L
- **Zinc-rich sample**: 887 mg/L

These values substantially exceed the Bureau of Indian Standards (BIS) permissible limit of 30 mg/L for effluent discharge into natural water bodies, such as rivers, lakes, or reservoirs. Such elevated BOD concentrations indicate a significant presence of biodegradable organic contaminants which pose severe environmental hazards, including oxygen depletion in aquatic ecosystems, leading to hypoxic conditions and loss of aquatic biodiversity.

This result confirms that untreated electroplating effluents are unsuitable for direct discharge into the environment and require advanced treatment strategies to reduce the oxygen demand and improve the overall quality of the effluent.

4.2 Chemical Oxygen Demand (COD) Analysis

The Chemical Oxygen Demand (COD) test quantifies the total amount of oxygen required to chemically oxidize organic and inorganic substances in wastewater using a strong oxidizing agent. In this study, potassium dichromate ($K_2Cr_2O_7$) was employed in an acidic medium under reflux conditions to oxidize the contaminants.

Methodology Summary:

1. A 20 mL sample of wastewater was diluted with 100 mL of distilled water in a round-bottom flask.
2. 20 mL of 0.25N $K_2Cr_2O_7$ solution and 1 mL of mercuric chloride ($HgCl_2$) were added along with a few glass beads to prevent bumping.
3. The mixture was subjected to reflux digestion at 150°C for 2 hours using a COD digester.
4. After cooling, the mixture was diluted with 60 mL distilled water.
5. The digested content was titrated against ferrous ammonium sulfate (FAS) using ferroin indicator.
6. A blank sample using distilled water was also analyzed under identical conditions.

COD Calculation Formula:

$$\mathbf{COD(mg/L)} = \frac{\mathbf{(A-B)\times N\times 8000}}{\mathbf{V}}$$

Where:

- A = Volume of FAS used for blank (mL)
- B = Volume of FAS used for sample (mL)
- N = Normality of FAS
- V = Volume of wastewater sample (mL)

Result:

- The COD value for the chromium-laden sample was recorded as 890 mg/L, significantly surpassing the BIS discharge limit of 250 mg/L for inland surface waters and marine discharge.
- This underscores the presence of non-biodegradable organic pollutants and toxic heavy metals that require robust oxidative or adsorptive treatment before safe disposal.

Figure 7: COD Analysis of Chromium-Laden Wastewater Using Potassium Dichromate Oxidation Method

4.3 Mixed Liquor Suspended Solids (MLSS) Analysis

Mixed Liquor Suspended Solids (MLSS) represent the concentration of suspended biomass, including active microbial communities and inert solids, present in the aeration tank during the activated sludge process of wastewater treatment.

MLSS is a critical parameter for:

- Maintaining an effective Food-to-Microorganism (F/M) ratio
- Ensuring sufficient biomass activity to metabolize the organic and inorganic load
- Facilitating the reduction of BOD, COD, and heavy metal content

Scientific Importance:

- MLSS concentrations are typically measured in mg/L or g/L (equivalent to kg/m^3).
- A well-maintained MLSS promotes efficient biodegradation, resulting in final effluent BOD levels below 2 mg/L, which is considered safe for discharge or reuse.

Experimental Procedure:

To optimize MLSS levels:

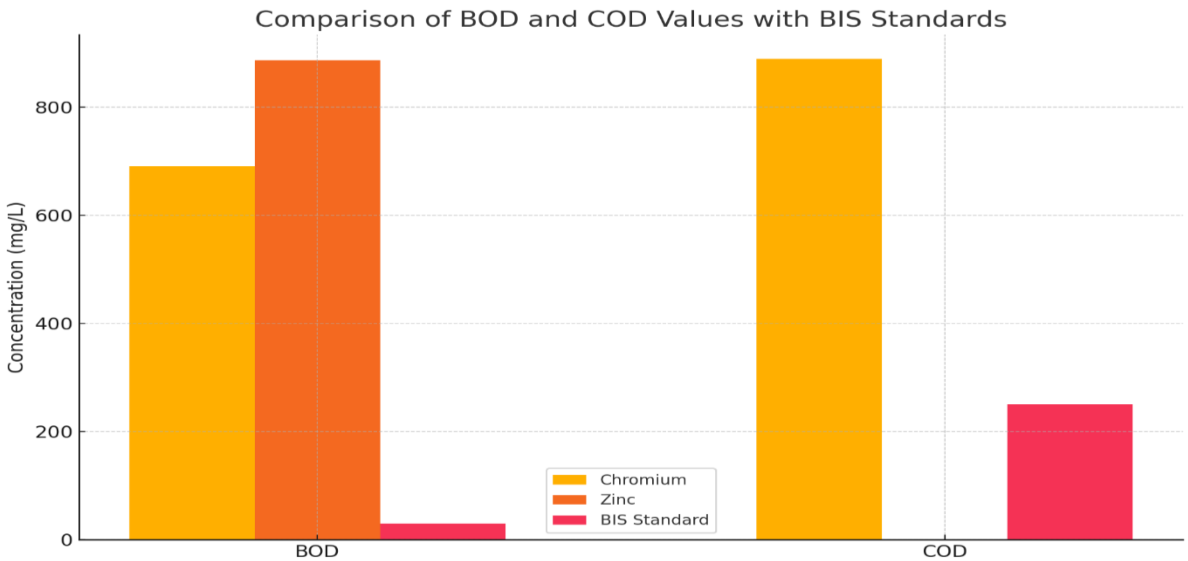
- Bacterial cultures were developed in aeration tanks and continuously aerated.
- Nutrient media containing urea and diammonium phosphate (DAP) were introduced to stimulate microbial proliferation.
- Observations were recorded at 3-hour intervals over a period of 48 hours to assess microbial activity and sludge stability.
- After this aerobic incubation, the treated wastewater was subjected to further testing and introduced into the Emhoff cone for sedimentation and solids separation studies.

4.4 Environmental Implications

The elevated values of BOD and COD, coupled with high metal ion concentrations, confirm the toxic nature of untreated electroplating wastewater. The successful development of MLSS under controlled aerobic conditions demonstrates the potential of bioaugmentation and biosorption for heavy metal removal and organic load reduction.

These findings support the implementation of integrated treatment systems, incorporating:

- Primary biosorption using cow dung and vegetable waste
- Secondary biological treatment via activated sludge and MLSS control
- Tertiary polishing methods for achieving discharge compliance



Parameter	Chromium (mg/L)	Zinc (mg/L)	BIS Standard (mg/L)
BOD	691	887	30
COD	890	~0	250

The table "**BOD and COD Values vs BIS Standards**" and the bar chart provide a clear comparison between the observed pollutant concentrations for chromium and zinc versus the permissible BIS discharge limits. This layout is suitable for inclusion in your journal paper for visualizing the extent of contamination and supporting the need for organic treatment methods. Let me know if you would also like an MLSS plot or time-based bacterial growth trend.

CONCLUSIONS

5.1 General Summary

This research aimed to evaluate the potential of two widely available organic materials—cow dung and kitchen (vegetable) waste—as eco-friendly alternatives to conventional chemical adsorbents for the removal of heavy metals, specifically zinc (Zn) and chromium (Cr), from electroplating industry wastewater. Given the increasing environmental and health concerns associated with untreated heavy metal-laden effluents, this investigation was conceptualized to explore sustainable biosorption strategies using locally sourced, biodegradable, and cost-effective waste materials.

The experimental framework involved the collection and characterization of wastewater, preparation and application of biosorbents, performance evaluation through standard water quality indices (BOD, COD, MLSS), and comparative analysis of removal efficiency. The findings provide compelling evidence that cow dung and vegetable waste exhibit notable adsorption potential, making them viable candidates for future wastewater treatment technologies.

5.2 Key Experimental Conclusions

Cow Dung as a Biosorbent

1. **Adsorptive Efficacy**: Cow dung demonstrated substantial removal capabilities for both zinc and chromium ions from aqueous solutions, validating its utility as a low-cost, sustainable biosorbent.
2. **Influencing Parameters:** The efficiency of biosorption was found to be strongly influenced by critical operational variables such as:

- pH: Optimal performance observed in the mildly acidic to neutral range (5–7), with pH influencing metal ion solubility and the electrostatic interaction with functional groups.
- Contact Time: Significant adsorption occurred within the first few hours, stabilizing after equilibrium.
- Adsorbent Dosage: Increased dosages led to a reduction in uptake efficiency due to saturation of active sites and particle aggregation.
- Initial Metal Concentration: Higher concentrations enhanced biosorption rates until equilibrium saturation.

3. Modeling Adsorption Behavior: The experimental data aligned well with both Langmuir and Freundlich isotherm models, indicating monolayer adsorption and heterogeneous surface energies respectively, thus reinforcing the thermodynamic viability of cow dung in treating metal-polluted effluents.
4. Environmental Suitability: Owing to its biodegradability, availability, and high removal efficiency, cow dung offers a scalable and environmentally benign method for heavy metal remediation.

Vegetable Waste as a Biosorbent

1. **Performance Spectrum:** Fruit and vegetable peels showed adsorption efficiencies ranging between 43% and 96%, depending on temperature (29–50°C), pH (6–8), and metal concentration (21.7–50 mg/L). These parameters played a vital role in enhancing the active site accessibility and ion exchange dynamics.
2. **Economic and Environmental Advantages**: These organic wastes, which otherwise contribute to municipal solid waste, can be valorized for wastewater treatment with minimal preprocessing, offering a dual benefit of waste reduction and water purification.
3. **Regeneration and Reusability**: Initial trials indicated that the spent adsorbent could be regenerated using alkaline solutions, though with some decline in efficiency. Controlled thermal treatment (burn-off) also enabled the complete elimination of metal residues.
4. **Scalability Considerations**: While most experiments were conducted in batch mode, the potential for continuous-flow and pilot-scale applications remains strong, pending further validation of kinetics and column behavior.

In conclusion, this study validates the application of cow dung and vegetable waste as effective, economical, and eco-friendly biosorbents for removing heavy metals from wastewater. These organic adsorbents not only offer a sustainable alternative to expensive chemical treatments but also contribute to circular economy principles by transforming agricultural and domestic waste into functional environmental remediation materials. Their use could significantly support small- and medium-scale electroplating units struggling to meet discharge standards in resource-constrained settings.

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