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# Comparative Analysis of Biomass-Based Adsorbents for Heavy Metal Ion Removal

Beta Cahaya Pertiwi<sup>1,a\*</sup>, Noni Firginia<sup>2</sup>, Muhammad Fauzan Satyasauqi<sup>3</sup>, Maudy Pratiwi Novia Matovanni<sup>4</sup>

<sup>1,2,3,4</sup> Department of Chemical Engineering, Faculty of Engineering and Science, Universitas Pembangunan Nasional “Veteran” Jawa Timur, Surabaya 60294, Indonesia

E-mail: <sup>a</sup>bpertiwi.ft@upnjatim.ac.id

\*Corresponding author: bpertiwi.ft@upnjatim.ac.id | Phone number: +6281330710398

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## Abstract

This study investigates the adsorption capabilities of various biomass-based adsorbents for the removal of heavy metal ions from industrial wastewater. This research focusses on the comparative effectiveness of chemical and steam activation methods. Steam-activated adsorbents derived from wine sector waste exhibited a maximum adsorption capacity for Pb<sup>2+</sup> ions of 399 mg/g. Adsorbents derived from walnut shells and chemically activated with HNO<sub>3</sub> ions exhibited a maximum adsorption capacity of 204.08 mg/g for Cu<sup>2+</sup> ions. Steam-activated spruce sawdust adsorbents achieved optimal adsorption of Fe<sup>2+</sup> ions at a capacity of 329 mg/g. The adsorption capacity for Cd<sup>+</sup> ions was determined to be 116 mg/g, achieved through microwave-assisted steam activation of palm kernel shell-based adsorbents. The research emphasizes the necessity of selecting appropriate activation techniques based on specific heavy metal ions and the desired adsorption properties. Additionally, there is a necessity for further investigation into the processes of pore structure development and their impact on adsorption effectiveness. The findings suggest that developing adsorbent from biomass waste represents a sustainable and effective method for reducing heavy metal contamination in industrial wastewater, thereby advancing environmental protection and resource efficiency.

**Keywords:** biomass, heavy metal removal, sustainable remediation

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## 1. Introduction

Heavy metals in industrial wastewater pose serious environmental and health risks due to their toxicity, persistence, and bioaccumulation. Nickel (Ni), Lead (Pb), Mercury (Hg), are particularly concerning, given its extensive use in electroplating, battery manufacturing, and stainless steel production [1], [2]. For example, classified as a Group 1 carcinogen by the IARC, nickel exposure is linked to respiratory issues, kidney damage, and increased cancer risks, while its environmental contamination disrupts aquatic ecosystems and biodiversity. In 2024, Indonesia's Central Statistics Agency (BPS) shows that nickel exports will increase by up to 45.85% [3]. In

Sulawesi and Maluku, nickel concentrations in water exceed safe limits, and over 5,300 hectares of deforestation intensifies climate change [4], [5]. Industrial hubs like Morowali also experience high PM<sub>2.5</sub> levels beyond WHO standards, highlighting the need for stricter regulations.

Biomass waste composed of lignocellulosic materials like lignin, cellulose, and hemicellulose, holds promise for sustainable energy and bioadsorbents with cellulose providing mechanical strength and lignin enhancing structural integrity while resisting microbial degradation [6][7][8]. In Indonesia, with a biomass energy potential of 49,810 MW, utilization remains suboptimal due to competing industrial demands [9]. Agricultural waste such as

sugarcane sludge, palm shells, rice husks, and corn cobs offers significant bioadsorbent potential due to functional groups like phenolic, hydroxyl, and carboxyl which facilitate heavy metal adsorption [10], [11]. Heavy metal pollution from mining and electroplating industries has increased interest in adsorption as a cost-effective, eco-friendly alternative to chemical precipitation, and ion exchange. Lignocellulose-based sludge, with its porous structure and active functional groups, effectively removes hazardous metals while repurposing waste. Additionally, biomass waste management mitigates methane emissions which have 21 times the atmospheric impact of CO<sub>2</sub>, reinforcing its role in pollution control [12]. Integrating lignocellulose-based bioadsorbents into remediation efforts benefits both environmental protection and sustainable resource utilization, necessitating further research and policy support.

Adsorbents capture and retain molecules or ions on their surface through physical or chemical interactions, making them essential in wastewater treatment, air purification, and catalysis. Adsorption, a surface-based process, enables contaminant removal via materials like activated carbon, zeolites, and silica gels, each with distinct mechanisms based on porosity and surface properties [13]. Bioadsorbents derived from biomass offer a sustainable alternative for heavy metal remediation due to their abundance and eco-friendliness. Cellulose-based adsorbents, particularly poly(hydroxamic acid) and poly(amidoxime) ligands, achieve up to 90% nickel removal from electroplating wastewater [14]. Their high reusability enhances economic viability in wastewater treatment. Nanocellulose-based adsorbents further improve adsorption efficiency with a high surface area and tunable surface chemistry, especially when functionalized with carboxylate groups for metal ion removal [15]. These materials also offer superior mechanical stability for industrial applications. As renewable, modifiable, and non-toxic materials, cellulose-based adsorbents align with green chemistry principles, making them a cost-effective and sustainable solution for heavy metal contamination.

The simplest bio adsorbent production method involves biomass carbonization through pretreatment including cleaning and drying, followed by pyrolysis at 300–700°C under low

oxygen to remove volatiles and increase carbon content[16]. Activation uses chemical agents like KOH, ZnCl<sub>2</sub>, or H<sub>3</sub>PO<sub>4</sub>, or physical methods like steam or CO<sub>2</sub> heating, though lignin hinders carbonization and reduces adsorption capacity [17]. To improve adsorption with NaOH or H<sub>2</sub>O<sub>2</sub> before carbonization enhances pore structure but adds processing time and chemical waste management challenges.

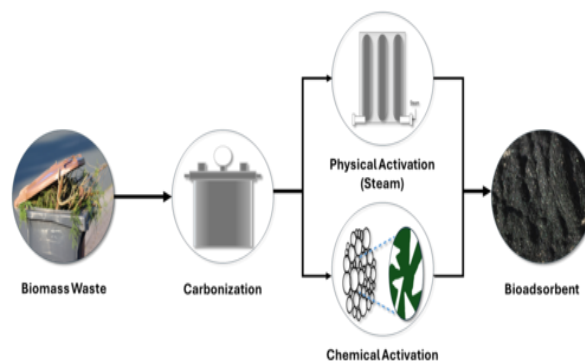


Fig 1. Biomass based adsorbent production.

This study compares two biomass based adsorbent production methods to identify the most effective technique for creating environmentally friendly bio adsorbents with superior adsorption capacity as shown on Figure 1.

The study evaluates chemical activation, physical activation, and surface modification based on adsorption efficiency, raw material availability, and environmental and economic impacts. While activated carbon has a large surface area and strong adsorption capacity, its regeneration requires high energy, increasing costs. Its adsorption ability declines at high heavy metal concentrations, and spent activated carbon poses disposal challenges. This research aims to identify a more sustainable, efficient, and cost-effective bio adsorbent production method for industrial wastewater treatment with minimal environmental impact.

## 2. Materials and Method

### 2.1. Materials

The global accessibility of biomass provides a sustainable basis for the development of novel functional materials. Biomass resources derived from plant, animal, and microbial sources offer

considerable potential as renewable feedstocks in various geographical areas. These organic compounds consist of complex biopolymers, including cellulose, hemicellulose, and lignin, which provide carbon frameworks and functional groups for material applications.

Biomass presents in various specific forms amenable to valorisation: (1) forestry residues (wood chips, sawdust, and associated lignocellulosic byproducts), (2) agricultural wastes (crop residues, straw, and husks), (3) industrial processing byproducts (food waste, paper sludge), and (4) aquatic biomass (macroalgae and hydrophytes)[18], [19], [20], [21], [22], [23]. Agricultural residues like rice straw and wheat straw exhibit significant potential as biomass-based adsorbents owing to their low economic value, widespread availability, and advantageous physicochemical characteristics.

Likewise, underutilised soybean hulls demonstrate considerable capacity for heavy metal absorption, especially for Pb(II) and Cd(II) ions, due to their abundant surface functionalities, which include carbonyl, phenolic, acetamido, alcoholic, amido, amino, and sulfhydryl groups that promote metal coordination[24].

Biomass ash, a waste of agroindustrial processing, when modified with chitosan and graphene oxide composites, has improved adsorption efficiencies of 69.5% for Cu(II) and Table 1. Comparison between biomass materials and production method

74.7% for Cr(VI)[25]. Aquatic macrophytes represent a significant resource; *Lemna minor* (duckweed) accumulates metals via indirect absorption mechanisms, translocating toxic metals from roots to shoots, whereas *Ceratophyllum demersum* demonstrates substantial adsorption capacities for aqueous heavy metals: 6.17 mg/g (Cu(II)), 13.98 mg/g (Zn(II)), and 44.8 mg/g (Pb(II))[26], [27].

## 2.2. Method

Referring to these problems, several discussions on heavy metal adsorption using biomass have led to the identification of two primary methods. These methods focus on enhancing the adsorption efficiency and sustainability of biomass-based adsorbents.

### a. Carbonization - Activation using steam Method

Carbonization using the steam activation method involves heating carbon-rich materials in an inert atmosphere followed by exposure to steam at high temperatures (700–1000°C) to enhance porosity and surface area[28], [29], [30].

### b. Carbonization - Chemical Activation Method

Carbonization using the chemical activation method involves impregnating raw biomass with

No.	Materials	Method	Adsorption Capacity (mg/g)	Activation Agent	Ref.
1	Grape Industrial Waste	Carbonization → Physical Activation	75 (Cd <sup>2+</sup> ); 399 (Pb <sup>2+</sup> )	Steam	[50]
2	Spruce Sawdust	Carbonization → Physical Activation	17.2 (Zn <sup>2+</sup> ); 6.6 (Ni <sup>2+</sup> ); 4.5 (Co <sup>2+</sup> )	Steam	[54]
3	Date Pits	Carbonization → Physical Activation	165 (Cu <sup>2+</sup> ); 329 (Fe <sup>2+</sup> )	Steam	[55]
4	Tobacco Biomass	Carbonization → Physical Activation	62.23 (Cr(VI))	Microwave Steam	[52]
5	Palm Kernel Shell	Carbonization → Physical Activation	116 (Cd <sup>2+</sup> ); 59.9 (Pb <sup>2+</sup> )	Microwave Steam	[53]
6	Olive Stone	Carbonization → Chemical Activation	186.77 (Pb <sup>2+</sup> )	KOH	[56]
7	Almond Shells	Carbonization → Chemical Activation	182.69 (Pb <sup>2+</sup> )	KOH	[56]
8	Walnut Shells	Carbonization → Chemical Activation	204.08 (Cu <sup>2+</sup> )	HNO <sub>3</sub> ;KOH	[51]
9	Walnut Shells	Carbonization → Chemical Activation	210.14 (Pb <sup>2+</sup> )	KMnO <sub>4</sub> , n-hexane, acrylic acid, acetone	[57]

chemical agents such as potassium hydroxide (KOH), phosphoric acid ( $\text{H}_3\text{PO}_4$ ), or zinc chloride ( $\text{ZnCl}_2$ ) before thermal treatment. During carbonization at moderate temperatures (400–1000°C)[36], [37], the activating agents enhance the porous structure by dehydrating and oxidizing the material, thereby improving its surface area and adsorption capacity. This method is widely used for producing activated carbon with high surface area and tunable pore structures, making it ideal for applications in adsorption, catalysis, and energy storage.

The formation of pore structures is determined by the physicochemical interactions between the activating agent and the carbon framework, which encompass the adsorption energies of both reactants and products [47], [48]. The increased adsorption energy of products correlates with enhanced pore activity. Finally, the flow rate of the activating medium influences the textural and fractal properties of the carbon, where increased flow rates result in smoother fractal structures and a decrease in the surface fractal dimension[49].

### 3. Results and Discussion

The difference between the two methods can be compared based on their efficiency and adsorption capacity. The phenomenon that occurs can also be explained in detail regarding the results obtained. Based on the Table 1. The adsorption process of heavy metals occurs when metal ions from a solution bind to the surface of an adsorbent material through physical and chemical mechanisms. In this study, several biomass show the highest performance in adsorbing toxic heavy metal ions such as  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ , and  $\text{As}^{3+}$ .

Data from table 1 indicate that numerous heavy metal ions demonstrate considerable adsorption capacities on diverse biomass-based adsorbents.  $\text{Pb}^{2+}$  ions exhibited the maximum adsorption capacity of 399 mg/g when utilising adsorbents derived from wine industry waste[50], which underwent carbonisation and steam activation at 973 K for 165 minutes, with a steam flow rate of 11.7 g/(g·hour).

Optimal adsorption of  $\text{Fe}^{2+}$  ions (329 mg/g) was attained using steam-activated spruce sawdust adsorbents [52]. Alternative physical activation methods yielded satisfactory outcomes,

exemplified by the adsorption of  $\text{Cd}^{2+}$  ions (116 mg/g) utilising palm kernel shell-based adsorbents activated through microwave-assisted steam. The process duration was 45 minutes at 700°C, utilising a flow rate of 5 g/minute, thereby enhancing thermal efficiency relative to traditional methods[53].

The steam activation process facilitates the formation of oxygenated surface functional groups, including carboxyl, lactone, and phenolic hydroxyl moieties, which significantly improve heavy metal uptake via multiple interaction mechanisms [31], [32]. These surface functionalities promote metal ion adsorption through both ion exchange processes and chemisorption interactions, as evidenced by enhanced  $\text{Pb}(\text{II})$  and  $\text{Cd}(\text{II})$  removal efficiencies. The presence of these oxygen-containing groups has been demonstrated to be a critical determinant of adsorption performance, serving as active sites for metal ion coordination and complexation [31], [33].

The adsorption kinetics of heavy metal ions onto steam-activated carbon surfaces typically exhibit strong correlation with pseudo-second-order kinetic models, suggesting a predominance of chemisorption mechanisms. This behavior reflects rate-limiting surface reactions involving electron sharing or exchange between metal cations and oxygen-containing functional groups on the activated carbon matrix [33], [34], [35].

The properties of activated carbon are influenced by various factors, including activation temperature, duration, method and ratio, precursor material type, pretreatment techniques, activation atmosphere, physicochemical interactions, and the flow rate of the activating agent.

Higher activation temperatures encourage the formation of microporous and mesoporous structures, which enhance the surface area and total pore volume [38], [39], [40]. Prolonged activation durations enhance pore size distribution, facilitating the development of more sophisticated pore networks [39], [41], [42].

On the other side, Walnut shell-based adsorbents, chemically activated with  $\text{HNO}_3$  and KOH, exhibited a maximum adsorption capacity of 204.08 mg/g for  $\text{Cu}^{2+}$  ions [51]. The use of KOH in chemical activation methods is notably effective for the formation of microporous structures, with pore development efficiency

being significantly influenced by the precursor-to-activator ratio [41], [43], [44], [45]. Biomass-based precursors typically produce more uniform and well-developed pore structures owing to their aliphatic characteristics, in contrast to those derived from coal [46].

Pretreatment techniques, including milling, sieving, and ash elimination, improve the quality of carbon by enhancing surface area and the hierarchical structure of pores. The composition of the activation atmosphere is significant; for instance, the presence of CO<sub>2</sub> can enhance mesopore formation by affecting reaction kinetics [41], [42].

#### 4. Conclusions

This study underscores the considerable efficacy of biomass-derived adsorbents in the extraction of heavy metal ions from industrial effluents. The comparative analysis of steam activation and chemical activation methods indicates that both procedures possess significant adsorption capacities, with steam activation often necessitating elevated temperatures and chemical activation allowing for adjustable pore shapes. The maximum adsorption capacity for Pb<sup>2+</sup> ions was recorded at 399 mg/g utilising steam-activated adsorbents sourced from wine industry waste. Adsorbents derived from walnut shells and chemically activated with HNO<sub>3</sub> and KOH

The comparison of steam activation and chemical activation involves not only adsorption capacity but also the characteristics of pore surfaces. Steam activation typically necessitates elevated temperatures ranging from 600 to 1000°C, whereas chemical activation functions within a temperature range of 600 to 900°C. Despite the relatively similar temperature ranges, it is essential to investigate the fundamental differences in mechanisms and their effects on pore structure for specific applications in heavy metal adsorption.

exhibited a maximum adsorption capacity of 204.08 mg/g for Cu<sup>2+</sup> ions.

The results highlight the necessity of choosing suitable activation techniques according to particular heavy metal ions and targeted adsorption capabilities. The result underscores the necessity for additional research into the fundamental mechanisms of pore structure creation and their influence on adsorption efficiency. Incorporating biomass waste into sustainable remediation initiatives alleviates environmental degradation, enhances resource utilisation, and diminishes carbon footprints.

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