

COMPARATIVE STUDY OF NATURAL AND CHEMICALLY MODIFIED ADSORBENTS FOR PHENOL REMOVAL

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³soomro93mustajab@gmail.com ⁴ameerjan@uomp.edu.pk,DOI: <https://doi.org/10.5281/zenodo.19875929>**Keywords**

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Copyright @Author**Corresponding Author: *****Fozia Khatoon Soomro****Abstract**

The contamination of water resources by phenolic compounds represents a significant environmental and public health concern due to their toxicity, persistence, and resistance to conventional biological degradation. This study provides a comprehensive comparative evaluation of natural and chemically modified adsorbents for the removal of phenol from aqueous systems. Adsorption is identified as an efficient and economically viable technique compared to alternative treatment methods. Natural adsorbents derived from agricultural biomass and mineral sources exhibit moderate adsorption capacities, primarily due to the presence of functional groups such as hydroxyl and carboxyl. However, their performance is substantially enhanced through chemical modification techniques, including alkaline and acid activation, as well as surface functionalization. Modified adsorbents demonstrate improved surface area, pore structure, and active site availability, resulting in significantly higher adsorption capacities. Advanced materials, particularly nanostructured adsorbents, show exceptional performance with capacities exceeding 1600 mg/g. The study further explores adsorption mechanisms, distinguishing between physisorption and chemisorption, and evaluates the influence of key operational parameters such as pH, temperature, and contact time. Kinetic and isotherm analyses reveal that the adsorption process predominantly follows pseudo-second-order kinetics and is well described by the Langmuir model. Overall, chemically modified adsorbents offer a highly effective and sustainable solution for phenol removal in wastewater treatment applications.

1. INTRODUCTION

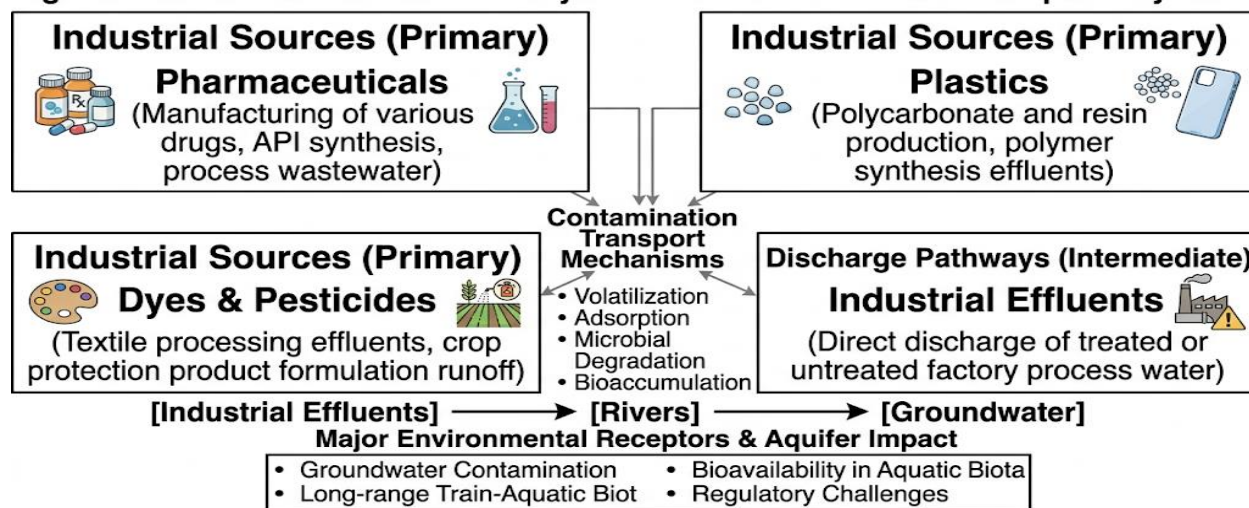
The contemporary industrial landscape is defined by a paradox where technological advancement frequently occurs at the expense of environmental equilibrium (El-Bery et al., 2022). Among the myriad challenges facing modern environmental

engineering, the contamination of aqueous systems by phenolic compounds represents a critical bottleneck for sustainable development (Rathod et al., 2024). Phenol C₆H₅-OH and its complex derivatives are not merely industrial byproducts; they are pervasive structural

components in the manufacturing of resins, pharmaceuticals, dyes, plastics, and agricultural chemicals (Brandão et al., 2017). The discharge of untreated or inadequately treated phenolic wastewater into natural water bodies triggers a cascade of ecological and public health crises (Al-Sakkaf et al., 2023). Even at trace concentrations, these compounds exhibit high toxicity, mutagenicity, and a resistance to conventional biological degradation that necessitates the deployment of advanced physicochemical remediation strategies (Afsharnia et al., 2016). Adsorption has emerged as the most viable methodology for the sequestration of phenol from industrial effluents, distinguishing itself from competitive techniques such as membrane filtration, ion exchange, and advanced oxidation through its operational simplicity and economic

flexibility (Ho, 2022). While commercial activated carbon remains the benchmark for adsorptive performance, its prohibitive production and regeneration costs have catalyzed a global research initiative to identify and refine low-cost alternatives (Ahmad & Alrozi, 2011). This report provides an exhaustive comparative analysis of natural and chemically modified adsorbents, evaluating their structural evolution, mechanistic performance, and long-term viability within a circular economy framework (Ali et al., 2022). The diverse industrial origins and environmental pathways of phenol contamination are illustrated in Figure 1. This schematic highlight how untreated effluents contribute to the widespread distribution of phenolic pollutants in aquatic ecosystems.

Figure 1: Global Sources and Pathways of Phenol Contamination in Aquatic Systems



2. Toxicological Profile and Regulatory Framework of Phenolic Compounds

The environmental persistence of phenol is fundamentally linked to its chemical stability and high water solubility, which reaches approximately 82,800 mg/L at 25 °C (Southworth & Keller, 1986). This mobility allows phenolic pollutants to infiltrate both surface and groundwater resources with relative ease. The United States Environmental Protection Agency (EPA) and the European Union have classified phenol as a priority pollutant due to its deleterious effects on aquatic life and human physiology (U.S. EPA,

1980). Chronic exposure in humans is associated with severe damage to the liver, kidneys, and central neurological functions (ATSDR, 2008), while its presence in aquatic ecosystems can disrupt reproductive cycles in fish and invertebrates (Saputera et al., 2021).

Regulatory standards for phenol discharge are exceptionally stringent, reflecting the compound's high-risk profile. The World Health Organization (WHO) recommends a limit of 0.001 mg/L for total phenolic content in potable water to prevent adverse health outcomes (WHO, 1994). In industrial contexts, toxicity thresholds are often

cited between 9 and 25 mg/L, but even concentrations as low as 5.6 g/m³ are known to disrupt the natural self-purification mechanisms of water bodies. At concentrations exceeding 30 g/m³, phenol has been observed to completely inhibit photosynthesis in aquatic organisms, thereby collapsing local primary production (Park et al., 2012).

3. The Adsorption Paradigm: Theoretical and Practical Advantages

The selection of adsorption as a preferred remediation technology is rooted in a multifaceted set of advantages that address the shortcomings of alternative methods. Techniques such as electrokinetic coagulation suffer from high sludge production, while ion exchange is often characterized by low adsorption capacity for non-

polar organics (Aichour et al., 2021). Advanced oxidation processes (AOPs), though highly effective, involve excessive chemical consumption and the potential generation of secondary toxic intermediates (Saleem et al., 2022).

Adsorption, by contrast, is a surface phenomenon driven by the deposition of solute molecules onto a solid matrix through physical or chemical forces (Dąbrowski, 2001). The primary appeal of this process lies in its design flexibility, lower capital and operating costs, and the availability of diverse precursor materials ranging from agricultural residues to industrial byproducts (Aichour et al., 2021). Furthermore, the kinetics of adsorption are notably rapid compared to biological treatments; while biodegradation may require days or weeks, equilibrium in a well-designed adsorption system can often be achieved within hours (Beyer, 2025).

Table 1. Comparison of Wastewater Treatment Techniques

Treatment Technique	Primary Disadvantages	Relative Cost	Phenol Removal Efficiency	Source
Biological Treatment	Very slow, sensitive to toxicity	Low	Variable	(Michałowicz & Duda, 2007)
Membrane Filtration	High operational cost, fouling	High	High	(Ogunniyi & Emenike, 2024)
Advanced Oxidation	Secondary pollutants, energy-intensive	High	High	(Bibi et al., 2023)
Coagulation	Heavy chemical consumption, sludge	Medium	Low	(Aichour et al., 2021)
Adsorption	Regeneration challenges	Low	Very High	(Beyer, 2025)

4. Mechanistic Fundamentals of Phenol Capture

The efficacy of an adsorbent is determined by the interplay between the physicochemical properties of the solid surface and the molecular characteristics of phenol. Adsorption mechanisms are generally categorized into physisorption and chemisorption, though many real-world systems exhibit a hybrid behavior (Ayoob et al., 2024).

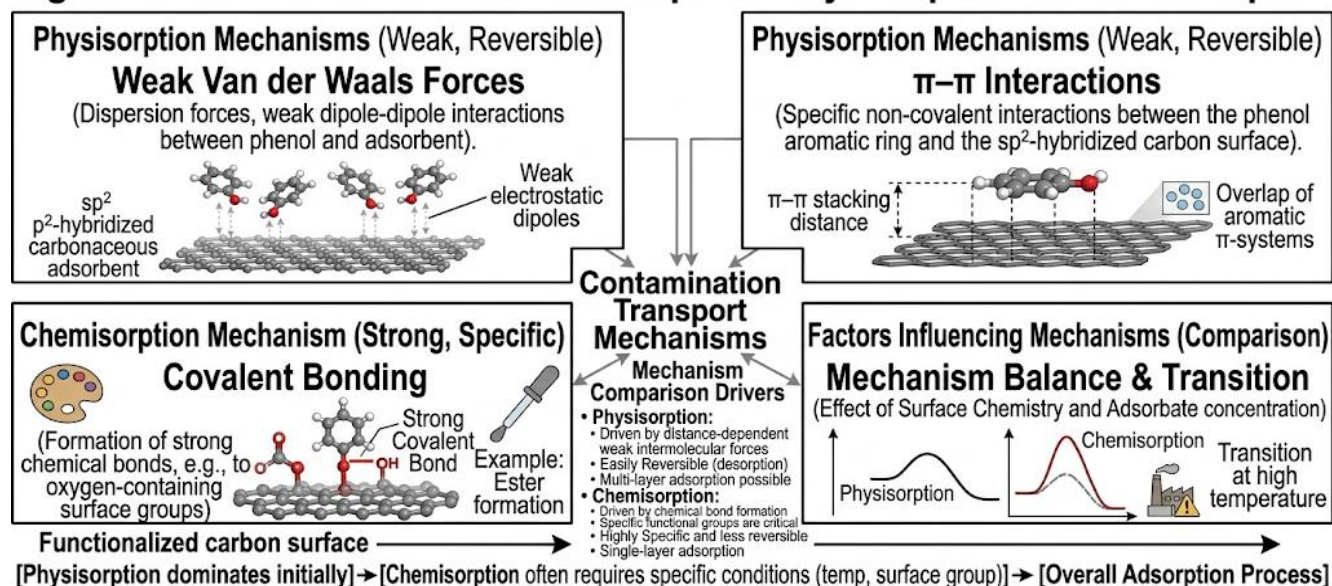
4.1 Physical vs. Chemical Adsorption

Physisorption is governed by weak Van der Waals forces and electrostatic interactions. It is

characterized by its reversibility, low heat of adsorption, and the formation of molecular multilayers. In the context of phenol, physisorption often occurs via π - π interactions between the aromatic ring of the phenol molecule and the basal planes of carbonaceous adsorbents (Bibi et al., 2022). The fundamental mechanisms governing phenol adsorption are depicted in Figure 2.

This illustration differentiates between reversible physisorption and irreversible chemisorption processes at the molecular level.

Figure 2: Mechanisms of Phenol Adsorption: Physisorption vs. Chemisorption



Chemisorption, conversely, involves the formation of strong covalent bonds between the phenol and specific functional groups on the adsorbent surface. This process is typically irreversible, requires higher activation energy, and is restricted to a monolayer formation (Borthakur et al., 2016).

Table 2. Fundamental Differences Between Physisorption and Chemisorption

Property	Physisorption	Chemisorption
Interaction Type	Weak (Van der Waals/Electrostatic)	Strong (Covalent bonds)
Enthalpy (ΔH)	Low (< 20 kJ/mol)	High (> 80 kJ/mol)
Reversibility	High	Low
Layering	Multilayer possible	Monolayer only
Temperature Effect	Favored at low temperatures	Often requires activation energy
Source	(Dąbrowski, 2001; Bibi et al., 2022)	(Dąbrowski, 2001; Bibi et al., 2022)

4.2 Intraparticle Diffusion and Boundary Layer Effects

The rate at which phenol is removed from the bulk solution is determined by a sequence of mass transfer steps: film diffusion, pore diffusion, and final adsorption at the active site. Empirical modeling using the Weber-Morris intraparticle diffusion model frequently identifies pore diffusion as the rate-determining step for highly porous modified adsorbents, such as NaOH-modified Luffa fibers (Ogunniyi & Emenike, 2024).

5. Raw Natural Adsorbents: Precursor Selection and Inherent Constraints

The utilization of raw natural materials represents a fundamental application of adsorption technology. Precursors such as agricultural residues, mineral clays, and animal wastes are attractive due to their local availability and negligible cost (Adeogun et al., 2022).

5.1 Agricultural Biomass

Lignocellulosic materials, including rice husks, coconut shells, walnut shells, and date stones, are rich in cellulose, hemicellulose, and lignin. These polymers contain numerous oxygen-containing functional groups, such as hydroxyl (-OH) and

carboxyl (-COOH), which can interact with phenol via hydrogen bonding (Siva Kumar et al., 2023). Pomegranate peel in its raw ash form has demonstrated a maximum adsorption capacity of 148.38 mg/g at pH 7 (Puzskarewicz et al., 2018).

5.2 Mineral and Industrial Waste

Natural clays, such as bentonite and attapulgite, are characterized by high surface areas and ion-exchange capacities. Bentonite is primarily composed of montmorillonite. However, natural bentonite is inherently hydrophilic due to the presence of exchangeable inorganic cations between its layers, which limits its effectiveness in adsorbing hydrophobic organic pollutants like phenol (Al-Sultani & Al-Seroury, 2012)

6. Chemical Modification Pathways for Performance Enhancement

Chemical modification aims to overcome the limitations of raw materials by tailoring their pore architecture and surface chemistry. Strategies range from simple acid/base etching to sophisticated surface functionalization (Dehmani et al., 2021).

6.1 Alkaline and Acid Activation

Fourier transform infrared (FTIR) spectroscopy provides a primary diagnostic of the oxidation state. Typical spectra exhibit a broad band at

approximately 3400 cm⁻¹ (O-H stretching of hydroxyl/carboxyl groups) and a peak at around 1720 cm⁻¹ (C=O carbonyl stretching) (Obayomi et al., 2023). Raman spectroscopy serves as a sensitive probe for structural disorder; the G-band (at approximately 1580 cm⁻¹) represents sp² carbon domains, while the D-band (at approximately 1350 cm⁻¹) is disorder-induced. A higher I_D/I_G ratio signifies a more disordered structure with a greater density of functional groups (Bibi et al., 2025).

6.2 Surface Oxidation and Functionalization

Oxidizing agents such as potassium permanganate (KMnO₄) are used to introduce oxygen-containing functional groups onto the carbon surface. Modified granular activated carbon (GAC) using 30 mg/L of KMnO₄ for 90 minutes revealed a 20% increase in phenol removal efficiency. Amino-functionalization is also effective; amino-silica modified date palm fibers (Si-DPF) increased adsorption capacity from 19.57 mg/g to 31.25 mg/g (Saleem et al., 2022).

7. Comparative Analysis of Adsorption Capacity and Performance

The disparity between raw and modified adsorbents is evident in their maximum adsorption capacities (q_m) (Manyangadze et al., 2020).

Table 3. Comparison of Phenol Adsorption Capacities for Natural and Modified Adsorbents

Adsorbent Matrix	Modification Method	Initial Conc. (mg/L)	Max Capacity (qm, mg/g)	Source
Date Palm Fiber	Raw	100	19.57	(Saleem et al., 2022)
Date Palm Fiber	Amino-Silica	100	31.25	(Saleem et al., 2022)
Orange Peel Char	KOH Activation	50-250	467.0	(Siva Kumar et al., 2023)
Pomegranate Ash	Thermal (450 °C)	100	148.38	(Saleem et al., 2022)
Cow Dung	Calcination	280	89.3	(Adeogun et al., 2022)
Coconut Shell AC	Thermal (1000 °C)	10-400	212.96	(Xie et al., 2020)
Graphene Oxide	Raw	30	7.69	(Bibi et al., 2022)
NPC@ZIF-8	Core-Shell Nano	300	1670.0	(Saleem et al., 2022)

8. Influence of Physicochemical Parameters on Efficiency

The pH of the aqueous solution is a critical factor; most carbonaceous adsorbents exhibit maximum phenol removal in the acidic to neutral range (pH 3–7), where neutral phenol molecules interact via hydrogen bonding. Temperature also plays a role; most physisorption-dominated systems are exothermic, whereas endothermic behavior is observed in systems where pore diffusion is limited, such as calcined cow dung (Hameed & Rahman, 2008).

9. Kinetic and Equilibrium Modeling: Insights into Surface Interaction

The Langmuir and Freundlich models are the most widely applied isotherms. Langmuir fits

suggest a homogeneous surface where phenol forms a monolayer, such as for NaOH -modified Luffa and Si-DPF (Ogunniyi & Emenike, 2024). The pseudo-second-order kinetic model is universally reported as the best fit for modified adsorbents, indicating a chemisorption-controlled process (Siva Kumar et al., 2023).

10. Regeneration, Reusability, and Economic Feasibility

Industrial viability depends on an adsorbent's life cycle. Chemical regeneration using solvents like ethanol can desorb over 99% of the adsorbate. Economic feasibility is determined by precursor acquisition and modification costs; agricultural waste-based adsorbents are among the most cost-effective options (Beyer, 2025).

Table 4. Economic and Technical Evaluation of Adsorbent Classes

Adsorbent Class	Synthesis Complexity	Estimated Cost	Regeneration Potential	Source
Raw Biomass	Very Low	Negligible	Moderate	(Beyer, 2025)
Chemical AC	Moderate	Medium	High	(Siva Kumar et al., 2023)
Organo-Clays	Moderate	Medium	Low	(Dehmani et al., 2021)
Nanocarbon/MOF	Very High	Very High	High	(Saleem et al., 2022)

11. Life Cycle Assessment (LCA) and Environmental Sustainability

Life Cycle Assessment (LCA) provides a "cradle-to-grave" analysis of environmental impacts. Sourcing materials from waste provides environmental credits by avoiding disposal impacts, and bioadsorbents derived from residues generally emerge as sustainable options within a circular bio-economy (Aichour et al., 2021).

12. Challenges and Future Perspectives in Phenol Remediation

Technical hurdles include structural degradation during modification and the biological variability of natural precursors. Future research involves the rational design of multifunctional "smart" materials and advanced computational modeling, such as Density Functional Theory (DFT) and molecular docking, to predict electronic interactions (Sindhushree et al., 2025).

13. Conclusions

This study highlights the critical role of adsorption technology in addressing phenol contamination in wastewater. While natural adsorbents provide a low-cost and environmentally sustainable option, their relatively lower efficiency limits their practical application in high-load systems. Chemical modification significantly enhances adsorption performance by improving surface characteristics, pore distribution, and functional group availability. Among the various approaches, alkaline activation and advanced nanostructured materials demonstrate superior adsorption capacities and faster kinetics. The findings confirm that modified adsorbents are more effective and suitable for large-scale applications compared to raw materials. Nevertheless, challenges related to regeneration efficiency, economic feasibility, and structural stability must be carefully addressed to ensure long-term

sustainability. Future research should focus on the development of cost-effective and scalable modification techniques, integration of life cycle assessment, and the application of advanced computational tools to optimize adsorbent design and performance for real-world wastewater treatment systems.

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