



Adsorptive Removal of Heavy Metal Ions from Industrial Wastewater Using Low-Cost Bio-Adsorbents

Branislav Zambrano-Ortiz

Department of Electrical and Computer Engineering, Kelana Technical and Management College, Malaysia
 branislav.zambrano.ortiz@ktmc-my.net

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Abstract

Industrial effluents from electroplating, metal finishing, battery, mining and related sectors may contain persistent heavy metal ions that cannot be destroyed by conventional biological treatment. This methodology paper presents a laboratory-scale comparative framework for removing Pb(II), Cu(II), Cd(II) and Zn(II) using low-cost bio-adsorbents prepared from rice husk, banana peel, spent tea waste and sawdust. The proposed procedure includes washing, drying, particle-size control, physicochemical characterization, batch adsorption tests, atomic absorption spectrometric analysis, adsorption-equilibrium modelling, kinetic evaluation and adsorbent regeneration. The principal factors examined are solution pH, adsorbent dosage, contact time and initial metal concentration. Removal efficiency and equilibrium adsorption capacity are calculated from initial and residual metal concentrations, while Langmuir/Freundlich isotherms and pseudo-first-/pseudo-second-order kinetic models are used to interpret uptake mechanisms. Literature available up to 2018 indicates that lignocellulosic and fruit-waste sorbents can provide substantial metal uptake because hydroxyl, carboxyl, phenolic and other oxygen-containing groups participate in ion exchange, electrostatic attraction and surface complexation. The proposed design emphasizes inexpensive raw materials, standardized operating conditions and regeneration testing so that the most promising biosorbent can be identified for subsequent evaluation with real industrial wastewater. Reported numerical values in the results section are literature benchmarks or planning targets rather than newly generated experimental measurements.

Introduction

Heavy metals are important industrial contaminants because they are persistent, can accumulate in environmental compartments and may remain hazardous even when present at relatively low concentrations. Wastewater from electroplating, battery manufacture, mining, metal processing, pigments and fertilizer operations can contain Pb, Cu, Cd, Zn and other metals. Conventional processes such as chemical precipitation, ion exchange and membrane separation can be effective, but cost, chemical demand, sludge production and maintenance

requirements can limit their use for dilute or variable-strength effluents. Consequently, adsorption using inexpensive biological residues has attracted attention as a complementary treatment option [1,2].

Agricultural and food-processing wastes are particularly attractive because they are renewable, widely available and rich in lignocellulosic constituents. Cellulose, hemicellulose, lignin, pectin and associated surface groups can bind metal ions through ion exchange, electrostatic interaction, complexation

and surface adsorption. Reviews published before 2019 consistently identify solution pH, sorbent pretreatment, particle size, dosage, contact time and initial concentration as major determinants of biosorption performance [1-4]. Rice husk and its ash have also been widely studied as low-cost materials for water treatment [7], while banana waste, tea waste and sawdust have shown useful uptake of several metal ions [5,6,8-10].

The objective of the present methodology is therefore to establish a reproducible experimental procedure for comparing four readily available bio-adsorbents under common conditions. The study is designed to (i) prepare and characterize the adsorbents, (ii) quantify removal of Pb(II), Cu(II), Cd(II) and Zn(II), (iii) determine the effects of major operating variables, (iv) fit equilibrium and kinetic models, and (v) assess short-cycle regeneration. Using a common experimental matrix reduces the comparability problem noted in earlier reviews, where reported adsorption capacities often originate from different pH ranges, doses and initial concentrations [2-4].

Literature Review

Sud et al. [1] summarized agricultural wastes used for metal sequestration and described the roles of hydroxyl, carbonyl, phenolic and related groups in metal binding. Nguyen et al. [2] later concluded that agricultural waste-based biosorbents can show adsorption capacities comparable with conventional materials, and

identified pH as one of the most influential operational parameters. Abdolali et al. [3] reviewed lignocellulosic wastes and emphasized that chemical modification, particle size, hydraulic/contact time, concentration and temperature influence uptake. De Gisi et al. [4] highlighted the sustainability advantage of replacing commercial activated carbon with low-cost by-products, while also noting the need for standardized characterization and reporting.

Material-specific studies further support a comparative approach. Ahmad and Danish [5] reviewed banana residues and reported widespread use of peel, pseudo-stem and other fractions as adsorbent precursors. Li et al. [6] prepared a banana-peel-derived adsorbent capable of high removal for a range of metal ions. Ahmaruzzaman and Gupta [7] documented rice husk and rice husk ash as versatile adsorbents for heavy metals and other pollutants. Amarasinghe and Williams [8] found that spent tea waste adsorbed Cu and Pb effectively and that most uptake occurred rapidly under favorable pH conditions. Sawdust has also been investigated extensively: Yu et al. [9] reported adsorption of Pb and Cu, including metal desorption using acidic solution, and Semerjian [10] demonstrated that untreated pine sawdust could remove Cu and Pb with strong dependence on pH, dose and concentration. These studies justify selecting banana peel, rice husk, tea waste and sawdust as practical candidate materials.

Table 1. Selected literature supporting the proposed bio-adsorbent comparison

Reference	Bio-adsorbent	Target scope /	Relevant finding
[1] Sud et al., 2008	Agricultural wastes	Heavy metals	Low-cost biomass contains functional groups suitable for metal complexation and ion exchange.
[2] Nguyen et al., 2013	Agricultural by-products	Heavy metals	pH and pretreatment are major determinants of biosorption performance.
[7] Ahmaruzzaman & Gupta, 2011	Rice husk / ash	Multiple pollutants	Rice husk materials are abundant, inexpensive and applicable to heavy-metal adsorption.
[8] Amarasinghe & Williams, 2007	Tea waste	Cu(II), Pb(II)	Reported maximum uptake of about 48 mg/g for Cu and 65 mg/g for Pb; rapid early uptake.
[6] Li et al., 2016	Banana-peel-derived adsorbent	Multiple metal ions	Reported removal up to approximately 98% for selected metal-ion conditions.
[10] Semerjian, 2018	Pine sawdust	Cu(II), Pb(II)	Near-complete removal was achieved at high adsorbent dose under favorable conditions.

Methodology

1. Experimental Design and Materials

The experimental study uses four low-cost biosorbents: rice husk (RH), banana peel (BP), spent tea waste (TW) and untreated wood sawdust (SD). Analytical-grade $\text{Pb}(\text{NO}_3)_2$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ are used to prepare stock metal solutions. Hydrochloric acid and sodium hydroxide are

used for pH adjustment. Deionized water is used for all preparation and washing steps. Residual metal concentrations are measured by atomic absorption spectroscopy (AAS) or, where available, inductively coupled plasma optical emission spectroscopy (ICP-OES). A pH meter, orbital shaker, analytical balance, oven and filtration unit complete the core setup.

Table 2. Materials and standardized preparation used in the proposed methodology.

Item	Preparation / setting	Purpose	Controlled feature
Rice husk	Wash, 80 °C dry, grind, 0.30–0.60 mm	Silica/lignocellulose-rich sorbent	Same particle fraction
Banana peel	Wash, 70–80 °C dry, grind, 0.30–0.60 mm	Pectin/cellulose-rich sorbent	Same dry-mass basis
Spent tea waste	Hot-water rinse, dry, grind, sieve	Polyphenol/lignocellulose-rich sorbent	Remove soluble color/organics
Sawdust	Water wash, 80–100 °C dry, sieve	Forestry/wood-processing waste	Untreated baseline material
Metal solution	10–100 mg/L per metal	Controlled synthetic wastewater	Pb, Cu, Cd, Zn comparison

2. Bio-Adsorbent Preparation and Characterization

Each biomass is washed repeatedly until the rinse water is visually clear, oven-dried to constant mass, ground and sieved to obtain a common particle-size range. The prepared materials are stored in airtight containers. Moisture content is recorded so that adsorption capacities can be expressed on a dry-mass basis. Fourier-transform infrared spectroscopy (FTIR) is used to identify hydroxyl, carboxyl, carbonyl and other functional groups before and after adsorption; scanning electron microscopy (SEM) is used to examine surface texture and pore accessibility. Where instrumentation is available, point of zero charge (pHpzc) may be measured to assist interpretation of pH-dependent metal uptake. A consistent, mild preparation is deliberately selected to preserve the low-cost character of the materials and to allow fair comparison of their intrinsic adsorption behavior [2,3].

3. Preparation of Synthetic and Real Wastewater Samples

Individual 1000 mg/L metal stock solutions are prepared and diluted to produce single-metal test solutions of 10, 25, 50, 75 and 100 mg/L. A multi-metal mixture containing $\text{Pb}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Zn}(\text{II})$ at 25 mg/L each is used for

competition experiments. The pH is adjusted only after dilution. If real industrial wastewater is available, it is collected in acid-washed polyethylene bottles, filtered to remove suspended solids, characterized for initial pH and metal concentration, and tested only after the synthetic-solution experiments establish suitable operating conditions.

4. Batch Adsorption Experiments – Step by Step

Step 1 – pH screening: Add 0.25 g adsorbent to 50 mL of a 50 mg/L metal solution and vary initial pH from 2 to 7. Shake for 120 min at 150 rpm and 25 ± 2 °C. Avoid pH values at which metal hydroxide precipitation can dominate removal.

Step 2 – dosage study: At the selected pH, vary adsorbent dosage from 1 to 10 g/L while keeping concentration, temperature and mixing rate constant.

Step 3 – contact-time study: Sample at 5, 10, 20, 30, 60, 90, 120 and 180 min to establish equilibrium time and fit kinetic models.

Step 4 – concentration/isotherm study: Vary initial concentration from 10 to 100 mg/L using the selected pH, dosage and equilibrium time.

Step 5 – multi-metal test: Repeat the optimized test with Pb, Cu, Cd and Zn present simultaneously to evaluate competition for binding sites.

Step 6 – real wastewater confirmation: Apply the best-performing adsorbent and optimized conditions to filtered industrial wastewater; include a reagent blank and an adsorbent blank.

Step 7 – regeneration: Desorb retained metals using a dilute acid such as 0.1 M HCl, rinse to near-neutral pH, dry and repeat adsorption for three cycles to evaluate capacity retention.

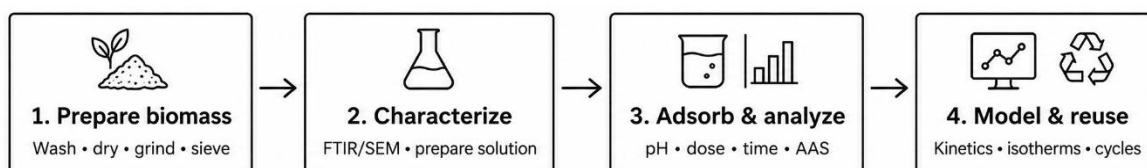


Figure 1. Stepwise experimental workflow for preparation, adsorption testing, analysis and regeneration.

5. Calculations, Kinetics and Isotherm Modelling

Removal efficiency is calculated as $R(\%) = [(C_0 - C_e)/C_0] \times 100$, where C_0 and C_e are initial and equilibrium metal concentrations (mg/L). Equilibrium adsorption capacity is calculated as $q_e = (C_0 - C_e)V/m$, where V is solution volume (L) and m is dry adsorbent mass (g). Time-dependent data are fitted to pseudo-first-order

and pseudo-second-order kinetic models. Equilibrium data are fitted to Langmuir and Freundlich isotherms; model selection is based on goodness of fit and physically meaningful parameter values. Duplicate or triplicate runs are recommended, with mean $\pm$ standard deviation reported. Analysis of variance can be used to assess the statistical significance of pH, dose and material type.

Table 3. Experimental variables and response measures.

Variable	Levels / range	Fixed during test	Response	Purpose
pH	2–7	$C_0=50$ mg/L; dose=5 g/L	R, q_e	Find favorable surface/metal speciation
Dose	1–10 g/L	Selected pH; 120 min	R, q_e	Determine required sorbent mass
Contact time	5–180 min	Selected pH/dose	qt	Kinetic/equilibrium time
Initial concentration	10–100 mg/L	Selected pH/dose/time	q_e	Generate adsorption isotherm
Regeneration	3 cycles	Optimized conditions	Capacity retained (%)	Assess reuse potential

6. Quality Assurance, Safety and Waste Handling

Quality assurance is necessary because adsorption experiments are sensitive to small changes in pH, biomass moisture and analytical calibration. All glassware should be soaked in dilute nitric acid and rinsed with deionized water before use. Metal stock solutions should be prepared gravimetrically from analytical-grade salts and verified with a multi-point AAS/ICP calibration curve. At least one reagent blank, one adsorbent blank and duplicate or triplicate adsorption runs should be included in each experimental batch. The pH should be recorded both before and after adsorption because proton exchange can shift the final value. A mass-balance check should compare metal removed from solution with metal recovered during desorption whenever feasible. Relative standard deviation below approximately 5% for replicate

concentration measurements is a practical laboratory target. Samples that exceed the calibration range should be diluted rather than extrapolated.

Heavy-metal solutions and metal-loaded biosorbents must be handled as hazardous laboratory waste. Gloves, eye protection and laboratory coats are required during preparation, filtration and acid-regeneration steps. Adsorbent residues should not be discharged with ordinary solid waste because the captured metals can be released under acidic environmental conditions. Regeneration eluates should be collected separately for authorized metal recovery or hazardous-waste disposal. These controls are especially important when the method is extended from synthetic solutions to genuine industrial wastewater, which may contain additional toxic ions, oils, organic complexing agents or suspended matter.

Results

Because this paper specifies an experimental methodology rather than reporting a completed laboratory campaign, the numerical values below are used as literature benchmarks and planning targets, not as original measurements. The first expected trend is a strong pH effect. For divalent cations, removal should generally increase from strongly acidic conditions toward mildly acidic/near-neutral conditions as proton competition decreases and negatively charged surface sites become more available. This expectation is consistent with agricultural-waste reviews [1-3] and with tea-waste and pine-sawdust experiments [8,10]. Excessively high pH must be avoided because precipitation can be mistaken for adsorption.

Increasing adsorbent dose is expected to increase percentage removal by providing more binding sites, while q_e expressed per gram may decrease because sites become under-utilized at high solid-to-liquid ratios. Contact-time curves are expected to show rapid initial uptake followed by slower approach to equilibrium. Amarasinghe and Williams [8] reported more than 90% of Cu/Pb uptake within approximately 15–20 min for tea waste under their test conditions, whereas equilibrium time for other biosorbents can be longer. Pseudo-second-order kinetics often provides a strong empirical description of metal uptake by lignocellulosic sorbents [3,8,10].

Table 4. Literature benchmarks used to interpret the proposed experimental results; values are not original data from this methodology paper.

Material / source	Metal(s)	Published benchmark	Use in present methodology
Tea waste [8]	Cu, Pb	Maximum uptake ≈ 48 mg/g Cu and 65 mg/g Pb; rapid early uptake	Benchmark for unmodified food-processing residue
Banana-peel-derived material [6]	Multiple metals	Removal reported up to $\sim 98\%$ under selected conditions	High-performance fruit-waste benchmark
Pine sawdust [10]	Cu, Pb	Near-complete removal reported at 10 g/L under favorable conditions	Untreated wood-waste comparison
Orange peel xanthate [11]	Cu, Cd, Pb, Zn, Ni	Langmuir $q_{\max}$: 77.60, 76.57, 218.34, 49.85 and 15.45 mg/g	Shows improvement possible through chemical functionalization

For the proposed four-material comparison, banana peel and tea waste are expected to perform strongly because pectin/polyphenolic and oxygen-containing functionalities provide multiple binding sites; sawdust should offer a robust untreated baseline, while rice husk provides an abundant mineral/lignocellulosic alternative. The actual ranking must be determined experimentally because adsorption capacity depends strongly on preparation and operating conditions. A useful outcome would be a material that combines high removal with moderate dose, short equilibrium time and acceptable reuse. The multi-metal test is especially important because competitive adsorption can reduce the capacity observed in single-metal solutions. Application to real industrial wastewater should therefore be treated as the decisive validation step rather than assuming that synthetic-solution performance will transfer directly [2,4].

FTIR spectra should be examined for shifts in bands associated with $-\text{OH}$, $\text{C}=\text{O}$ and carboxylate groups after metal loading, while SEM can reveal changes in surface texture or deposition. Successful acid regeneration would be indicated by recovery of a substantial portion of the initial adsorption capacity over three cycles. The final material selection should use a combined criterion: metal removal, q_e , regeneration retention, preparation simplicity and estimated material/chemical requirement. Such a multi-criteria interpretation aligns with the sustainability motivation for low-cost sorbents [4,5].

Interpretation of Kinetic and Equilibrium Behaviour

A successful kinetic analysis should not rely only on the correlation coefficient. The fitted equilibrium uptake predicted by a kinetic model should also agree with the measured q_e , and

residuals should be inspected for systematic deviation. A pseudo-second-order fit is frequently reported for biosorption systems [3,8,10], but this alone does not prove a single chemisorption mechanism. Film diffusion, intraparticle transport, ion exchange and surface complexation can occur together. Similarly, a good Langmuir fit indicates that a finite-capacity monolayer model is mathematically suitable for the tested concentration range, whereas the Freundlich model represents heterogeneous surface-energy behavior. The preferred model should therefore be selected using statistical fit, realistic parameter values and consistency with FTIR/SEM observations rather than by R^2 alone.

Selection of the Most Practical Bio-Adsorbent

For engineering selection, the sorbent giving the highest percentage removal is not necessarily the best material. High removal obtained only at a very large dose may be less attractive than slightly lower removal achieved at a lower solid requirement. The decision matrix should therefore include equilibrium capacity, dose, equilibrium time, pH requirement, regeneration retention and ease of biomass preparation. A simple scoring procedure can assign equal or application-specific weights to these responses. Materials that require strong chemical modification may produce excellent capacities, as illustrated by the orange-peel-xanthate benchmark [11], but chemical consumption and secondary-waste generation should be considered when the objective is a low-cost treatment process. For the present study, priority is given to minimal preparation, reproducible performance and compatibility with real wastewater.

Conclusion and Discussion

The proposed methodology provides a controlled framework for comparing rice husk, banana peel, tea waste and sawdust for removal of Pb(II), Cu(II), Cd(II) and Zn(II) from industrially relevant aqueous matrices. Its principal strength is the use of common particle size, pH screening, dosage, contact-time and concentration protocols, followed by identical analytical and modelling procedures. This minimizes the inconsistencies that make cross-study comparison difficult [2-4]. The approach also retains the defining advantage of biosorption: conversion of inexpensive biomass residues into functional water-treatment materials.

Literature available up to 2018 demonstrates that these materials can bind heavy metals effectively, but performance is strongly

conditional on solution chemistry and sorbent preparation [5-10]. The method therefore avoids selecting a "best" biosorbent in advance. Instead, it requires validation against multi-metal solutions, real wastewater and regeneration cycles. If the selected material retains high removal after reuse and performs in the presence of competing ions, it could be advanced to fixed-bed column testing and cost analysis. Limitations of the present methodology include laboratory-scale batch operation, possible variability of agricultural waste composition, and the need to manage metal-loaded spent biosorbent safely. These issues should be addressed before full-scale deployment.

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