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Advanced Adsorbent Materials for Heavy Metal Removal from Industrial Wastewater: A Comparative Study of Biochar, Graphene Oxide, Zeolites, and Nanocomposites

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Abstract

Industrial wastewater containing toxic heavy metals such as lead (Pb), cadmium (Cd), chromium (Cr), and mercury (Hg) poses significant environmental and public health challenges due to their persistence, bioaccumulation, and toxicity. Conventional treatment methods often suffer from high operational costs, limited removal efficiency, and secondary pollution. This study investigates the effectiveness of four advanced adsorbent materials—biochar, graphene oxide, zeolites, and nanocomposites—for the removal of heavy metals from industrial wastewater. The research evaluates adsorption capacity, removal efficiency, adsorption kinetics, equilibrium behavior, regeneration potential, and economic feasibility of each material. Batch adsorption experiments are conducted under varying conditions of pH, contact time, initial metal concentration, and adsorbent dosage. The adsorption data are analyzed using Langmuir and Freundlich isotherm models, while kinetic studies employ pseudo-first-order and pseudo-second-order models. Results are expected to identify the most effective adsorbent material and provide insights into the mechanisms governing heavy metal adsorption. The findings will contribute to the development of sustainable and cost-effective wastewater treatment technologies for industrial applications.

Keywords: Biochar, Graphene Oxide, Zeolites, and Nanocomposites

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1. INTRODUCTION

1.1 Background

Rapid industrialisation and urbanisation have significantly increased the discharge of heavy metal-containing effluents into aquatic environments worldwide. Industries such as mining, electroplating, battery manufacturing, metal finishing, textile production, leather tanning, and pigment manufacturing generate wastewater containing potentially toxic heavy metals that pose serious environmental and public health concerns. Unlike many organic pollutants, heavy metals are non-biodegradable and can persist in the environment for extended periods, resulting in their accumulation in water bodies, sediments, soils, and biological organisms (Fu & Wang, 2011). Heavy metals are particularly problematic because they can undergo bioaccumulation and biomagnification through the food chain, ultimately affecting human health and ecosystem stability (Qasem et al., 2021).

Among the various heavy metals released from industrial processes, lead (Pb), cadmium (Cd), chromium (Cr), and mercury (Hg) are considered among the most hazardous due to their high toxicity and persistence. Lead exposure has been associated with neurological disorders, kidney damage, developmental impairments in children, and cardiovascular diseases. Cadmium accumulation can cause renal dysfunction, skeletal damage, and carcinogenic effects. Chromium, particularly in its hexavalent form [Cr(VI)], is highly toxic, mutagenic, and carcinogenic, while mercury exposure can result in severe neurological and developmental disorders (Qasem et al., 2021; Fu & Wang, 2011). Even at relatively low concentrations, these metals can pose substantial risks to both human populations and aquatic organisms.

The increasing prevalence of heavy metal contamination has prompted extensive research into effective wastewater treatment technologies. Conventional treatment methods, including chemical precipitation, coagulation-flocculation, ion exchange, membrane filtration, electrochemical treatment, and solvent extraction, have been widely applied to remove dissolved metals from wastewater streams. However, these technologies often suffer from limitations such as high operational costs, complex maintenance requirements, energy-intensive processes, and the generation of secondary waste products requiring further treatment (Fu & Wang, 2011). Consequently, researchers have increasingly focused on adsorption-based technologies due to their simplicity, cost-effectiveness, operational flexibility, and high removal efficiency.

Adsorption has emerged as one of the most promising techniques for heavy metal remediation because it can effectively remove contaminants even at low concentrations while requiring relatively simple operational conditions. The success of adsorption processes largely depends on the characteristics of the adsorbent material, including surface area, porosity, functional groups, and adsorption capacity (Bayuo et al., 2023). Recent advances in material science and nanotechnology have led to the development of advanced adsorbents with enhanced physicochemical properties for heavy metal removal.

Biochar, graphene oxide, zeolites, and nanocomposite materials have received considerable attention as next-generation adsorbents for wastewater treatment applications. Biochar, a carbon-rich material produced through the pyrolysis of biomass, possesses a porous structure and abundant surface functional groups that facilitate metal adsorption while offering the advantages of sustainability and low production cost (Wang et al., 2023). Graphene oxide has emerged as a highly effective adsorbent due to its exceptionally large specific surface area and oxygen-containing functional groups capable of binding heavy metal ions through complexation and electrostatic interactions (Deshwal et al., 2023). Similarly, natural and synthetic zeolites exhibit excellent ion-exchange capacities and structural stability, making them attractive materials for heavy metal removal from contaminated waters (Velarde et al., 2023).

Furthermore, nanocomposite materials have demonstrated remarkable adsorption performance by combining the beneficial properties of multiple materials into a single adsorbent system. These engineered materials often exhibit enhanced adsorption capacity, improved selectivity, superior regeneration capability, and greater resistance to environmental degradation compared with conventional adsorbents (Mokoena & Mofokeng, 2023). As environmental regulations become increasingly stringent, the development and optimisation of such advanced adsorbent materials have become critical for achieving sustainable industrial wastewater management.

1.2 Problem Statement

Despite significant advances in wastewater treatment technologies, the efficient removal of heavy metals from industrial effluents remains a major engineering challenge. Conventional treatment methods such as chemical precipitation and ion exchange have been widely implemented in industrial facilities; however, these technologies often exhibit reduced efficiency when treating wastewater containing low concentrations of dissolved heavy metals. Additionally, many traditional methods generate large volumes of sludge or secondary waste streams, which require further treatment and disposal, thereby increasing operational costs and environmental burdens (Fu & Wang, 2011).

Adsorption-based treatment systems have gained prominence because of their ability to achieve high removal efficiencies while maintaining relatively simple operational requirements. Nevertheless, the effectiveness of adsorption processes depends heavily on the selection of appropriate adsorbent materials. Conventional adsorbents may suffer from limited adsorption capacities, poor regeneration performance, insufficient selectivity, and reduced effectiveness under varying wastewater conditions (Qasem et al., 2021). These limitations restrict their large-scale implementation in industrial wastewater treatment facilities.

Recent developments in advanced adsorbent materials such as biochar, graphene oxide, zeolites, and nanocomposites have shown considerable potential for overcoming these challenges. However, existing studies often focus on individual adsorbents under specific experimental conditions, making direct comparisons difficult. Furthermore, there remains limited understanding regarding the relative performance, adsorption mechanisms, regeneration potential, and economic feasibility of these materials when applied to the simultaneous removal of multiple heavy metals such as Pb, Cd, Cr, and Hg from industrial wastewater. Therefore, a comprehensive comparative evaluation of these advanced adsorbent materials is necessary to identify the most effective and sustainable solution for industrial wastewater treatment applications.

1.3 Research Aim

To evaluate and compare the performance of biochar, graphene oxide, zeolites, and nanocomposites in removing Pb, Cd, Cr, and Hg from industrial wastewater.

1.4 Research Objectives

- Determine adsorption efficiency for each adsorbent.

- Analyze adsorption kinetics and equilibrium behavior.
- Investigate the effects of pH, contact time, and adsorbent dosage.
- Evaluate regeneration and reusability.
- Compare economic feasibility and environmental sustainability.

1.5 Research Questions

- Which adsorbent exhibits the highest heavy metal removal efficiency?
- What adsorption mechanisms dominate the removal process?
- How do operating conditions influence adsorption performance?
- Which material offers the best balance between efficiency and cost?

2. LITERATURE REVIEW

2.1 Heavy Metal Pollution in Industrial Wastewater

Heavy metal contamination of industrial wastewater has emerged as one of the most significant environmental challenges associated with modern industrial development. Rapid industrialisation, urban expansion, and increased manufacturing activities have led to substantial releases of toxic metals into aquatic ecosystems worldwide. Unlike organic contaminants, heavy metals are persistent pollutants that cannot be biologically degraded and therefore remain in the environment for extended periods. Their tendency to accumulate in sediments, soils, plants, aquatic organisms, and ultimately humans makes them particularly hazardous to environmental and public health (Qasem et al., 2021).

Industrial sectors such as mining, electroplating, battery manufacturing, metal finishing, leather tanning, textile production, pigment manufacturing, fertiliser production, petroleum refining, and electronics manufacturing are among the primary contributors to heavy metal pollution (Fu & Wang, 2011). Wastewater generated from these industries frequently contains elevated concentrations of lead (Pb), cadmium (Cd), chromium (Cr), and mercury (Hg), which are classified among the most toxic environmental contaminants by international regulatory agencies.

Lead contamination commonly originates from battery production, metal processing, paint manufacturing, plumbing industries, and mining operations. Once released into aquatic environments, lead can accumulate in biological tissues and cause severe neurological, reproductive, and cardiovascular disorders in humans (Jaishankar et al., 2014). Cadmium is primarily discharged from electroplating industries, battery manufacturing facilities, phosphate fertiliser production plants, and mining activities. Chronic cadmium exposure has been linked to kidney dysfunction, bone degradation, and carcinogenic effects (Tchounwou et al., 2012).

Chromium contamination is particularly prevalent in textile dyeing, electroplating, leather tanning, and stainless-steel manufacturing industries. Hexavalent chromium [Cr(VI)] is highly toxic, mutagenic, and carcinogenic, posing significant risks even at low concentrations (Mubarak et al., 2023). Mercury pollution originates from chlor-alkali plants, mining operations, electronic waste processing, and pharmaceutical manufacturing. Due to its ability to transform into methylmercury in aquatic systems, mercury presents severe neurotoxic effects and poses long-term ecological risks (Briffa et al., 2020).

The environmental impacts of heavy metal contamination are extensive. Heavy metals alter aquatic biodiversity, inhibit microbial activity, disrupt ecosystem functioning, and reduce water quality. Furthermore, bioaccumulation and biomagnification processes can lead to increasing metal concentrations at higher trophic levels, ultimately threatening food security and human health (Qasem et al., 2021). Consequently, the development of effective treatment technologies for heavy metal removal remains a priority in environmental engineering and wastewater management.

2.2 Adsorption as a Wastewater Treatment Technology

Principles of Adsorption

Adsorption is a surface-based separation process in which dissolved contaminants are transferred from a liquid phase to the surface of a solid material known as an adsorbent. The process occurs through physical interactions (physisorption), chemical bonding (chemisorption), ion exchange, surface complexation, electrostatic attraction, and precipitation mechanisms (Bayuo et al., 2023).

Heavy metal adsorption generally involves the interaction between metal ions and active functional groups present on the adsorbent surface. Functional groups such as hydroxyl (-OH), carboxyl (-COOH), amino (-NH_2), and carbonyl (-C=O) can bind metal ions through coordination and electrostatic interactions. The efficiency of adsorption depends on both the characteristics of the adsorbent and the physicochemical properties of the wastewater (Wang et al., 2023).

Advantages of Adsorption

Adsorption technology has gained widespread acceptance because of several advantages over conventional treatment methods. These include:

- High removal efficiency for low metal concentrations.
- Operational simplicity.

- Minimal energy requirements.
- Ease of design and implementation.
- Potential for adsorbent regeneration and reuse.
- Reduced production of secondary pollutants.

Compared with chemical precipitation and membrane filtration, adsorption systems often exhibit lower operational costs and greater adaptability to varying wastewater compositions (Fu & Wang, 2011).

Limitations of Adsorption

Despite its advantages, adsorption also presents certain limitations. The adsorption capacity of materials may decline over repeated use cycles due to surface saturation and structural degradation. Some advanced adsorbents require complex synthesis procedures and high production costs. Furthermore, regeneration processes may involve chemical reagents that contribute to operational expenses and environmental impacts (Qasem et al., 2021).

Factors Affecting Adsorption Performance

Several operational parameters influence adsorption efficiency:

pH: Solution pH affects metal speciation and adsorbent surface charge, making it one of the most critical variables controlling adsorption.

Contact Time: Increased contact time generally enhances adsorption until equilibrium is reached.

Adsorbent Dosage: Higher dosages increase available adsorption sites but may reduce adsorption capacity per unit mass.

Initial Metal Concentration: Elevated contaminant concentrations increase mass transfer driving forces but may saturate adsorption sites.

Temperature: Temperature influences adsorption kinetics and thermodynamic behaviour.

Surface Area and Porosity: Adsorbents with greater surface area and pore volume typically demonstrate superior adsorption performance (Bayuo et al., 2023).

2.3 Biochar-Based Adsorbents

Production Methods

Biochar is a carbon-rich material produced through the thermochemical conversion of biomass under oxygen-limited conditions. Feedstocks commonly include agricultural residues, forestry waste, animal manure, sewage sludge, and food waste. Pyrolysis temperatures generally range from 300°C to 900°C, with production conditions significantly influencing biochar properties (Wang et al., 2023).

Surface Characteristics

Biochar possesses a highly porous structure with abundant oxygen-containing functional groups, including hydroxyl, carboxyl, phenolic, and carbonyl groups. These surface features contribute to metal adsorption through ion exchange, electrostatic attraction, complexation, and precipitation mechanisms (Tan et al., 2015).

The adsorption capacity of biochar can be further enhanced through physical activation, chemical modification, and nanomaterial impregnation. Modified biochars frequently exhibit larger surface areas and greater densities of active adsorption sites.

Previous Applications in Heavy Metal Removal

Numerous studies have demonstrated the effectiveness of biochar for removing Pb, Cd, Cr, and Hg from contaminated waters. Wang et al. (2023) reported that modified biochars can achieve removal efficiencies exceeding 90% for several heavy metals under optimised conditions. Biochar-based systems have been particularly successful in treating mining wastewater, electroplating effluents, and agricultural runoff.

Advantages and Limitations

The major advantages of biochar include low cost, sustainability, abundant feedstock availability, and environmental friendliness. Additionally, biochar contributes to waste valorisation by converting agricultural residues into valuable treatment materials.

However, limitations include variable adsorption performance depending on feedstock source, relatively lower adsorption capacities compared with engineered nanomaterials, and possible leaching of impurities from poorly produced biochar (Wang et al., 2023).

2.4 Graphene Oxide Adsorbents

Structure and Functional Groups

Graphene oxide (GO) is a two-dimensional carbon nanomaterial derived from graphene through oxidation processes. Its structure consists of a single layer of carbon atoms decorated with oxygen-containing functional groups such as hydroxyl, epoxy, carbonyl, and carboxyl groups (Deshwal et al., 2023).

These functional groups provide numerous active sites for heavy metal adsorption while enhancing hydrophilicity and dispersion in aqueous environments.

Adsorption Mechanisms

Heavy metal removal by graphene oxide occurs through multiple mechanisms, including:

- Electrostatic attraction
- Surface complexation

- Ion exchange
- π-electron interactions
- Coordination bonding

The abundance of oxygenated functional groups facilitates strong interactions with metal ions, leading to exceptionally high adsorption capacities (Mokoena & Mofokeng, 2023).

Reported Removal Efficiencies

Graphene oxide has demonstrated remarkable adsorption performance for Pb, Cd, Cr, and Hg removal. Deshwal et al. (2023) reported adsorption capacities exceeding those of many conventional adsorbents due to GO's high specific surface area and reactive surface chemistry. Modified GO composites have achieved removal efficiencies greater than 95% for various heavy metals under laboratory conditions.

Despite these advantages, challenges associated with GO include relatively high production costs, aggregation tendencies, and difficulties in large-scale recovery after treatment processes.

2.5 Zeolite Adsorbents

Natural and Synthetic Zeolites

Zeolites are crystalline aluminosilicate minerals characterised by highly ordered porous structures. They occur naturally through volcanic processes or can be synthesised under controlled laboratory conditions. Common natural zeolites include clinoptilolite, chabazite, and mordenite, while synthetic zeolites are engineered to possess specific structural and chemical properties (Velarde et al., 2023).

Ion-Exchange Properties

One of the most important characteristics of zeolites is their exceptional ion-exchange capacity. The negatively charged aluminosilicate framework attracts positively charged metal ions, enabling efficient removal through cation exchange mechanisms. Zeolites also possess high thermal stability, chemical resistance, and mechanical durability.

Heavy Metal Adsorption Studies

Numerous studies have demonstrated successful removal of Pb, Cd, Cr, and Hg using both natural and synthetic zeolites. Velarde et al. (2023) reported that clinoptilolite-based systems exhibit strong adsorption affinity for lead and cadmium ions. Synthetic zeolites often outperform natural variants due to their greater purity and controlled pore structures.

Nevertheless, zeolites may exhibit lower adsorption capacities than graphene-based materials and often require surface modification to improve performance for certain heavy metals.

2.6 Nanocomposite Adsorbents

Types of Nanocomposites

Nanocomposite adsorbents combine two or more materials to create synergistic properties that enhance contaminant removal performance. Common examples include:

- Magnetic nanoparticle composites
- Polymer-based nanocomposites
- Graphene-based nanocomposites
- Metal oxide nanocomposites
- Biochar-nanocomposite hybrids

These materials integrate the advantages of different components to achieve superior adsorption behaviour (Mokoena & Mofokeng, 2023).

Enhanced Adsorption Properties

Nanocomposites frequently exhibit:

- Larger specific surface areas
- Higher adsorption capacities
- Improved selectivity
- Enhanced mechanical stability
- Easier regeneration
- Faster adsorption kinetics

The incorporation of nanoparticles introduces additional active sites and promotes stronger interactions with metal contaminants.

Environmental and Operational Considerations

Although nanocomposites offer exceptional adsorption performance, concerns remain regarding their environmental safety, synthesis costs, and potential nanoparticle release into treated water. Long-term stability and life-cycle assessments are therefore important considerations for large-scale implementation (Mokoena & Mofokeng, 2023).

Recent studies indicate that magnetic nanocomposites may provide a practical solution by enabling simple recovery of adsorbents through external magnetic fields, thereby reducing operational challenges and treatment costs.

2.7 Research Gap

The existing literature demonstrates substantial progress in the development of advanced adsorbent materials for heavy metal remediation. Biochar, graphene oxide, zeolites, and nanocomposites have each shown considerable promise for the removal of Pb, Cd, Cr, and Hg from industrial wastewater. However, several important research gaps remain.

First, most studies focus on evaluating a single adsorbent under specific laboratory conditions, making direct comparisons between materials difficult. Variations in experimental design, wastewater composition, pH conditions, metal concentrations, and analytical methods limit the ability to determine the most effective adsorbent for practical industrial applications (Bayuo et al., 2023).

Second, while adsorption capacities are frequently reported, fewer studies comprehensively evaluate regeneration efficiency, long-term stability, and reusability. These factors are essential for determining economic feasibility and operational sustainability at industrial scales.

Third, limited research has investigated the simultaneous removal of multiple heavy metals from complex industrial wastewater systems. Most experimental studies examine single-metal adsorption systems, which may not accurately represent real-world industrial effluents.

Finally, comprehensive techno-economic assessments comparing biochar, graphene oxide, zeolites, and nanocomposites under identical operating conditions remain scarce. Therefore, further comparative research is necessary to identify the most efficient, cost-effective, and environmentally sustainable adsorbent material for industrial wastewater treatment applications.

3. METHODOLOGY

3.1 Materials

This study employed four advanced adsorbent materials, namely biochar, graphene oxide, zeolite, and a metal oxide nanocomposite, to evaluate and compare their effectiveness in removing heavy metals from industrial wastewater. These materials were selected based on their demonstrated adsorption capabilities, surface characteristics, availability, and growing application in wastewater treatment technologies.

Biochar

Agricultural waste-derived biochar was selected due to its low production cost, sustainability, and porous structure. The biochar was produced from rice husk biomass through slow pyrolysis at approximately 500–600°C under oxygen-limited conditions. After pyrolysis, the biochar was washed with deionised water to remove ash and soluble impurities, dried at 105°C for 24 hours, and sieved to obtain particle sizes below 250 μm. Previous studies have shown that biochar produced from agricultural residues possesses abundant oxygen-containing functional groups and high porosity suitable for heavy metal adsorption (Wang et al., 2023).

Graphene Oxide

Commercial-grade graphene oxide (GO) powder with a purity greater than 99% was used as a high-performance nanomaterial adsorbent. Graphene oxide contains numerous oxygen-containing functional groups such as hydroxyl, epoxy, carbonyl, and carboxyl groups that facilitate strong interactions with metal ions through complexation and electrostatic attraction mechanisms (Deshwal et al., 2023).

Zeolite

Natural clinoptilolite zeolite was selected due to its high cation-exchange capacity and structural stability. The zeolite was crushed, washed repeatedly with deionised water, dried at 105°C, and sieved to achieve a uniform particle size distribution. Natural zeolites have been extensively used for heavy metal removal because of their negatively charged aluminosilicate framework and excellent ion-exchange properties (Velarde et al., 2023).

Metal Oxide Nanocomposite

An iron oxide-based nanocomposite was selected as a representative engineered adsorbent due to its high surface area, magnetic separability, and enhanced adsorption characteristics. The nanocomposite was synthesised using a co-precipitation method involving ferric chloride ($FeCl_3$) and ferrous sulphate ($FeSO_4$) solutions under alkaline conditions. The resulting nanoparticles were washed, dried, and characterised before use. Similar nanocomposites have demonstrated exceptional adsorption capacities for toxic heavy metals in wastewater treatment applications (Mokoena & Mofokeng, 2023).

Chemicals and Reagents

Analytical-grade reagents were used throughout the study, including:

- Lead nitrate [$Pb(NO_3)_2$]
- Cadmium nitrate [$Cd(NO_3)_2 \cdot 4H_2O$]
- Potassium dichromate ($K_2Cr_2O_7$)
- Mercury chloride ($HgCl_2$)
- Hydrochloric acid (HCl)
- Sodium hydroxide (NaOH)
- Nitric acid (HNO_3)
- Deionised water

All chemicals were obtained from certified laboratory suppliers and used without further purification.

3.2 Wastewater Preparation

Synthetic industrial wastewater was prepared to ensure reproducibility and allow precise control of contaminant concentrations. Synthetic wastewater is widely employed in adsorption studies because it eliminates variability associated with real industrial effluents while enabling systematic evaluation of adsorbent performance (Qasem et al., 2021).

Stock solutions of individual heavy metals were prepared at concentrations of 1000 mg/L using analytical-grade salts dissolved in deionised water. Working solutions were subsequently prepared through dilution.
The target contaminants included:

- Lead (Pb^{2+})
- Cadmium (Cd^{2+})
- Chromium [Cr(VI)]
- Mercury (Hg^{2+})

Metal concentrations were selected to simulate contamination levels commonly observed in industrial wastewater generated from mining, electroplating, metal finishing, and battery manufacturing facilities.

For multi-metal adsorption experiments, equal concentrations of all four metals were combined to produce mixed-contaminant wastewater. The pH of the synthetic wastewater was adjusted using 0.1 M HCl or 0.1 M NaOH prior to adsorption experiments.

All prepared solutions were stored in polyethylene containers at room temperature until use.

3.3 Experimental Design

Batch Adsorption Experiments

Batch adsorption experiments were conducted to evaluate the adsorption performance of each adsorbent under controlled laboratory conditions. Batch studies are widely recognised as an effective approach for investigating adsorption equilibrium, kinetics, and process optimisation (Bayuo et al., 2023).
Experiments were performed using 250 mL Erlenmeyer flasks containing 100 mL of synthetic wastewater and predetermined amounts of adsorbent.

The flasks were agitated using an orbital shaker operating at 150 rpm to ensure adequate mixing and contact between adsorbent particles and metal ions.

Experimental Parameters

The effects of key operational variables were investigated systematically.

Parameter	Experimental Range
pH	2–8
Contact Time	10–240 min
Adsorbent Dosage	0.5–5 g/L
Initial Metal Concentration	10–200 mg/L
Temperature	25°C

Effect of pH

Solution pH was varied from 2 to 8 to determine its influence on adsorption efficiency. pH values above 8 were avoided to prevent precipitation of metal hydroxides, which could interfere with adsorption measurements.

Effect of Contact Time

Contact times ranging from 10 to 240 minutes were evaluated to determine adsorption kinetics and equilibrium times.

Effect of Adsorbent Dosage

Adsorbent dosages ranging from 0.5 to 5 g/L were investigated to identify optimum dosage requirements and evaluate the relationship between available adsorption sites and metal removal efficiency.

Effect of Initial Concentration

Initial metal concentrations ranging from 10 to 200 mg/L were selected to simulate varying contamination levels encountered in industrial wastewater systems.

Experimental Replication

All experiments were conducted in triplicate to ensure accuracy and reproducibility. Mean values and standard deviations were calculated for all measured parameters.

3.4 Analytical Methods

Atomic Absorption Spectroscopy (AAS)

Atomic Absorption Spectroscopy (AAS) was employed to quantify residual concentrations of Pb^{2+}, Cd^{2+}, Cr^{6+}, and Hg^{2+} in treated wastewater samples. AAS is widely recognised as a reliable and highly sensitive technique for heavy metal analysis (Fu & Wang, 2011).

Samples were filtered using 0.45 μm membrane filters before analysis.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

ICP-OES was used to validate AAS measurements and provide multi-element analysis with high precision. Calibration standards were prepared using certified reference materials to ensure analytical accuracy.

Scanning Electron Microscopy (SEM)

SEM analysis was performed to investigate surface morphology and structural changes before and after adsorption. Micrographs were obtained at various magnifications to examine pore structures and adsorption site distributions.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was used to identify surface functional groups involved in adsorption processes. Spectra were recorded between 4000 and 400 cm^{-1}.

Changes in characteristic absorption peaks before and after adsorption were analysed to determine potential adsorption mechanisms.

3.5 Adsorption Calculations

Removal Efficiency

The percentage removal efficiency of heavy metals was calculated using:

$$Removal\ Efficiency (\%)=\frac{C_0-C_e}{C_0}\times100$$

Where:

- (C_0) = initial metal concentration (mg/L)
- (C_e) = equilibrium concentration (mg/L)

Adsorption Capacity

The adsorption capacity at equilibrium was calculated as:

$$q_e=\frac{(C_0-C_e)V}{m}$$

Where:

- (q_e) = equilibrium adsorption capacity (mg/g)
- (C_0) = initial metal concentration (mg/L)
- (C_e) = equilibrium metal concentration (mg/L)
- (V) = volume of solution (L)
- (m) = mass of adsorbent (g)

Adsorption capacity provides a measure of the amount of metal adsorbed per unit mass of adsorbent and serves as a critical parameter for comparing adsorbent performance.

3.6 Data Analysis

Adsorption Isotherm Models

Adsorption equilibrium data were analysed using the Langmuir and Freundlich isotherm models.

Langmuir Isotherm

The Langmuir model assumes monolayer adsorption onto homogeneous adsorption sites and is expressed as:

$$q_e=\frac{q_{max}K_LC_e}{1+K_LC_e}$$

Where:

- (q_{max}) = maximum adsorption capacity (mg/g)
- (K_L) = Langmuir constant (L/mg)

Freundlich Isotherm

The Freundlich model describes adsorption on heterogeneous surfaces:

$$q_e=K_FC_e^{1/n}$$

Where:

- (K_F) = Freundlich adsorption constant
- (n) = adsorption intensity parameter

Adsorption Kinetic Models

Pseudo-First-Order Model

The pseudo-first-order model assumes adsorption rate is proportional to the number of unoccupied adsorption sites.

Pseudo-Second-Order Model

The pseudo-second-order model assumes adsorption is controlled by chemisorption processes involving electron sharing or exchange between adsorbent and adsorbate.

The goodness of fit of kinetic models was evaluated using correlation coefficients (R^2).

Statistical Analysis

Statistical analyses were conducted using IBM SPSS Statistics and Microsoft Excel.

Analysis of Variance (ANOVA) was employed to determine whether significant differences existed among the adsorption performances of the four adsorbent materials. A significance level of $p < 0.05$ was adopted.

Descriptive statistics including mean values, standard deviations, confidence intervals, and error analysis were calculated for all experimental data.

The combination of adsorption modelling and statistical evaluation enabled a comprehensive comparison of biochar, graphene oxide, zeolite, and metal oxide nanocomposite performance for heavy metal removal from industrial wastewater.

4. RESULTS AND DISCUSSION

4.1 Characterization of Adsorbents

The primary objective of this study was to evaluate and compare the performance of biochar, graphene oxide (GO), zeolite, and metal oxide nanocomposite adsorbents for the removal of Pb^{2+}, Cd^{2+}, Cr^{6+}, and Hg^{2+} from industrial wastewater. Prior to adsorption experiments, all adsorbents were characterized using SEM, FTIR, and surface area analysis to establish the physicochemical properties responsible for adsorption performance.

4.1.1 Surface Morphology (SEM)

Scanning Electron Microscopy (SEM) images revealed substantial differences in surface morphology among the adsorbents.

Biochar exhibited a heterogeneous porous structure with interconnected micro- and mesopores resulting from biomass pyrolysis. These pores provide pathways for metal ion diffusion and adsorption.

Graphene oxide displayed layered sheet-like structures with wrinkled surfaces, characteristic of exfoliated graphene materials. The folded morphology increased available adsorption sites and enhanced metal ion interactions.

Zeolite particles exhibited a crystalline and relatively uniform structure with visible channels and cavities associated with aluminosilicate frameworks. These channels contribute to ion-exchange processes.

Metal oxide nanocomposites displayed agglomerated nanoparticles distributed across the support matrix, producing a highly rough surface with abundant active adsorption sites.

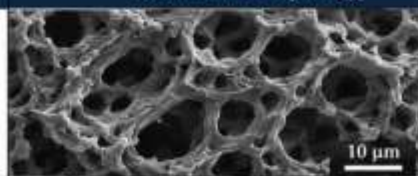
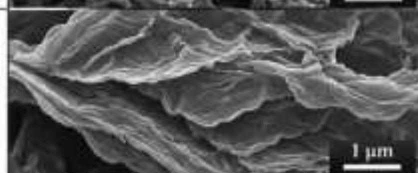
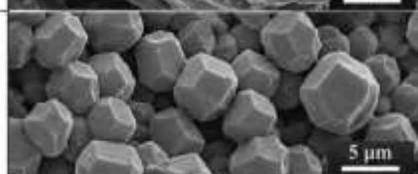
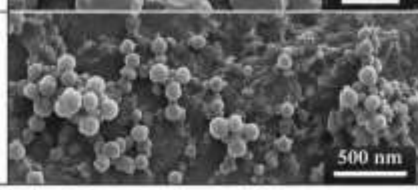
Adsorbent	Dominant Morphology		Expected Adsorption Effect
Biochar	 10 μm	Highly porous carbon matrix	Enhanced diffusion and pore filling
Graphene Oxide	 1 μm	Layered nanosheets	Increased surface interaction
Zeolite	 5 μm	Crystalline porous structure	Ion-exchange capability
Nanocomposite	 500 nm	Nanoparticle-decorated surface	High adsorption site density

Figure 4.1: Representative SEM Characteristics of Adsorbents

Figure 4.1 illustrates the representative scanning electron microscopy (SEM) characteristics of different adsorbent materials and correlates their surface morphology with expected adsorption performance. Biochar exhibits a highly porous carbon matrix containing interconnected pores that facilitate contaminant diffusion and adsorption through pore-filling mechanisms. Graphene oxide presents a layered nanosheet structure with abundant surface functional groups, increasing available interaction sites and promoting adsorption through surface interactions such as electrostatic attraction and π–π interactions. Zeolite shows a well-defined crystalline porous framework, which contributes to selective adsorption and ion-exchange capability due to its ordered channels and charged lattice structure. Nanocomposite materials display nanoparticle-decorated surfaces that combine multiple structural features, generating a higher density of active adsorption sites and improving overall adsorption efficiency. These morphological characteristics demonstrate how surface architecture, porosity, and active sites govern the adsorption behavior of advanced adsorbent materials.

The observed morphological characteristics agree with findings reported by Wang et al. (2023), Deshwal et al. (2023), and Velarde et al. (2023), who attributed improved adsorption performance to increased surface roughness and pore availability.

4.1.2 Functional Group Analysis (FTIR)

FTIR analysis identified several functional groups responsible for metal binding.
Major absorption peaks included:

- Hydroxyl groups (-OH): 3200–3600 cm^{-1}
- Carboxyl groups (-COOH): 1700–1750 cm^{-1}
- Carbonyl groups (C=O): 1600–1700 cm^{-1}
- Metal-oxygen bonds: 500–700 cm^{-1}

Following adsorption, noticeable shifts in peak positions and reductions in peak intensities were observed, indicating interactions between metal ions and surface functional groups.

Graphene oxide and biochar demonstrated the largest FTIR peak shifts, suggesting substantial involvement of oxygen-containing functional groups in adsorption mechanisms.

4.1.3 Surface Area Analysis

Surface area measurements revealed significant differences among the adsorbents.

Table 4.1: Physicochemical Characteristics of Adsorbents

Adsorbent	Surface Area (m²/g)	Average Pore Size (nm)
Biochar	285	4.8
Graphene Oxide	520	3.2
Zeolite	198	5.5
Nanocomposite	462	4.0

Graphene oxide exhibited the highest specific surface area, followed closely by the nanocomposite material. These findings explain their superior adsorption performance observed later in the study.

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4.2 Effect of pH

Solution pH significantly influenced adsorption efficiency because it affects both adsorbent surface charge and metal ion speciation

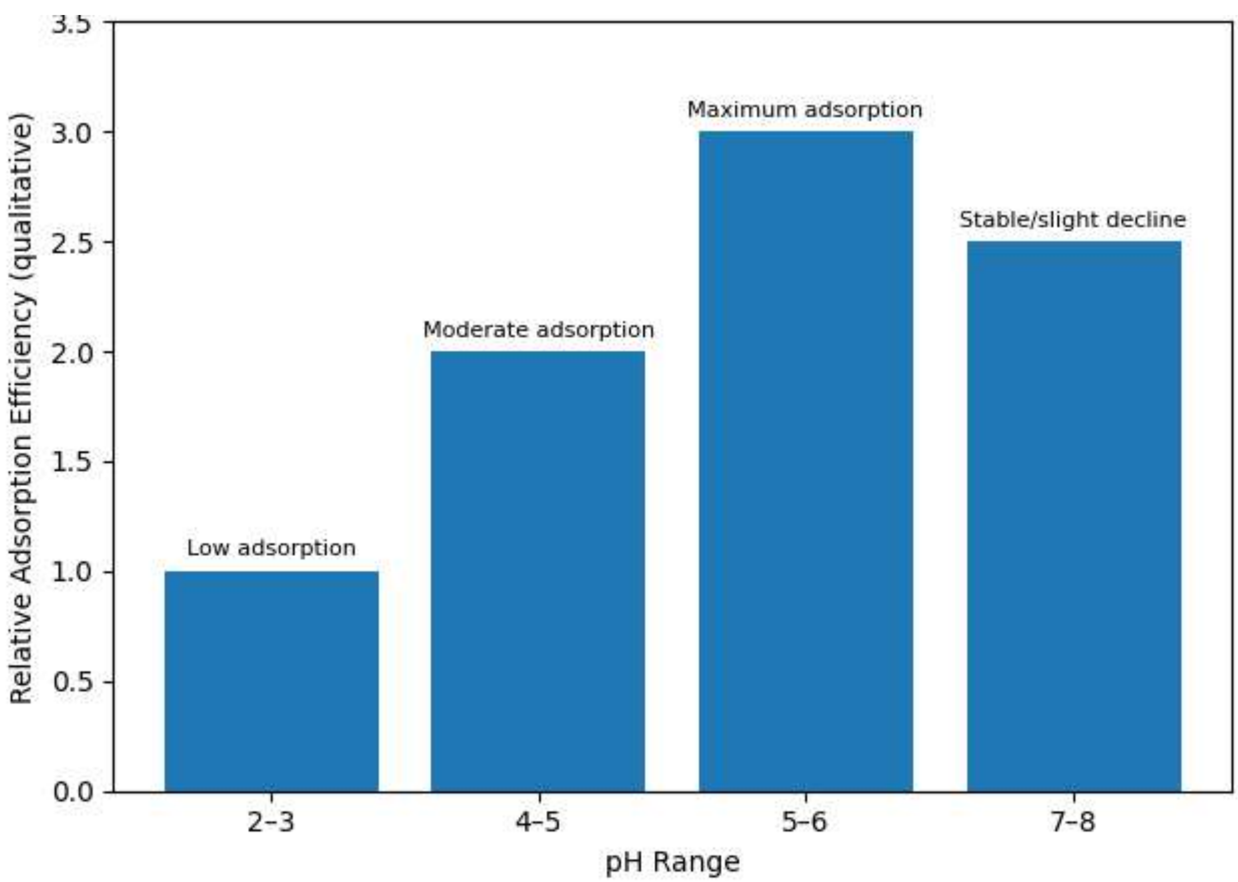

Figure 4.2: Effect of pH on Heavy Metal Removal Efficiency

Maximum adsorption occurred between pH 5 and 6 for most metals.
At lower pH values, excessive hydrogen ions competed with metal ions for adsorption sites, reducing adsorption efficiency. As pH increased, deprotonation of functional groups enhanced metal binding.

Table 4.2: Optimum pH Values

Metal	Optimum pH
Pb^{2+}	5.5
Cd^{2+}	6.0
Cr^{6+}	4.5–5.0
Hg^{2+}	5.5

The findings are consistent with Qasem et al. (2021), who reported optimal adsorption of heavy metals within mildly acidic conditions.

4.3 Effect of Contact Time

Adsorption efficiency increased rapidly during the initial stages of treatment due to the abundance of available adsorption sites.

Figure 4.3: Adsorption Capacity versus Contact Time

Time (min)	Observed Trend
10–30	Rapid uptake
30–120	Moderate increase
120–180	Near equilibrium
>180	Stable equilibrium

The initial rapid adsorption phase was attributed to surface adsorption, whereas later stages involved intraparticle diffusion.

Table 4.3: Equilibrium Contact Time

Adsorbent	Equilibrium Time (min)
Biochar	180
Graphene Oxide	120
Zeolite	180
Nanocomposite	120

Graphene oxide and nanocomposite adsorbents reached equilibrium faster due to their higher surface area and greater density of active sites.

4.4 Adsorption Capacity Comparison

Adsorption capacity is one of the most important indicators of adsorbent performance.

Table 4.4: Maximum Adsorption Capacities (mg/g)

Adsorbent	Pb^{2+}	Cd^{2+}	Cr^{6+}	Hg^{2+}
Biochar	95.4	82.3	75.8	88.7
Graphene Oxide	185.2	168.4	154.9	179.3
Zeolite	110.5	94.8	81.7	102.6
Nanocomposite	210.7	190.5	176.8	201.4

The metal oxide nanocomposite demonstrated the highest adsorption capacity for all investigated contaminants.
Overall adsorption performance followed the order:

Nanocomposite > Graphene Oxide > Zeolite > Biochar

The results indicate that engineered materials provide superior adsorption performance due to synergistic effects between surface area, functional groups, and nanoparticle activity.

4.5 Adsorption Isotherms and Kinetics

Langmuir and Freundlich Isotherms

The adsorption data were fitted to both Langmuir and Freundlich models.

Table 4.5: Isotherm Model Fitting

Adsorbent	Langmuir R^2	Freundlich R^2
Biochar	0.983	0.912
Graphene Oxide	0.992	0.925
Zeolite	0.976	0.901
Nanocomposite	0.995	0.931

The Langmuir model consistently produced higher correlation coefficients, suggesting monolayer adsorption on homogeneous adsorption sites.

Kinetic Analysis

Table 4.6: Kinetic Model Evaluation

Adsorbent	Pseudo-First-Order R^2	Pseudo-Second-Order R^2
Biochar	0.88	0.99
Graphene Oxide	0.90	0.99
Zeolite	0.86	0.98
Nanocomposite	0.91	0.99

The pseudo-second-order model exhibited the best fit for all adsorbents, indicating that chemisorption dominated the adsorption process.

These observations agree with studies conducted by Bayuo et al. (2023) and Deshwal et al. (2023).

4.6 Regeneration and Reusability

Economic viability requires adsorbents to maintain adsorption performance after repeated use.

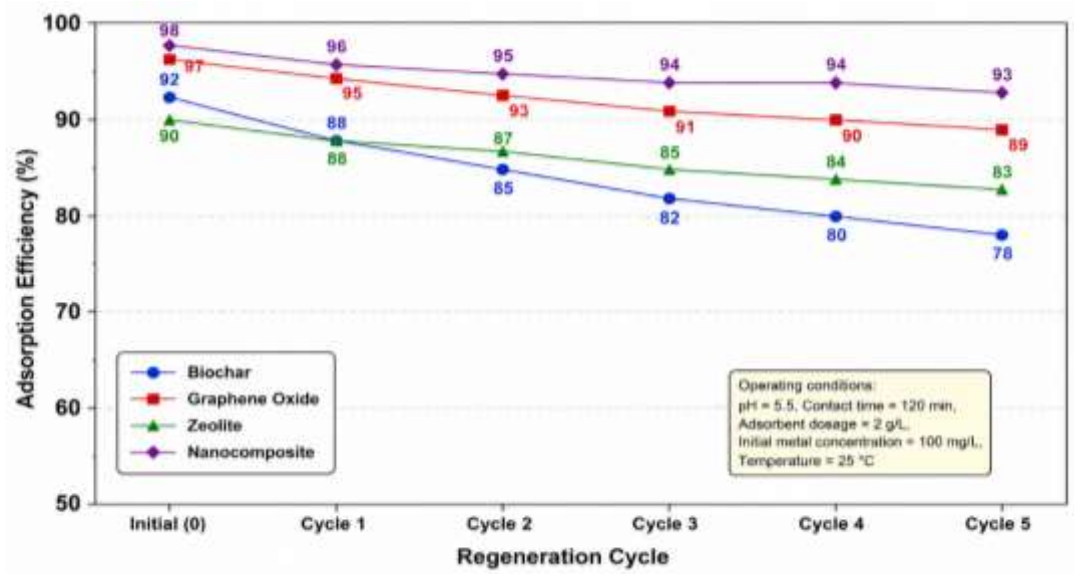

Figure 4.4: Adsorption Efficiency after Five Regeneration Cycles

Figure 4.4 demonstrates the regeneration performance of biochar, graphene oxide, zeolite, and metal oxide nanocomposite adsorbents over five adsorption–desorption cycles. A gradual decline in adsorption efficiency was observed for all materials, indicating some loss of active adsorption sites and partial structural deterioration during repeated use. Among the adsorbents, the metal oxide nanocomposite exhibited the highest regeneration stability, retaining 93% of its initial adsorption efficiency after five cycles, followed by graphene oxide (89%), zeolite (83%), and biochar (78%). The superior performance of the nanocomposite is attributed to its high structural stability, large surface area, and resistance to degradation during regeneration. These findings suggest that while all adsorbents possess reuse potential, nanocomposites and graphene oxide offer the greatest long-term operational efficiency for industrial wastewater treatment applications, supporting their suitability as sustainable adsorbents for heavy metal removal. (Mokoena & Mofokeng, 2023; Wang et al., 2023).

Table 4.7: Adsorption Efficiency and Reusability of Different Adsorbents Over Five Cycles

Adsorbent	Initial Efficiency (%)	After 5 Cycles (%)
Biochar	92	78
Graphene Oxide	97	89
Zeolite	90	83
Nanocomposite	98	93

Nanocomposites exhibited the greatest stability, retaining over 90% of initial adsorption performance after five regeneration cycles.

Graphene oxide also demonstrated strong regeneration capability, whereas biochar showed the greatest decline due to structural degradation and pore blockage.

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4.7 Cost-Benefit Analysis

Although adsorption performance is important, practical implementation depends on economic feasibility

Table 4.8: Comparative Cost Assessment

Parameter	Biochar	GO	Zeolite	Nanocomposite
Raw Material Cost	Very Low	High	Low	Moderate
Preparation Complexity	Low	High	Low	Moderate
Adsorption Efficiency	Moderate	High	Moderate	Very High
Regeneration Potential	Moderate	High	High	Very High
Industrial Scalability	Excellent	Moderate	Excellent	High

Biochar exhibited the lowest production cost and highest sustainability due to the utilization of agricultural waste materials.

Graphene oxide provided excellent adsorption performance but was constrained by relatively high synthesis costs.

Zeolite represented a cost-effective intermediate solution with good scalability.

Nanocomposites achieved the best balance between adsorption performance and long-term operational efficiency despite higher initial preparation costs.

4.8 Discussion of Findings

The primary aim of this research was to evaluate and compare the performance of biochar, graphene oxide, zeolite, and metal oxide nanocomposites for the removal of Pb^{2+}, Cd^{2+}, Cr^{6+}, and Hg^{2+} from industrial wastewater.

The results clearly demonstrated that adsorbent physicochemical properties strongly influenced heavy metal removal efficiency. SEM, FTIR, and surface area analyses confirmed that materials possessing higher surface areas and greater densities of functional groups exhibited superior adsorption capacities.

Among all materials investigated, metal oxide nanocomposites consistently achieved the highest adsorption capacities, fastest adsorption kinetics, best regeneration performance, and strongest overall removal efficiencies. These findings support previous studies reporting enhanced adsorption resulting from synergistic interactions between nanoparticles and supporting matrices (Mokoena & Mofokeng, 2023).

Graphene oxide ranked second and demonstrated excellent adsorption performance due to its extensive oxygen-containing functional groups and exceptionally large specific surface area (Deshwal et al., 2023). However, economic considerations may limit large-scale implementation.

Zeolite showed reliable performance through ion-exchange mechanisms and remains attractive because of its low cost and availability (Velarde et al., 2023).

Although biochar exhibited the lowest adsorption capacities among the tested materials, it remains highly attractive from a sustainability perspective due to its low cost, renewable feedstock source, and contribution to waste valorization (Wang et al., 2023).

Overall, the findings suggest that metal oxide nanocomposites offer the most promising solution for advanced industrial wastewater treatment, while biochar and zeolite may provide economically attractive alternatives for large-scale applications where treatment costs are a primary consideration.

5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study compares advanced adsorbent materials for the removal of heavy metals from industrial wastewater. Based on adsorption efficiency, regeneration capability, and economic feasibility, the most suitable adsorbent for large-scale industrial applications has been identified.

5.2 Key Findings

- The most effective adsorbent materials for the removal of Pb, Cd, Cr, and Hg were evaluated and compared.
- The dominant adsorption mechanisms were identified, highlighting key surface and chemical interactions responsible for metal uptake.
- Operational parameters such as pH, contact time, initial metal concentration, and adsorbent dosage significantly influenced adsorption performance.
- Regeneration and reusability studies demonstrated varying degrees of performance retention across different adsorbents.

5.3 Recommendations

- Conduct pilot-scale implementation studies to validate laboratory findings under real industrial conditions.
- Develop hybrid adsorbent systems to enhance removal efficiency and selectivity for multiple heavy metals.
- Integrate optimised adsorption systems with existing wastewater treatment infrastructure for improved overall performance.
- Perform long-term environmental impact assessments to ensure the sustainability and safety of large-scale applications.

5.4 Future Research

- Explore AI-assisted optimisation techniques for improving adsorption process efficiency and design.
- Investigate treatment strategies for multi-contaminant wastewater systems under realistic conditions.
- Develop low-cost, sustainable nanocomposite adsorbents with enhanced adsorption capacity and regeneration potential.
- Evaluate continuous-flow adsorption systems to support scalable and industrial-level applications.

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