

Review

# Nature-Based Hybrid Adsorbents for Emerging Contaminant Removal: Integrating Low-Cost Bioresources in the Water–Energy–Food Nexus

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**Abstract:** The pervasive presence of emerging contaminants (ECs), including pharmaceuticals, heavy metals, dyes, and personal care products in water systems, poses a critical threat to environmental and public health. Conventional treatment methods often fail to remove these pollutants efficiently due to high costs, energy intensity, and limited selectivity. This review highlights the transformative potential of nature-based hybrid adsorbents, which synergistically combine biopolymers such as chitosan and alginate, agricultural wastes including banana peel and rice husk, and biochar with functional components like metal oxides, enzymes, or magnetic nanoparticles. These systems achieve relatively high removal efficiencies, often exceeding 90%, and record-breaking adsorption capacities, such as 586 mg/g for lead and 394 mg/g for pharmaceuticals, far surpassing conventional alternatives. By leveraging low-cost, renewable materials, they reduce operational expenses by 30–80% and minimise energy use and secondary waste. Furthermore, their integration within the water–energy–food (WEF) nexus supports resource recovery, water reuse, and progress toward multiple UN Sustainable Development Goals. Remaining challenges, including scalability, regeneration stability, and the ecological safety of nano-enhanced adsorbents, are critically addressed, with forward-looking insights into AI-assisted design and circular economy integration. Ultimately, this work highlights how bridging natural bioresources with advanced hybrid engineering can redefine sustainable water treatment paradigms.

**Keywords:** nature-based adsorbents; emerging contaminants; wastewater treatment; water–energy–food nexus; sustainable technologies

## 1. Introduction

The increasing detection of emerging contaminants (ECs) in freshwater, marine, and terrestrial ecosystems has become a critical global environmental challenge, as their persistence and complex ecotoxicological effects threaten both planetary and human health. ECs, including pharmaceuticals, personal care products, pesticides, microplastics, per- and polyfluoroalkyl substances (PFAS), and antibiotic resistance genes (ARGs), enter the environment mainly through industrial effluents, agricultural runoff, and municipal wastewater discharges. Recent studies report that the Chemical Abstract Service Registry has expanded from 20 million substances in 2002 to over 204 million by 2023, with nearly 15,000 new chemicals added daily [1], intensifying the risk of ecological imbalance and human exposure. Their presence has been widely confirmed in rivers, lakes, groundwater, oceans, and soils worldwide, with concentrations ranging from nanograms to micrograms per litre, where they accumulate in food chains, disrupt endocrine systems, alter soil nutrient cycles, and drive antibiotic resistance [2]. Global initiatives, such as the UN’s Intergovernmental Science-Policy Panel on Chemicals, Waste, and Pollution Prevention,



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emphasise adopting a One Health approach to address EC impacts through cross-sectoral collaboration, source control, and sustainable remediation [3]. However, conventional wastewater treatment technologies, including coagulation, activated sludge, and advanced oxidation, remain insufficient due to high energy demands, operational costs, and incomplete removal, especially for persistent compounds like PFAS and microplastics [4]. Consequently, recent advances focus on integrated and sustainable treatment strategies, including membrane filtration, constructed wetlands, bio-based adsorbents, and algae-assisted systems, which demonstrate improved EC removal efficiency and economic feasibility [5]. Urgent regulatory frameworks, advanced detection techniques, and interdisciplinary policies are required to mitigate EC risks and safeguard environmental and public health for future generations.

The growing prevalence of ECs carries profound implications for human health, ecosystem services, and sustainable development goals (SDGs) [6,7]. Chronic exposure to pharmaceuticals and endocrine-disrupting compounds has been linked to reproductive abnormalities, metabolic disorders, genotoxicity, and neurological dysfunctions in humans [8]. Similarly, microplastics and PFAS bioaccumulate through food webs, affecting aquatic organisms, soil productivity, and biodiversity. The disruption of ecosystem services; such as water purification, nutrient cycling, and food security; further complicates socio-economic development and threatens the achievement of several SDGs, particularly SDG 3 (Good Health and Well-being) [9,10], SDG 6 (Clean Water and Sanitation) [11], SDG 12 (Responsible Consumption and Production) [12], and SDG 14 (Life Below Water) [13,14]. Addressing EC contamination, therefore, represents a critical global priority.

Despite growing recognition of EC-related risks, conventional wastewater treatment technologies remain largely inadequate in effectively removing these pollutants. Processes such as activated sludge treatment, coagulation-flocculation, and advanced oxidation often face limitations, including high operational costs, elevated energy consumption, and incomplete degradation of persistent compounds [15]. In many cases, these technologies produce secondary sludge that requires additional treatment and disposal, further exacerbating environmental burdens [16]. Moreover, their application in resource-limited regions is constrained by infrastructure, cost, and technical expertise, leaving significant populations vulnerable to water quality deterioration and associated health risks. To address these limitations, nature-based hybrid adsorbent systems have emerged as promising solutions for sustainable remediation [17,18]. These systems leverage locally available bioresources, such as agricultural residues [19], biochar [20], biopolymers [21], and plant-derived mucilage [22], and integrate them with advanced functional materials, including nanomaterials, enzyme-functionalized surfaces, and electro-bioreactor technologies. This hybrid approach enhances adsorption performance by improving surface area, selectivity, and regeneration potential while minimising costs and environmental footprints. In this work, adsorption is defined as the surface-based process where atoms, ions, or molecules (the adsorbate, such as a heavy metal ion or pharmaceutical molecule) from a liquid phase accumulate on the solid surface of a material (the adsorbent). Moreover, the scalability and adaptability of such systems make them particularly attractive for decentralised wastewater treatment, especially in low- and middle-income regions where conventional methods are economically unfeasible.

The objective of this review is to critically evaluate recent advances in hybrid bio-based adsorbents and highlight their potential for emerging contaminant removal within the broader framework of the water–energy–food (WEF) nexus. By exploring cutting-edge innovations, sustainability benefits, and integration pathways, this review seeks to demonstrate how nature-based hybrid systems can transform wastewater treatment paradigms and support global efforts to achieve environmental sustainability, resource efficiency, and resilient ecosystem management.

## 2. Methodology

This review was executed following a structured and transparent methodological framework to ensure a comprehensive and critical appraisal of the current literature. The process was designed to systematically capture, evaluate, and synthesise research concerning nature-based hybrid adsorbent systems for the remediation of ECs from aqueous environments. The methodology was delineated into four sequential phases: literature search and collection, screening and selection, data extraction, and thematic synthesis.

### 2.1. Literature Search and Collection

A systematic literature search was conducted utilising the Scopus and Web of Science core databases to identify pertinent peer-reviewed articles. The temporal scope was restricted to publications from January 2018 to May 2024, a period selected to encapsulate the most recent and innovative advancements in this rapidly evolving field. The search strategy employed a Boolean logic query, structured around the core concepts of the review. The population was defined by terms such as “wastewater” and “aqueous environment”. The intervention was captured using keywords including “nature-based”, “hybrid adsorbent”, “bioresource”, “biochar”, “biopolymer”, “mucilage”,

“enzyme-functionalized”, and “electro-bioreactor”. The desired outcome was specified with terms like “emerging contaminant”, “pharmaceutical”, “PFAS”, “microplastic”, “antibiotic resistance gene”, and “personal care product”. This rigorous initial search strategy returned an extensive corpus of 1852 publications for preliminary consideration.

## 2.2. Screening and Selection

The identified records underwent a stringent, two-stage screening process to refine the collection to studies of the highest relevance and methodological quality, a procedure inspired by the PRISMA guidelines. The initial stage involved a triage of all 1852 records based on their titles and abstracts. This screening was performed against strict inclusion criteria, which mandated that studies must: (a) focus explicitly on hybrid systems integrating biological materials with advanced engineered components; (b) demonstrate application for the removal of ECs from water; and (c) report quantitative performance data, such as removal efficiency or adsorption capacity. Studies confined to conventional adsorbents or single-technology approaches were systematically excluded. This process yielded 218 articles for a more in-depth evaluation. The second stage consisted of a detailed, full-text assessment of these remaining articles. Publications were excluded at this juncture if they lacked sufficient methodological detail to assess validity, failed to discuss the synergistic mechanisms central to hybrid systems, or were not available in English. This meticulous screening and selection protocol culminated in a final corpus of 89 high-quality, highly relevant articles that constitute the foundational evidence for this critical review.

## 2.3. Data Extraction and Thematic Synthesis

From the final selection of 89 articles, key data were systematically extracted into a standardised matrix to facilitate a consistent and critical analysis. The extracted information encompassed several critical dimensions: the composition of the adsorbent, detailing both the base bioresource (e.g., agricultural residue, biochar) and the advanced functional component (e.g., nanomaterial type, immobilized enzyme); the specific classes and identities of the target contaminants; critical performance metrics including removal efficiency, adsorption capacity, reusability, and relevant cost or energy comparisons; and finally, the key findings related to synergistic mechanisms, reported challenges, and integration within broader frameworks such as the Water-Energy-Food (WEF) Nexus. The subsequent synthesis was not merely descriptive but critically analytical. The extracted data were interrogated to identify dominant trends, reconcile performance claims with documented limitations, elucidate overarching scientific and technological barriers, and articulate coherent and impactful future research directions, which are presented thematically in the body of this review.

## 3. Emerging Contaminants in the Anthropocene

The Anthropocene era is marked by the rapid proliferation of synthetic chemicals and novel pollutants, collectively termed ECs, which are increasingly detected in freshwater, marine, and terrestrial ecosystems. Pharmaceuticals such as ciprofloxacin, diclofenac, and paracetamol are extensively used in human and veterinary medicine and frequently enter aquatic environments through sewage effluents, household disposal, and agricultural runoff. In Malaysia, a scoping review by Arumugam et al. [23] reported 65 active pharmaceutical compounds across multiple therapeutic classes, with surface water being the most studied matrix ( $n = 23$ ), followed by wastewater treatment plant effluent ( $n = 10$ ) and tap water ( $n = 11$ ), highlighting both the prevalence and uneven monitoring of pharmaceuticals. Per- and polyfluoroalkyl substances (PFAS) and microplastics are persistent environmental pollutants; a field study of four landfill-wastewater treatment systems in Illinois, USA, found microplastic concentrations in influent at approximately  $10^2$   $\mu\text{g/L}$ , whereas PFAS ranged from parts-per-trillion in WWTP influent to parts-per-billion in landfill leachate, demonstrating their resistance to degradation and potential bioaccumulation [24]. Antibiotic resistance genes (ARGs), prevalent in soil, water, and sediments, pose critical biological threats by facilitating horizontal gene transfer; urban soil samples revealed quinolone ARGs at 50.56%, aminoglycosides at 21.91%, and tetracyclines at 9.56%, emphasising the scale of environmental antimicrobial resistance [25]. Additionally, personal care products (PPCPs), including cosmetics, fragrances, and detergents, and agricultural pesticides contribute substantially to EC loads, with persistent compounds such as carbamazepine exhibiting resistance to conventional wastewater treatment processes [26].

Recent regional and global monitoring studies indicate that ECs, particularly pharmaceuticals, are widespread in freshwater systems, with surface water and groundwater frequently showing trace concentrations ranging from a few nanograms to several micrograms per litre. In Europe, groundwater from Gdańsk, Poland, contained 16 pharmaceuticals, including caffeine, diclofenac, sulfamethoxazole, and ketoprofen, with concentrations up to 1528.2 ng/L [27], while Lake Mälaren, Sweden, had 76 pharmaceuticals, with lamotrigine reaching 140 ng/L [28]. Rivers in Spain showed diverse pharmaceutical contamination: the Barcelona River had sulfamethoxazole and

related sulfonamides (0–30.5 ng/L) [29], while the Mijares River contained 69 pharmaceuticals, including tramadol, acetaminophen, and ciprofloxacin at concentrations up to 1949 ng/L [30]. In India, groundwater in Patna harboured 73 emerging organic contaminants, including carbamazepine, tramadol, and lamotrigine at 0–360 ng/L [31]. Brazilian tap water from the Federal District contained 35 micropollutants such as diclofenac, carbamazepine, and caffeine, with concentrations up to 7.8 ng/L [32]. In Africa, surface water in the peri-urban Mfoundi watershed in Yaoundé, Cameroon, showed 15 pharmaceuticals at 0–74 ng/L, while urban surface water in the same watershed reached 5660 ng/L, with acetaminophen being the highest [33]. Groundwater from the Mfoundi watershed contained 15 pharmaceuticals at 0–73 ng/L, with sulfamethoxazole highest [33], and Kisumu, Kenya groundwater had sulfamethoxazole in 14.3% of sources at concentrations up to 258.2 ng/L [34]. In Hungary, Lake Balaton contained 46 active compounds, including caffeine and diclofenac, with caffeine reaching 2675.1 ng/L [35]. Across the United States, 103 pharmaceuticals were detected in groundwater systems at 0–677 ng/L, with caffeine highest [36], while Pennsylvania groundwater contained seven pharmaceuticals up to 122.7 ng/L, with ofloxacin highest [37]. These findings collectively highlight the pervasive occurrence of pharmaceuticals in freshwater across continents, demonstrating widespread anthropogenic influence on water quality and the urgent need for comprehensive monitoring and management strategies.

Persistent ECs pose multiple environmental and human health risks. These compounds, including pharmaceuticals, endocrine-disrupting chemicals (EDCs), microplastics, PFAS, and antibiotic residues, can interfere with the hormonal systems of aquatic organisms, reduce biodiversity, alter soil nutrient dynamics, and accumulate in food webs. Chronic exposure to low levels of ECs has been linked to neurological, carcinogenic, and reproductive effects in humans, while the presence of antibiotic-resistant genes contributes to the global antimicrobial resistance crisis. According to Thacharodi et al. [38], water serves as a major source of human and animal exposure to EDCs, which bioaccumulate and persist in the environment. Microplastics have been shown to bioaccumulate within marine trophic levels, though clear biomagnification at higher trophic levels remains unconfirmed, as reported by Miller et al. [39]. Despite these alarming trends, significant gaps remain in the detection, monitoring, and regulation of ECs. Analytical challenges stem from complex chemical structures, low environmental concentrations, and diverse environmental matrices, often necessitating advanced techniques such as high-resolution mass spectrometry and molecular tools for ARG quantification. Regulatory frameworks are limited or inconsistent globally, with many ECs still unregulated in drinking water and wastewater standards. Temporal and spatial monitoring is particularly sparse in low- and middle-income countries, hindering a comprehensive understanding of global contaminant dynamics. According to Naznine et al. [40], river waters serve as major reservoirs for antibiotic-resistant genes and bacteria, yet standardised methodologies, defined risk thresholds, and effective monitoring strategies remain lacking. Bridging these gaps through harmonised protocols, cross-disciplinary research, and improved surveillance is critical for mitigating ECs and AMR in aquatic ecosystems. Table 1 provides compiled data that reveals a vibrant landscape of research into nature-based adsorbents, highlighting a strategic balance between performance, cost, and sustainability. While advanced composites like the fish collagen-alginate gel achieve remarkable capacities exceeding 500 mg/g for lead, and specialised chitosan hydrogels demonstrate exceptional suitability for continuous-flow systems, a significant focus remains on unmodified or minimally processed agricultural wastes like banana peel and eggshells. These low-cost materials offer commendable removal efficiencies (>90%) and capacities (up to 100 mg/g for lead on banana peel), making them highly attractive for decentralised or resource-limited applications. The table highlights a clear trade-off: high-performance often requires sophisticated synthesis creating engineered hybrids, whereas maximal cost-effectiveness and minimal processing are achieved with raw, abundant wastes. This spectrum of materials, from simple peels to complex bionanocomposites, provides a versatile toolkit for tackling diverse aquatic pollutants, allowing for selection based on the specific requirements of contamination level, available budget, and technical infrastructure.

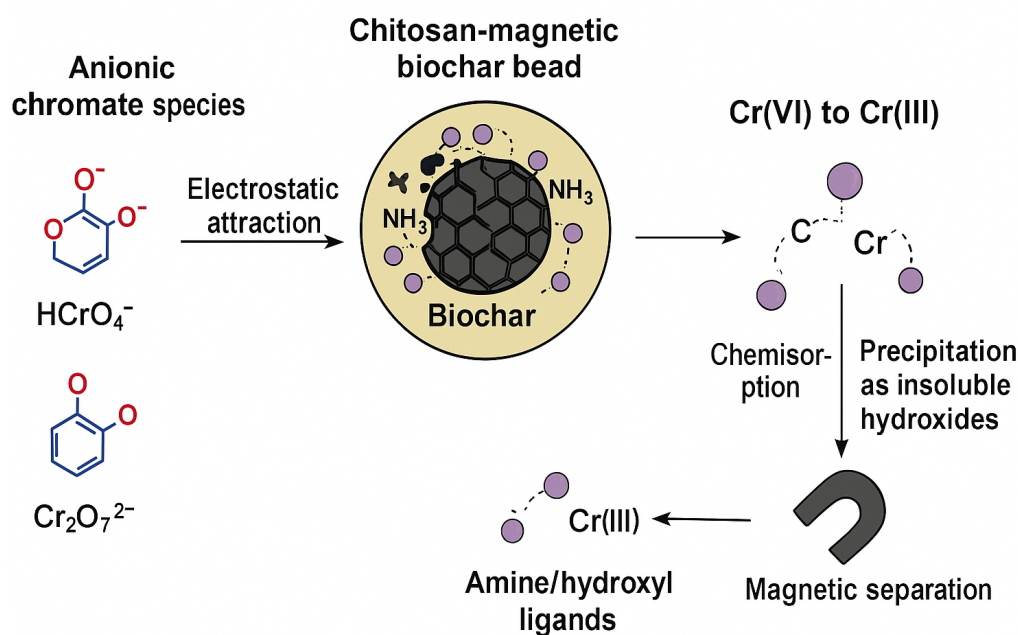
**Table 1.** Emerging nature-based and hybrid adsorbents for ECs.

| Adsorbent Material  | Target ECs                          | Removal Efficiency (%)        | Capacity (mg/g)                             | Regeneration Cycles    | Key Advantages  | Limitations   | Reference |
|---|-------------------------------------|-------------------------------|---|------------------------|---|---|-----------|
| Fish skin Collagen-Sodium Alginate-CMC gel (CMC-FC-SA)  | Heavy Metals (Pb <sup>2+</sup> )    | >88%<br>(in complex matrices) | 586.56                                      | 5                      | Very high capacity, uses food-grade/fishery by-products                     | Performance interfered with by specific organic compounds | [41]      |
| Lignin-intercalated WS <sub>2</sub> composite   | Heavy Metals (Pb <sup>2+</sup> )    | -                             | ~66.9                                       | -                      | Synergistic adsorption prevents nanosheet agglomeration                     | Lower capacity  | [42]      |
| Cationic Chitosan Hydrogel Bead (CHB-M)   | Heavy Metals (Cr(VI))               | >99%<br>(continuous flow)     | 234.99                                      | >6                     | Green synthesis, high mechanical strength, excellent for continuous flow    | Performance is pH-dependent                               | [43]      |
| Functionalized Clay-based Film (ENDFIL)   | Pharmaceuticals (Diclofenac)        | 95%                           | 286.2 (µg/g)                                | 6                      | Effective for trace-level contaminants, film form factor                    | Lower absolute capacity                                   | [44]      |
| Biochar-supported Co-Cu Oxide (CoCuO@BC)  | Pharmaceuticals (Bisphenol F)       | Degradation                   | Catalytic                                   | -                      | Activates PMS, generates superoxide radicals, and works under visible light | Complex system, potential metal leaching                  | [45]      |
| Chitosan-Lignin Biocomposite  | Dyes (RO16), Heavy Metals (Cr(VI))  | -                             | 59.43–79.76 (RO16),<br>52.06–72.61 (Cr(VI)) | -                      | Uses two abundant biopolymers, effective for multiple pollutants            | Moderate capacity   | [46]      |
| DESP-Modified Magnetic Cellulose Nanoparticles (DESP-MCN)   | Heavy Metals (Cr(VI), As(III))      | -                             | 337.5 (Cr),<br>89.21 (As)                   | Multiple               | One-step removal of multiple heavy metals, magnetic                         | -   | [47]      |
| Sodium Lignosulfonate-Functionalized Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @Polypyrrole (FSPL) | Dyes (MB, MG, CV), Metals (Mn(VII)) | >80% (after 5 cycles)         | -   | 5                      | Magnetic, high reusability, excellent selectivity                           | Capacity not specified                                    | [48]      |
| SnO <sub>2</sub> /BiOBr Lignin-based Carbon Nanofibrous Membrane  | Dyes (Rhodamine B)                  | 87.3–93.0%                    | - (Photocatalytic)                          | 5                      | Flexible, visible-light-driven, sustainable synthesis                       | Photocatalytic, not pure adsorption                       | [49]      |
| Chitosan/Ferrous Oxide Nanocomposite (CFON)   | Dyes (Acid Red 73)                  | 99.30%                        | -   | -                      | Sunlight-driven, effective in real aquaculture wastewater                   | Photocatalytic, not pure adsorption                       | [50]      |
| Sugarcane Bagasse Biochar/Sodium Alginate Monolith (SA@KBC)   | Pharmaceuticals (Nitrofurazone)     | 94% (within 60 min)           | 394.46                                      | -                      | Rapid removal, monolithic form for easy separation                          | -   | [51]      |
| Activated Banana Peel (ABP)   | Heavy Metals (Cr(III))              | 92.50%                        | -   | -                      | Sustainable, low-cost, from agricultural waste                              | Requires activation                                       | [52]      |
| Activated Orange Peel (AOP)   | Heavy Metals (Cr(III))              | 96%                           | -   | -                      | Superior performance to ABP, low-cost                                       | Requires activation                                       | [52]      |
| Palm Husk Powder  | COD, Chromium                       | 88.19% (COD),<br>83.69% (Cr)  | -   | Effective regeneration | Ultrasound-pretreated, high porosity, treats real wastewater.               | -   | [53]      |

Table 1. Cont.

| Adsorbent Material   | Target ECs  | Removal Efficiency (%) | Capacity (mg/g)          | Regeneration Cycles | Key Advantages   | Limitations  | Reference |
|--|---|------------------------|--------------------------|---------------------|--|--|-----------|
| Degummed Silk Fibres   | Dyes (Methylene Blue)   | -                      | 179.14                   | -                   | High capacity, biodegradable, sustainable                    | Requires degumming pre-treatment                               | [54]      |
| Banana Peel (BP)   | Heavy Metals (Pb <sup>2+</sup> )                                    | >90%                   | 100                      | -                   | Raw, unmodified, very high capacity for raw waste            | -  | [55]      |
| Eggshells (ES)   | Heavy Metals (Pb <sup>2+</sup> )                                    | >90%                   | 68.6                     | -                   | Raw, unmodified, effective                                   | -  | [55]      |
| Almond Shells (AS)   | Heavy Metals (Pb <sup>2+</sup> )                                    | >90%                   | 51.7                     | -                   | Raw, unmodified, effective                                   | -  | [55]      |
| Tea Waste (TW)   | Heavy Metals (Pb <sup>2+</sup> )                                    | >90%                   | 47.8                     | -                   | Raw, unmodified, effective                                   | -  | [55]      |
| Thermally Activated Clay (TAC)                                   | Pharmaceuticals (Levofloxacin)                                      | 72.60%                 | -                        | -                   | Simple thermal activation, from natural clay                 | Moderate removal efficiency                                    | [56]      |
| Algae-Alginate Beads (AASB)                                      | Heavy Metals (Pb <sup>2+</sup> )                                    | ~91%                   | 9.05                     | -                   | Immobilisation enhances stability and handling               | Low capacity   | [57]      |
| NaOH-Modified Clove Leaves (CL-NaOH)                             | Dyes (Methylene Blue)   | -                      | 9.8                      | Recyclable          | Cost-efficient, recyclable, from waste                       | Low capacity   | [58]      |
| Phytochelatin-PAN Blend (PC@PN)                                  | Heavy Metals (Hg <sup>2+</sup> /As <sup>3+</sup> /S <sup>5+</sup> ) | ~100%                  | -                        | 60                  | Extremely high selectivity and regeneration cycles           | Integrated in a hybrid electro-deionisation process            | [59]      |
| Dithizone-Immobilised Coal Bottom Ash (Dtz-CBA)                  | Heavy Metals (Pb <sup>2+</sup> )                                    | -                      | 21                       | -                   | Easier and more rapid adsorption than the base material      | Uses a synthetic modifier (dithizone)                          | [60]      |
| Ultrasonic Assisted Palm Shell AC (UAC)                          | PAHs (Acenaphthene)   | -                      | 52.75                    | -                   | High surface area, efficient for organic pollutants          | -  | [61]      |
| Silk Fibroin/Soursop Seed Composite (SF: SS)                     | Dyes (Crystal Violet), Heavy Metals (Cu <sup>2+</sup> )             | -                      | -                        | -                   | Tunable 3D porous structure, good thermal stability          | Capacity not specified   | [62]      |
| Tire Rubber/Polyurethane Composite                               | Dyes (Crystal Violet)   | -                      | 20.92                    | -                   | Made from polymer wastes, low-cost                           | Not entirely “nature-based”                                    | [63]      |
| Rice Husk Ash-Spirogyra Algae Composite                          | Heavy Metals (Fe(II), Pb(II))                                       | >48% (Fe), >58% (Pb)   | -                        | -                   | Effective in a fixed-bed column, it uses two low-cost wastes | Moderate removal efficiency                                    | [64]      |
| Carbonised Date Stone  | Heavy Metals (Pb <sup>2+</sup> )                                    | 88.50%                 | 9.03                     | -                   | Promising natural, low-cost adsorbent                        | Low capacity   | [65]      |
| Cobalt Ferrite-Supported AC (CF-AC)                              | Heavy Metals (Cr, Pb(II))   | 98.2% (Cr), 96.4% (Pb) | 23.6 (Cr), 6.27 (Pb)     | -                   | Magnetic for easy separation, high removal efficiency        | Low capacity for Pb(II)  | [66]      |
| H <sub>2</sub> SO <sub>4</sub> -Activated Cashew Nut Shell (CNS) | Heavy Metals (Cr, Mn(II))   | 56.4% (Cr), 53.1% (Mn) | 10.79 (Cr), 9.82 (Mn)    | -                   | Effective in a fixed-bed column, high surface area           | Moderate removal efficiency                                    | [66]      |
| Multiwall Carbon Nanotubes (from Castor Seed)                    | Heavy Metals (Cd(II), Cr(VI))                                       | -                      | 404.86 (Cd), 243.90 (Cr) | -                   | Exceptionally high capacity                                  | Synthetic material (MWCNTs), though derived from bio-precursor | [67]      |
| Nanche Stone Activated Carbon (AC)                               | Heavy Metals (Pb <sup>2+</sup> )                                    | -                      | -                        | -                   | Improved capacity over raw stone                             | Capacity not specified   | [68]      |
| Agricultural Waste Composite-AC (AWCAC)                          | Heavy Metals (Pb(II), As(III))                                      | -                      | 250 (Pb), 200 (As)       | -                   | Very high capacity, uses a composite of multiple wastes.     | -  | [69]      |

For instance, the removal of hexavalent chromium (Cr(VI)) by chitosan-magnetic biochar beads proceeds through a sophisticated multi-mechanistic pathway initiated by electrostatic attraction, where anionic chromate species ( $\text{HCrO}_4^-/\text{Cr}_2\text{O}_7^{2-}$ ) are drawn to protonated amine groups ( $-\text{NH}_3^+$ ) on the chitosan component under acidic conditions [70]; this surface concentration is subsequently followed by a critical chemisorption step involving electron transfer from the biochar's graphitic domains and chitosan's functional groups that reduces toxic Cr(VI) to less hazardous Cr(III), whereupon the newly formed cations become permanently immobilized through coordination complexes with amine/hydroxyl ligands and precipitation as insoluble hydroxides within the bead's porous architecture, while the embedded  $\text{Fe}_3\text{O}_4$  nanoparticles enable efficient magnetic separation from treated water (Figure 1).



**Figure 1.** Schematic illustration of the multi-mechanistic removal of hexavalent chromium (Cr(VI)) by chitosan-magnetic biochar beads.

#### 4. Nature-Based Hybrid Adsorbent Systems

##### 4.1. Locally Available Bio-Adsorbents

Locally available agricultural residues have been widely investigated as cost-effective bio-adsorbents for the removal of diverse contaminants from water. Pineapple leaf fibres, which are typically discarded after harvest, can be chemically modified to enhance their adsorption capacity. According to the study by Daochalermwong et al. [71], cellulose fibres extracted from pineapple leaves were functionalized with ethylenediaminetetraacetic acid (EDTA) and carboxymethyl groups, producing adsorbents capable of efficiently removing lead ( $\text{Pb}^{2+}$ ) and cadmium ( $\text{Cd}^{2+}$ ) ions, with maximum adsorption capacities ranging from 33.2 to 63.4 mg/g. The adsorption processes followed pseudo-first- and pseudo-second-order kinetics and were well described by Langmuir isotherms, indicating monolayer chemisorption. In a related study, Song et al. [72] demonstrated that biochar prepared from pineapple leaves at different pyrolysis temperatures (300–700 °C) exhibited significant variations in surface structure, porosity, and functional groups, which directly influenced its adsorption performance for phosphorus. Biochar prepared at 500 °C offered an optimal balance between energy consumption and adsorption efficiency, highlighting its potential as a precursor for further modification and composite development. Moreover, Ogheneochuko et al. [73] showed that pristine and modified pineapple wastes could effectively remove Co(II) from both simulated and real wastewater in batch and continuous flow systems, with column saturation values of 22.9 mg/g, and adsorption behaviour well fitted by Langmuir and pseudo-second-order models. Similarly, activated carbon derived from pyrolysed pineapple waste demonstrated a high surface area (914.7 m<sup>2</sup>/g) and strong adsorption of methylene blue, with a maximum uptake of 288.3 mg/g [74], underscoring the versatility of pineapple-based residues for diverse water treatment applications.

Biopolymers, particularly those derived from *Opuntia ficus-indica*, have also shown significant promise as bio-adsorbents. In the study by Asnam et al. [75], cactus extract was combined with sodium alginate to produce reinforced gelled porous composites. These materials exhibited strong mechanical properties, including breaking strength between 400 and 2200 Pa and bead rigidity of 5–11%, while maintaining adsorption capacities of 80–120 mg/g for pentachlorophenol. Hydrogen bonding between hydroxyl and carboxyl groups in the cactus polysaccharides and alginate matrix was found to enhance structural stability. In addition, hydrogel biocomposites composed of cactus mucilage and alginate have been successfully applied to the adsorption of methylene blue from aqueous solutions. According to Nazzari et al. [76], the hydrogel exhibited a maximum adsorption capacity of 760 mg/g at higher contaminant concentrations, with effective reusability over five cycles, demonstrating both high efficiency and environmental sustainability. Biochar and other bio-based composites represent another class of locally available adsorbents with wide applicability. In a recent review by Guo et al. [77], biochar was highlighted as a versatile adsorbent for carbon dioxide capture due to its tunable surface area, pore structure, and surface functional groups. Although pristine biochar can be used directly, modifications are often required to optimise physicochemical properties for specific contaminants.

Recent technological advances have further enhanced the potential of these locally available bio-adsorbents. Magnetic biochar composites, such as those derived from sesame seed cake and enhanced with polyaniline (PANI), have demonstrated high adsorption capacities for heavy metals, including  $\text{Hg}^{2+}$  (141.89 mg/g) and  $\text{Cu}^{2+}$  (124.78 mg/g), while allowing efficient magnetic recovery [78]. These materials combine high surface area, abundant functional groups, and magnetic responsiveness, enabling rapid adsorption and facile separation. Magnetic nanocomposites (MNCs) have also been developed using biochar and polymer matrices, exhibiting enhanced adsorption efficiency, selectivity, and recyclability [79]. These MNCs leverage synergistic effects between the magnetic core and functionalized surface to improve contaminant binding while maintaining structural stability, highlighting the importance of surface engineering and composite design. Additionally, surface modification and functionalization of magnetic nanomaterials, through techniques such as polymer grafting, amino functionalization, or biomolecule coating, address inherent limitations like aggregation, leaching, and poor stability in acidic conditions, while improving adsorption kinetics and electron mobility [80]. Carbon-based and metal oxide nanoparticles, including carbon nanotubes (CNTs), graphene-based nanoparticles (GNPs), carbon quantum dots (CQDs), and metal oxides such as CuO, ZnO,  $\text{TiO}_2$ , and  $\text{Fe}_2\text{O}_3$ , have been integrated with bio-adsorbents to enhance contaminant removal efficiency, achieving 60–99% pollutant removal within short contact times [81]. The combination of locally sourced biomass with nanomaterials creates multifunctional hybrid adsorbents capable of simultaneous removal of heavy metals, dyes, and emerging contaminants, while enabling reusability and potential scale-up for real-world applications. Mechanistically, these hybrid bio-adsorbents exploit ion exchange, electrostatic attraction, hydrogen bonding, complexation, and  $\pi$ – $\pi$  interactions, which can be tuned through surface functionalization, magnetic incorporation, or polymer modification. This strategic integration not only improves adsorption performance but also enhances operational feasibility by enabling magnetic separation, regeneration, and multi-cycle usage, addressing traditional limitations of raw biomass adsorbents.

#### 4.2. Synergistic Integration with Nanomaterials and Advanced Technologies

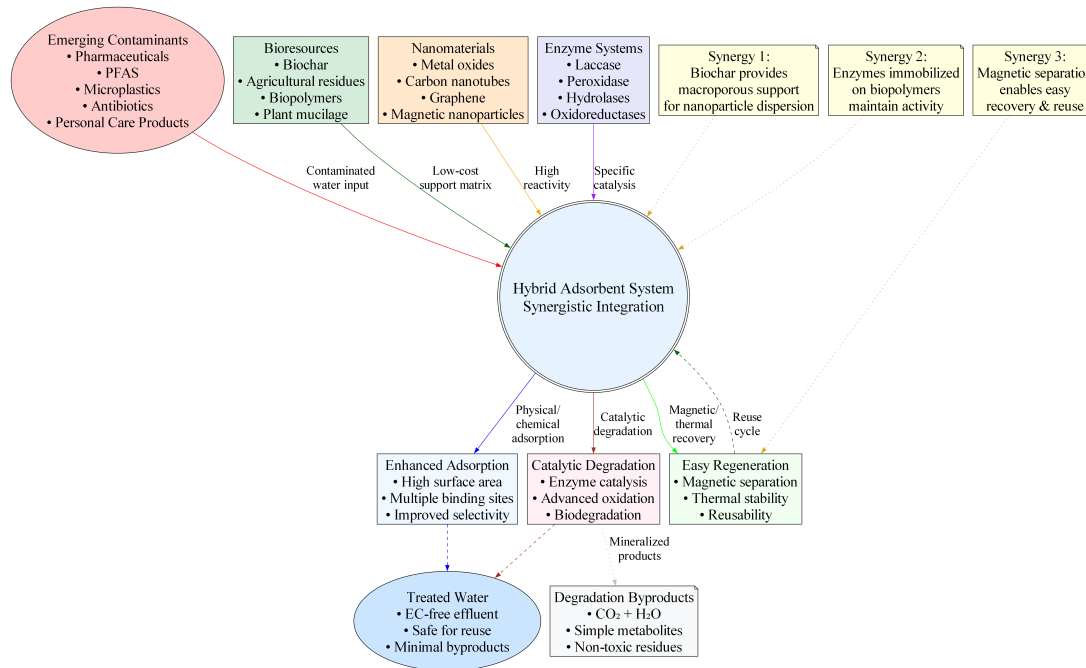
The integration of locally available bio-adsorbents with nanomaterials and advanced technologies has emerged as a promising strategy to enhance the removal efficiency of ECs while enabling resource recovery. According to the study by Arabzadeh Nosratabad et al. [82], nanomaterial-modified biochars, particularly biochar supported with metal nanoparticles (biochar-MNPs), significantly improve the adsorption and reactive properties of pristine biochar. Such modifications have been shown to effectively remove heavy metals, organic pollutants, and other toxic elements from aqueous environments, soil, and air by increasing surface reactivity, expanding the pH operating range, and improving structural stability. Similarly, Sani et al. [83] highlighted the advantages of waste-derived nano-biochar, demonstrating that its enhanced surface area, mobility, and adsorption capacity enable superior performance in soil and water applications compared to conventional biochar. These nano-biochars not only improve contaminant remediation but also contribute to sustainable agriculture, circular bioeconomy, and climate change mitigation through carbon sequestration and greenhouse gas reduction.

Enzyme-functionalized materials have also shown considerable promise for the selective degradation of persistent pollutants. In a recent study, Zhang et al. [84] developed enzyme-loaded porous hydrogels with tunable properties, which exhibited superior nanoplastic degradation performance compared to free enzymes. The immobilised enzymes retained 39.9% activity after five cycles and achieved a 104.1% greater PET removal rate (vs. free enzymes) at pH 5, demonstrating high efficiency and reusability. In a broader context, Bittencourt et al. [85] reviewed the application of enzyme and nanozyme-based processes for EC bioremediation, emphasising that



oxidoreductases and hydrolases, when immobilised or combined with nanomaterials, serve as green biocatalysts capable of high degradation efficiency with minimal toxic by-product formation. Such approaches hold potential for integration into conventional wastewater treatment systems to overcome current limitations in EC removal.

Advanced reactor configurations further enhance the performance of bio-adsorbent and enzyme-based systems. According to Sinharoy et al. [86], inverse fluidised bed bioreactors (IFBRs) enable simultaneous removal of selenite and heavy metals from wastewater while facilitating the recovery of these elements as elemental selenium and metal selenide nanoparticles. The study demonstrated removal efficiencies above 70% for most heavy metals and formation of nanoparticles ranging from 10 nm to 300 nm, highlighting the potential of integrating biological and electro-bioreactor approaches for both remediation and resource recovery (Figure 2).



**Figure 2.** Schematic illustration of hybrid adsorbent mechanisms.

#### 4.3. Sustainability Advantage

The increasing pressure on freshwater resources, coupled with the environmental and economic limitations of conventional chemical-based treatments, has driven the search for sustainable, low-cost, and scalable water purification technologies. In this context, biomass-derived bio-adsorbents have gained significant attention as a viable alternative due to their renewable nature, wide availability, and ability to convert agricultural and industrial residues into high-value functional materials. These bio-adsorbents can be produced from fruit and vegetable peels, crop residues, shells, husks, and other agro-industrial byproducts, often at minimal cost, making them suitable for large-scale applications while simultaneously addressing waste management challenges. According to Aguilar-Rosero et al. [87], bio-adsorbents derived from fruits, grains, seeds, and herbage exhibit remarkable adsorption capacities for heavy metals, nutrients, pharmaceuticals, and industrial organic pollutants, highlighting their versatility in diverse water treatment contexts. Supporting this, Karić et al. [88] demonstrated that thermally activated or chemically modified agricultural residues can effectively remove complex inorganic and organic pollutants, emphasising the dual benefit of environmental pollution mitigation and resource recovery. Teklemedhin et al. [89] further emphasised that bio-adsorbents derived from carbohydrates, lignin, and protein not only achieve high removal efficiency but also retain their adsorption performance over multiple regeneration cycles, confirming their long-term operational viability. Moreover, the application of biomass-derived biochar has been shown to lower the carbon footprint of water treatment processes compared to conventional chemical methods, providing a greener alternative while promoting energy efficiency [90]. Beyond environmental remediation, the production and use of bio-adsorbents align with circular economy principles, as they valorise waste streams, reduce reliance on virgin materials, and contribute to sustainable resource management [91]. By integrating waste valorisation, pollutant removal efficiency, scalability, and eco-friendly performance, bio-adsorbents offer a compelling solution that addresses both water scarcity and environmental sustainability challenges, establishing them as a transformative platform in the field of sustainable water and wastewater management (Table 2).

**Table 2.** Recent advances in nature-based hybrid adsorbent systems for emerging contaminant removal.

| EC Class & Examples                                      | Nature-Based Base Material                                     | Advanced Modifier/Hybrid Element                                     | Representative Performance (Reported)  | Primary Removal Mechanisms   | Regeneration & Reuse  | Scalability/Implementation Notes   | Environmental & Safety Concerns  | WEF Nexus Benefits  | SDG Relevance     | Reference |
|--|--|--|--|--|---|--|--|---|-------------------|-----------|
| Pharmaceuticals (ciprofloxacin, diclofenac, paracetamol) | Rice-husk biochar; pineapple leaf activated carbon             | ZnO or FeOx nanoparticles; cyclodextrin grafting; magnetic particles | Batch removals often 70–95%; $q_{\max}$ tens–hundreds $\text{mg}\cdot\text{g}^{-1}$ (e.g., 288 $\text{mg}\cdot\text{g}^{-1}$ MB on pineapple AC) | $\pi$ – $\pi$ interactions, H-bonding, electrostatic attraction, pore trapping | Chemical/thermal desorption, solvent wash; 70–90% retained over several cycles reported | Low-cost feedstock; pyrolysis and activation are scalable; QC for uniformity required  | NP leach risk if not immobilised; LCA for energy use required                                | Improves irrigation water quality; reduces downstream treatment needs | SDG6, SDG12, SDG2 | [92,93]   |
| PFAS (PFOA, PFOS)  | Coconut-shell AC; modified biochar                             | Cyclodextrin-functionalized chitosan; anion-exchange coatings        | Lab removals 70–92% for shorter chains; efficacy declines with chain variants  | Hydrophobic partitioning, inclusion complexation, and electrostatic binding    | Solvent extraction, high-T thermal treatment; regeneration energy-intensive             | High-cost modifiers limit low-resource use; pilot testing is essential                 | Spent adsorbent is considered hazardous; careful disposal/thermal destruction is needed      | Protects potable resources; reduces long-term soil/food contamination | SDG6, SDG3, SDG12 | [94–96]   |
| Microplastics & nanoplastics                             | Cactus (Opuntia) mucilage; magnetic biochar                    | Magnetic Fe <sub>3</sub> O <sub>4</sub> coatings; porous hydrogels   | Bench capture >90% particles <100 $\mu\text{m}$ ; enzyme-hydrogel degradation reports high PET removal increases vs free enzyme                  | Flocculation, physical entrapment, adsorption, and enzymatic degradation       | Magnetic recovery; hydrogel reuse with capacity decline over cycles                     | Decentralised, low-cost potential; processing and sludge handling challenge            | NP leaching from magnetic modifiers; microplastic fate in biosolids must be controlled       | Reduces marine pollution, supports water reuse for irrigation         | SDG14, SDG6       | [97,98]   |
| Antibiotic resistance genes (ARGs) & antibiotic residues | Biochar, engineered porous carbons                             | Immobilised nucleases or laccases; graphene oxide supports           | Enzymatic hybrids report 2–3 log ARG reduction; ARG reductions reported in WWTP effluents  | Enzymatic cleavage, ROS-mediated oxidation, adsorption + entrapment            | Enzyme immobilisation extends life; activity declines, but reuse is feasible            | Costs and enzyme stability limit field use; cold-chain and dosing control needed       | Carrier leaching; ARG mobilisation in biosolids must be prevented                            | Reduces AMR propagation risk; safer reuse of effluent in agriculture  | SDG3, SDG6        | [99–102]  |
| Personal care products (parabens, triclosan, EDCs)       | Algal biomass; chitosan; aloe mucilage                         | TiO <sub>2</sub> -doped biochar; photocatalytic coatings             | Sunlight-driven lab removals 80–93% for select PPCPs under optimised conditions  | Photocatalysis, oxidative degradation, adsorption, $\pi$ – $\pi$ stacking      | Photocatalyst reactivation via light; nanoparticle immobilisation critical              | Good for sun-rich, decentralised systems; photocatalyst production steps need scale-up | Photocatalyst particle release and toxic by-products from partial oxidation                  | Enables safe irrigation reuse; reduces endocrine load to ecosystems   | SDG6, SDG3, SDG15 | [103,104] |
| Heavy metals (Pb, Cd, Cr, Co)                            | Modified pineapple leaf cellulose; coconut shell AC; rice husk | EDTA/carboxymethyl functionalization; carbonisation-activation       | Adsorption capacities range tens to hundreds $\text{mg}\cdot\text{g}^{-1}$ ; column ts ~20–100 $\text{mg}\cdot\text{g}^{-1}$ depending on prep   | Ion exchange, complexation (carboxyl/amine groups), surface chelation          | Acid/base desorption; regenerable with efficiency depending on the modifier             | Readily scalable; pilot columns demonstrated; regeneration chemicals must be managed   | Regenerant waste (acidic solutions) requires neutralisation; a metal recovery path is needed | Enables recovery of metals (resource) and safer irrigation water      | SDG6, SDG12       | [105,106] |
| Dyes & textile organics                                  | Agricultural waste, AC; biochar; chitosan beads                | ZnCl <sub>2</sub> activation; polymer crosslinking; magnetic doping  | $q_{\max}$ often >100 $\text{mg}\cdot\text{g}^{-1}$ for methylene blue; some ACs report 200–300 $\text{mg}\cdot\text{g}^{-1}$                    | Electrostatic attraction, $\pi$ – $\pi$ stacking, porous trapping              | Thermal/chemical regeneration; good cycle retention for some ACs                        | Industry-scale adoption feasible; integration into dyehouse effluents                  | Regeneration generates high-T emissions or solvent wastes if not optimised                   | Improves industrial effluent quality and downstream reuse             | SDG6, SDG12       | [107–109] |
| Nutrients (ammonium, phosphate)—resource recovery        | Biochar, modified crop-residue chars                           | Mg/Al impregnations, Ca-loaded biochars for P capture                | Phosphate adsorption and slow-release behaviour; some biochars used as P-fertiliser alternatives   | Ion exchange, precipitation (Ca/Mg), surface complexation                      | Adsorbent can be reused as a soil amendment, providing slow-release nutrients           | Integrates directly with agriculture (circular loop); the pyrolysis scale affects cost | Risks of contaminants in biochar used on soils (e.g., PFAS); need QA/QC                      | Direct nutrient reclamation for crops reduces fertiliser demand       | SDG2, SDG12, SDG6 | [110–112] |

Table 2. Cont.

| EC Class & Examples                                   | Nature-Based Base Material                        | Advanced Modifier/Hybrid Element                            | Representative Performance (Reported)   | Primary Removal Mechanisms  | Regeneration & Reuse  | Scalability/Implementation Notes  | Environmental & Safety Concerns   | WEF Nexus Benefits   | SDG Relevance | Reference |
|---|---|---|---|---|---|---|---|--|---------------|-----------|
| Pesticides & herbicides                               | Agri-residue chars; chitosan beads                | Surface functionalization with $\beta$ -cyclodextrin, clays | Lab removals commonly 60–95% depending on molecule and polarity                         | Inclusion complexation (cyclodextrin), hydrophobic partitioning, and adsorption | Regeneration by solvent wash; long-term binding varies                                  | Low-cost feedstock; need target-specific tuning   | Persistent metabolites are sometimes generated; breakdown product toxicity must be checked. | Protects irrigation water and reduces crop uptake of toxicants | SDG6, SDG2    | [113,114] |
| Surfactants/detergents / personal-use surfactants     | Biosorbents from fruit peels, algal biomass       | Polymer grafting (polyaniline, PANI), crosslinked alginates | Removal efficiencies vary widely (50–95%) depending on chain length & CEC               | Micelle adsorption, electrostatic interactions, hydrophobic partitioning        | Regeneration via saline/solvent flush; polymer stability is important                   | Decentralised WW reuse is viable; surfactant loads may affect adsorbent lifetime        | Toxicity of discharged regenerants: foam and biological effects in downstream systems       | Improves reclaimed water quality for non-potable reuse         | SDG6, SDG12   | [115]     |
| Oil, hydrocarbons, and PFAS co-contaminated effluents | Biochar, activated carbon, oil-imbibing hydrogels | Aerogel composites, oleophilic surface treatments           | High removal for free-phase hydrocarbons (>95% sorption); PFAS co-removal variable      | Hydrophobic partitioning, sorption/entrapment, capillary uptake                 | Oil recovery by skimming; hydrogels reused with capacity loss; PFAS remains challenging | Industrial stormwater and refinery effluent applications; robust pre-treatment required | Hydrocarbon-laden spent adsorbent is combustible; PFAS persistence remains critical         | Protects surface waters and enables industrial water reuse     | SDG6, SDG12   | [116,117] |
| Cyanotoxins / algal toxins (microcystins)             | Chitosan, algal biomass, biochar                  | Oxidant-impregnated biochar; photocatalytic coatings        | Rapid adsorption and photodegradation reported; >80% removal under optimized conditions | Adsorption + oxidative degradation ( $\bullet\text{OH}$ ), photocatalysis       | Photocatalyst reactivation via light; spent material requires toxicity checks           | Beneficial for reservoir treatment; solar-driven designs are promising                  | By-product toxicity from incomplete oxidation; trophic transfer needs monitoring            | Secures drinking water sources and irrigation safety           | SDG6, SDG3    | [118,119] |

## 5. Materials Characterisation Techniques for Adsorbent Analysis

A fundamental tenet of materials science is that the performance of an adsorbent is intrinsically governed by its physical and chemical properties. To establish a reliable structure-property-performance relationship and validate the efficacy of the nature-based hybrid adsorbents discussed in this review, a suite of advanced characterisation techniques is employed. These methods provide critical insights into the morphology, structure, surface chemistry, and elemental composition of the materials, forming the essential foundation upon which adsorption mechanisms and capacity claims are based. The key techniques utilised across the cited studies are detailed below.

### 5.1. Structural and Morphological Analysis

The development of high-performance nature-based hybrid adsorbents is fundamentally reliant on a deep understanding of their physical architecture. Scanning Electron Microscopy (SEM) serves as an indispensable first line of investigation, providing a direct visual window into the micro- and nanoscale world that governs adsorption behaviour. As a multipurpose state-of-the-art instrument, SEM is primarily employed to observe surface phenomena, revealing critical information about topography, morphology, and texture [120]. This capability is paramount for confirming the successful synthesis of hybrid materials. For instance, SEM micrographs can visually validate the creation of a porous network within a biochar matrix, the intercalation of clay layers within a biopolymer, or the successful deposition of metallic nanoparticles onto a fibrous chitosan scaffold. The power of SEM in quantifying structural features is exemplified in work like that of Biessikirsi et al. [121], who used SEM to identify a parallel arrangement of tube-like structures and fibrous formations in microstructured charcoal, directly linking this distinct morphology to the material's high porosity. Without this direct morphological evidence, claims of successful hybrid formation would remain speculative.

While SEM reveals the exterior landscape of an adsorbent, Transmission Electron Microscopy (TEM) allows for a detailed investigation of its internal structure. TEM's unparalleled resolution, which can achieve the sub-nanometer scale, makes it a powerful tool for investigating the interior of nanoconstructs, providing detailed information on particle size, grain size, lattice type, and crystallographic details [122]. In the context of hybrid adsorbents, TEM is crucial for answering more nuanced questions about the integration of components at the atomic level. It can definitely confirm the formation of core-shell heterostructures by clearly resolving the distinct layers and their interfaces. Furthermore, TEM is the definitive technique for assessing the dispersion of nanoparticles within a biopolymeric matrix. This ability to probe internal structure and crystallography, as highlighted in nanomedical research for observing nanoparticle interactions with subcellular structures [123], is directly transferable to materials science, where it reveals how nanophases interact with their bio-support.

### 5.2. Surface Area and Porosity

The quantitative assessment of surface area and pore architecture is fundamental to understanding and predicting adsorbent performance, as these parameters directly govern the accessibility and density of active sites available for contaminant sequestration. The Brunauer-Emmett-Teller (BET) method stands as the predominant technique for determining the specific surface area of porous materials through the analysis of nitrogen physisorption isotherms. This analysis provides a critical numerical value, expressed in  $\text{m}^2/\text{g}$ , which serves as a primary indicator of adsorption potential. For instance, the exceptional adsorption capacity of a sugarcane bagasse biochar/sodium alginate monolith ( $394.46 \text{ mg/g}$  for nitrofurazone) is directly attributable to its extensive BET surface area of  $884.79 \text{ m}^2/\text{g}$ , a relationship consistently observed across high-performance adsorbents. The utility of BET analysis extends beyond mere characterisation, providing complementary insights into fouling mechanisms and structural changes in porous systems [124]. However, it is crucial to recognise the method's limitations, particularly for materials with complex pore geometries where surface area computations may require careful interpretation and potentially supplementary methods for validation [125].

While BET analysis quantifies total surface area, the Barrett-Joyner-Halenda (BJH) method provides essential complementary information by deriving pore size distribution and pore volume from the desorption branch of the isotherm. Classifying porosity into micropores ( $<2 \text{ nm}$ ), mesopores ( $2\text{--}50 \text{ nm}$ ), and macropores ( $>50 \text{ nm}$ ) is vital for understanding molecular transport and accessibility. Mesopores are particularly crucial as they facilitate efficient diffusion of pollutant molecules to internal adsorption sites, while micropores contribute significantly to ultimate capacity through their high surface energy. The evolution of porous networks under various treatments can be effectively tracked through BJH analysis, as demonstrated in studies of thermally modified nanoporous gold, where pore morphology changes were correlated with adsorption performance [126]. Recent advancements in pore size distribution modelling, such as the differential BJH approach, offer improved

accuracy by addressing limitations of traditional methods and providing more robust theoretical frameworks for interpreting complex adsorption mechanisms [127]. Together, BET and BJH analyses form an indispensable characterisation suite that bridges numerical surface area metrics with structural understanding of the porous network that dictates adsorption kinetics and capacity.

### 5.3. Chemical and Functional Group Identification

Understanding the chemical identity and bonding environment of functional groups on adsorbent surfaces is crucial for elucidating adsorption mechanisms and designing materials with targeted affinities for specific contaminants. Fourier-Transform Infrared Spectroscopy (FTIR) serves as a fundamental analytical technique for identifying characteristic organic functional groups through their specific absorption of infrared radiation. This method detects vibrational modes of bonds such as O-H, C=O, N-H, and C-O, which are ubiquitous in natural biopolymers like chitosan, alginate, and lignin [128]. The power of FTIR extends beyond mere identification; by comparing spectra before and after adsorption, researchers can observe peak shifts, intensity changes, or the disappearance of specific bands, providing direct evidence of chemical interactions such as complexation, hydrogen bonding, or ion exchange between the adsorbent and contaminant. The technique's utility in characterising complex materials is exemplified in studies of activated carbons, where it has been employed to quantitatively analyse surface oxygen groups that govern adsorption behaviour in water treatment applications [129].

While FTIR reveals molecular bonding information, X-ray Photoelectron Spectroscopy (XPS) provides complementary quantitative data about elemental composition and chemical states within the top 1–10 nanometers of a material's surface. This extreme surface sensitivity makes XPS particularly valuable for verifying successful functionalization processes and characterising thin coatings or nanoparticle surfaces [130]. In environmental adsorption studies, XPS proves indispensable for investigating redox-based removal mechanisms, such as confirming the reduction of toxic Cr(VI) to less hazardous Cr(III) on the surface of adsorbents containing iron or other reducing agents. The technique's ability to identify elemental oxidation states and quantify surface composition has established it as a powerful tool across multiple fields, including nanotechnology, materials science, and environmental engineering [131]. Together, FTIR and XPS form a comprehensive characterisation approach that bridges molecular-level bonding information with quantitative elemental analysis, providing critical insights into the chemical mechanisms governing contaminant adsorption and enabling the rational design of advanced adsorbent materials.

### 5.4. Crystallographic and Thermal Properties

The structural integrity and thermal stability of adsorbent materials are critical parameters that determine their practical applicability and regeneration potential. X-ray Diffraction (XRD) serves as a fundamental technique for characterising the crystalline structure of adsorbent components, providing essential information about phase composition, crystal structure, and crystallinity. This method enables researchers to identify specific mineral phases in natural clays, verify the successful synthesis of crystalline nanoparticles such as ZnO or Fe<sub>3</sub>O<sub>4</sub> within biocomposite matrices, and monitor structural transformations occurring during adsorption or regeneration cycles. The quantitative assessment of crystallinity is particularly valuable, as demonstrated by Chukhchin et al. [132], who developed a novel XRD-based method for determining crystallinity degree through analysis of diffraction pattern derivatives. This approach allows objective comparison of crystallinity across diverse material systems, providing crucial insights into how structural order influences adsorption performance and material stability.

Complementing structural analysis, Thermogravimetric Analysis (TGA) offers vital information about the thermal behaviour and composition of adsorbent materials. By measuring mass changes as a function of temperature under controlled atmospheres, TGA characterises thermal stability, moisture content, volatile components, and decomposition profiles of biopolymeric matrices like chitosan and alginate. The thermal parameters derived from TGA, particularly the temperature of maximum mass change rate ( $T_{\max}$ ), serve as reliable indicators of material composition and purity. As demonstrated in studies of graphene materials,  $T_{\max}$  values show systematic variations with particle size and material type, establishing TGA as a valuable quality control tool for characterising carbon-based adsorbents [133]. This thermal characterisation is essential for determining optimal regeneration conditions and predicting long-term stability under operational temperatures, thereby guiding the development of durable adsorbent systems.

### 5.5. Surface Charge and Magnetic Properties

The interfacial characteristics and separation efficiency of adsorbents play crucial roles in determining their practical implementation in water treatment systems. Zeta potential measurement provides fundamental insights

into the electrokinetic properties of adsorbent particles in suspension, reflecting the electrical potential at the slipping plane and governing colloidal interactions. This parameter is particularly significant for predicting pH-dependent adsorption behaviour, especially for ionizable pollutants where electrostatic interactions represent a primary removal mechanism. The point of zero charge (PZC), where zeta potential equals zero, serves as a key reference for optimising adsorption conditions. Recent comprehensive reviews have highlighted the complex temperature dependence of zeta potential, emphasising that thermal variations significantly influence electrokinetic behaviour through multiple mechanisms, including changes in dielectric constant, viscosity, and ion mobility [134]. Understanding these relationships is essential for designing adsorption processes that operate effectively across varying environmental conditions.

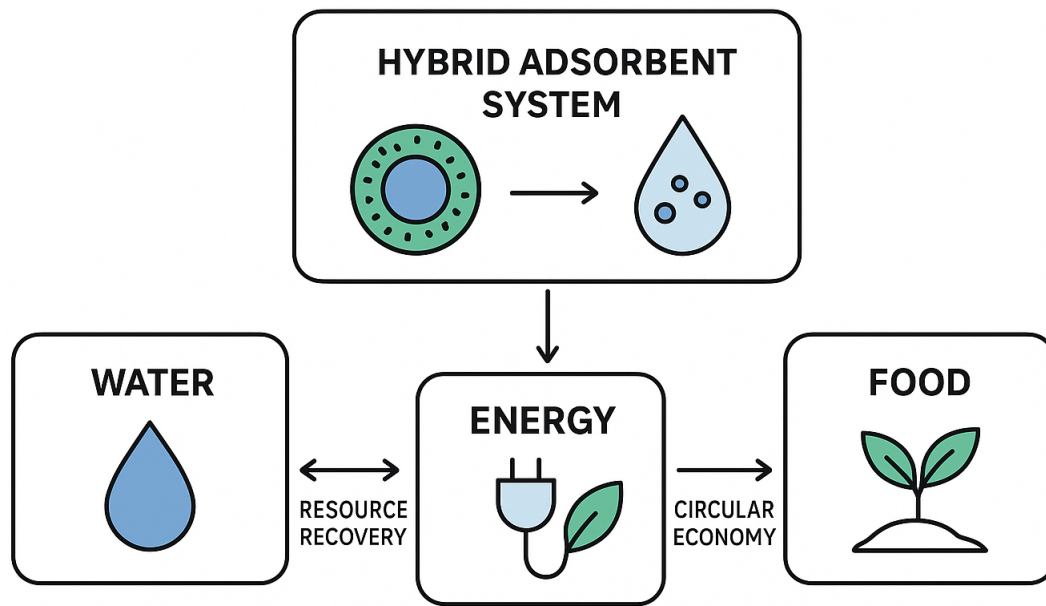
For magnetic adsorbents, Vibrating Sample Magnetometry (VSM) provides a quantitative assessment of magnetic properties that directly impact separation efficiency and reusability. VSM measures critical parameters, including saturation magnetisation, remanence, and coercivity, which collectively determine how readily materials can be recovered from treated water using external magnetic fields. The practical significance of these measurements is evident in applications such as magnetic cellulose nanoparticles and chitosan-magnetic beads, where optimal magnetic properties ensure efficient solid-liquid separation. Detailed VSM characterisation, as demonstrated in studies of vulcanised natural rubber nanocomposites, enables precise tuning of magnetic filler content to achieve desired separation characteristics while maintaining structural integrity [135]. This capability to quantitatively relate composition to magnetic performance is invaluable for designing adsorbents that combine high contamination removal efficiency with straightforward operational recovery, addressing a critical challenge in practical water treatment applications.

## 6. Integrating Hybrid Adsorbents into the Water–Energy–Food Nexus

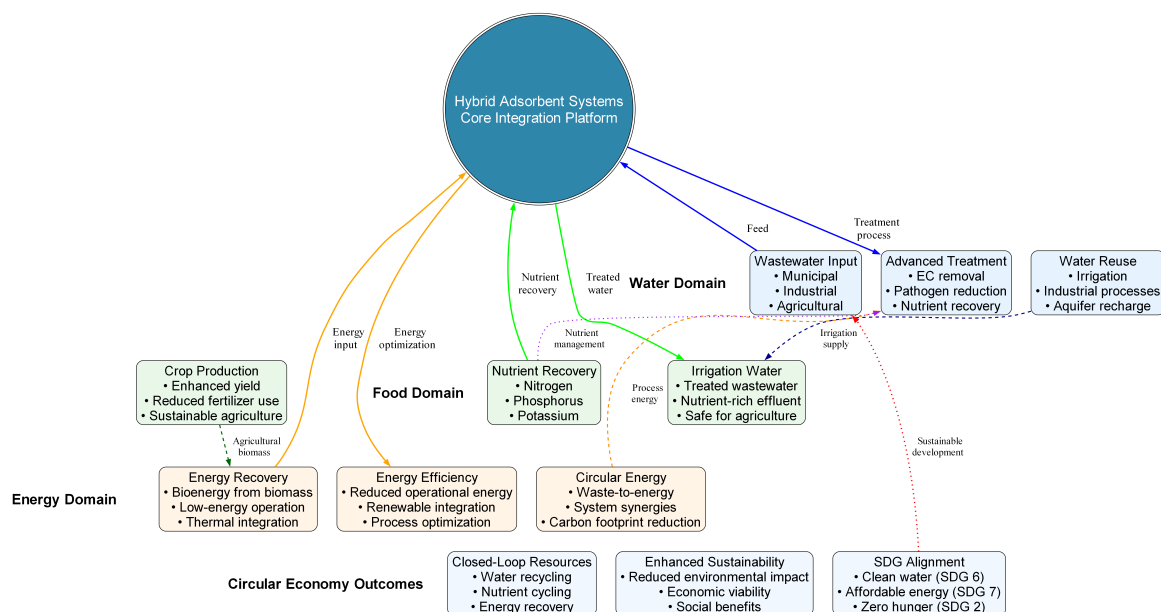
Wastewater is increasingly being recognised as a valuable resource rather than a disposable byproduct, offering tremendous potential for energy recovery, nutrient reclamation, and safe water reuse. As global water scarcity intensifies, sustainable wastewater recovery is becoming a cornerstone of circular economy strategies, where waste is transformed into inputs for other systems, thereby reducing environmental impacts and enhancing resource efficiency. Recent research highlights that adopting wastewater recovery pathways can significantly improve environmental sustainability while supporting agricultural productivity. For instance, according to a systematic review by Crovella et al. [136], wastewater can be effectively recovered for multiple purposes, including reclaiming irrigation water, extracting bio-based compounds from sludge, and recovering nutrient-rich biosolids for soil amendment and aquaculture feeds. These processes not only reduce greenhouse gas emissions but also close material loops, creating resilient and resource-efficient agricultural systems. In the study by Garcia and Pargament [137], a structured cost-benefit framework applied to a wastewater reuse project (Yarqon River, Israel) yielded a net present value of  $\approx$  USD 4.83 million under the base-case scenario; a Monte Carlo-based sensitivity analysis indicated a 64.28% probability of positive outcomes, emphasizing that properly accounting for externalities (e.g., recreational impacts) is pivotal to project feasibility. Figure 3 illustrates the structure and components of nature-based hybrid adsorbent systems and their integration within the water–energy–food (WEF) nexus.

Integration of adsorbent-based systems into sustainable water treatment frameworks represents a transformative approach to addressing global water scarcity and quality challenges. Adsorbent technologies have evolved rapidly, offering advanced capabilities to remove hazardous contaminants such as heavy metals, persistent organic pollutants, and emerging contaminants with high efficiency. According to the comprehensive review by Badran et al. [138], recent innovations in adsorbent materials such as starch-based composites, chitosan derivatives, metal-organic frameworks (MOFs), and magnetic nanomaterials have significantly enhanced adsorption capacities, in some cases doubling or even quadrupling pollutant removal efficiency compared to traditional adsorbents. These advanced materials also demonstrate exceptional reusability, with some systems maintaining up to 90% regeneration efficiency across multiple cycles, thereby reducing operational costs and improving environmental sustainability. Furthermore, when integrated with complementary technologies like electro-bioreactors, adsorbent-based systems enable simultaneous improvements in water quality, reduced energy consumption, and resource recovery, making them highly attractive for circular water management systems (Figure 4). Despite their technical promise, large-scale adoption of advanced adsorbents faces commercialisation barriers. A recent study by Kunwar et al. [139] highlights that a significant gap exists between laboratory-scale breakthroughs and market-ready products, primarily due to challenges associated with production scalability, quality control, regeneration costs, and compliance with stringent environmental regulations. The study underscores the need for robust productisation strategies and optimised business models to accelerate real-world deployment. Integrating adsorbent-based water treatment into sustainable frameworks not only supports energy-

efficient purification but also enables safe reuse of treated water for irrigation, contributing to agricultural productivity and aligning with the United Nations Sustainable Development Goals (SDGs) on clean water, climate action, and sustainable consumption.



**Figure 3.** Nature-based hybrid adsorbent systems within the WEF nexus.

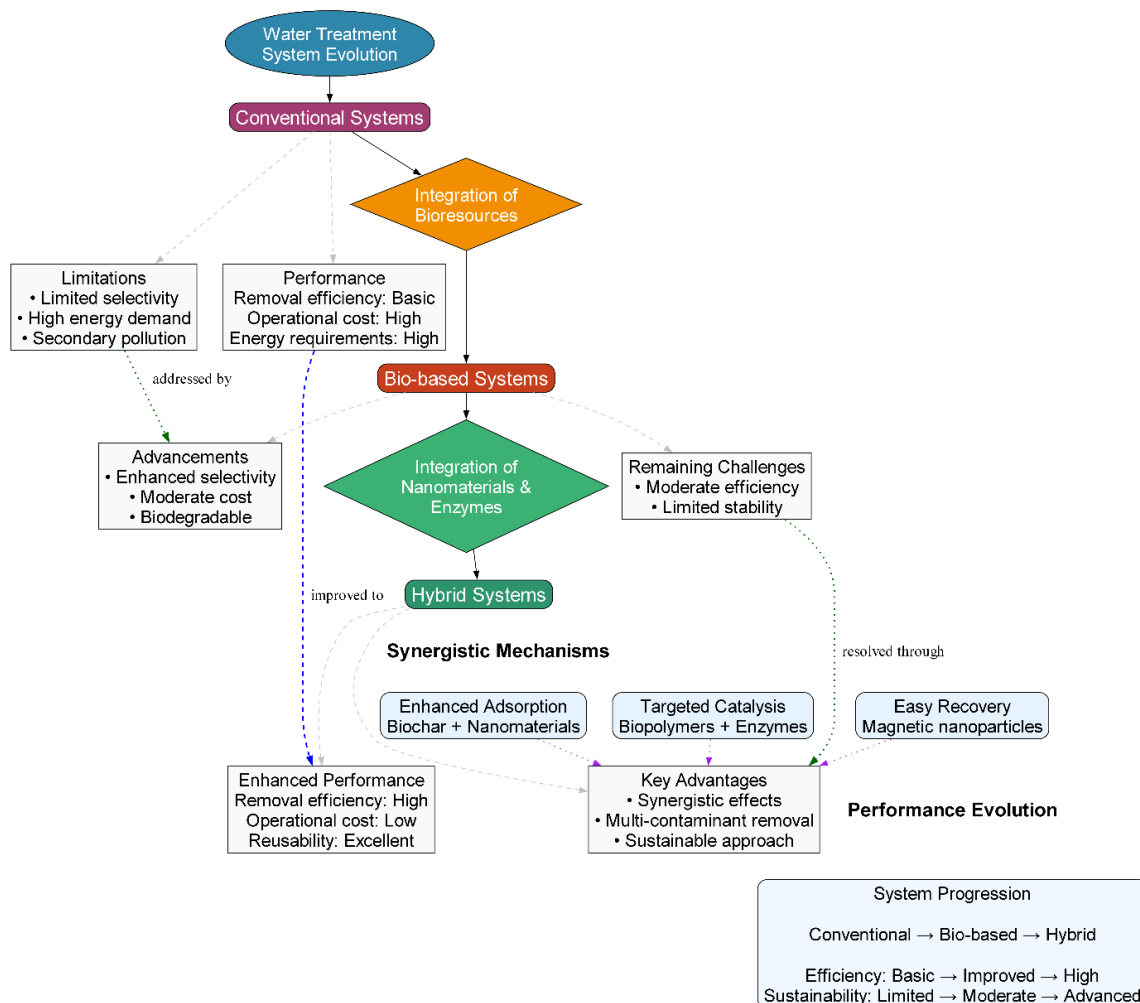


**Figure 4.** A flow diagram of hybrid systems enables resource recovery and the circular economy.

The role of policy frameworks and SDG alignment is central to advancing the development, implementation, and scalability of sustainable adsorbent-based water treatment technologies. The growing integration of these technologies within global sustainability agendas is strongly guided by international and national policies aimed at optimising water resource management and promoting circular economy principles. According to Faheem et al. [140], the sustainable regeneration and reuse of spent adsorbents (SPAs) significantly reduce secondary pollution while transforming SPAs into high-value products such as antimicrobial agents, fertilisers, catalysts, and construction materials. The study emphasises that integrating regeneration strategies with renewable energy solutions can further accelerate sustainability transitions, making adsorbent-based technologies a cornerstone of modern water treatment frameworks.

In addition, global policy evaluations underscore the strategic importance of aligning adsorbent-based water treatment innovations with SDG-driven objectives. A comprehensive study by Wang et al. [141] analysed 123 water resource policies across 15 Middle Eastern countries and revealed that advanced water treatment

technologies, including adsorption and desalination, are critical to achieving SDG 6 targets amid growing challenges such as water scarcity, rapid population growth, and climate variability. The findings highlight that countries leveraging technological innovations like the UAE and Kuwait, which derive more than 80% of their potable water from advanced treatment processes, achieve significantly greater progress in water security compared to nations with policy gaps in sanitation and transboundary cooperation. Furthermore, the importance of integrating policy frameworks with cross-SDG synergies is highlighted by Wang et al. [142], where 319 interactions between SDGs were identified, of which 286 were positive synergies. The study demonstrates that effective water pollution control requires coordinated strategies that simultaneously address clean water (SDG 6), climate action (SDG 13), food security (SDG 2), and responsible production (SDG 12). For instance, combining nutrient recovery from wastewater with improved water governance and climate mitigation strategies produces compounding benefits across environmental, agricultural, and social dimensions (Figure 5).



**Figure 5.** Evolution of adsorbent systems from conventional to hybrid approaches.

## 7. Mechanistic Insights and Theoretical Framework of Adsorption

### 7.1. Beyond Conventional Isotherms: Accounting for Surface Heterogeneity

The critical limitations of classical adsorption models, as highlighted in the provided paragraph, represent a fundamental challenge in accurately characterising the behaviour of nature-based hybrid adsorbents. While the Langmuir [143,144] and the Freundlich [145,146] isotherms have served as valuable preliminary tools in adsorption science, their application to complex bio-composite systems requires careful reconsideration. The Langmuir model's assumption of homogeneous binding sites is particularly problematic when applied to materials like biochar and chitosan composites, which inherently possess heterogeneous surfaces with multiple functional groups and pore structures exhibiting varying adsorption energies. Similarly, the purely empirical nature of the Freundlich model, while acknowledging heterogeneity, fails to provide meaningful physical insights into the actual adsorption mechanisms. This theoretical inadequacy is substantiated by experimental evidence, such as the study



by Obaid [147], where the Temkin isotherm demonstrated superior performance over both Langmuir and Freundlich models in describing chromium adsorption, indicating the significant role of adsorbate-adsorbate interactions that classical models neglect.

The integration of advanced isotherm models represents a necessary evolution in adsorption science toward more physically meaningful characterisation. The Sips isotherm effectively bridges the gap between Langmuir and Freundlich approaches, capturing the transition from heterogeneous site distribution at low concentrations to monolayer behaviour at saturation, thus providing a more accurate representation of real-world adsorption systems. The Temkin model's incorporation of decreasing heat of adsorption with coverage reflects the realistic scenario where the most favourable sites are occupied first, followed by progressively less energetically favourable interactions. Most significantly, the Dubinin-Radushkevich approach enables crucial mechanistic discrimination between physisorption and chemisorption through calculation of the mean free energy of adsorption [148]. Recent evaluations by Chu et al. [149] further validate the importance of proper DR model selection, demonstrating how different variants can yield substantially different parameter estimates and mechanistic interpretations for antibiotic adsorption systems. This sophisticated multi-model approach moves beyond mere curve-fitting to deliver genuine insights into the energetic landscape and binding mechanisms, ultimately enabling more rational design and optimization of advanced adsorbent materials for environmental remediation applications.

### 7.2. The Role of Nanoparticle Support and Leaching Mitigation

The paradigm of using support substrates in nano-enhanced hybrid adsorbents represents a fundamental advancement in environmental nanotechnology, addressing both performance optimisation and critical safety concerns. The dual role of substrates, serving as a stable foundation to prevent nanoparticle agglomeration while simultaneously functioning as a containment matrix, has been convincingly demonstrated in recent research. The study by Feng et al. [150] provides compelling evidence for this approach, where silver nanoparticles (AgNPs) were successfully immobilised within a biochar sodium alginate tannic acid composite matrix. Their characterisation using SEM, FTIR, and XRD confirmed excellent compatibility between the components, with the carbon silver interface significantly enhancing the dissolution, swelling, and expansion properties of the gel beads. This structural integrity directly contributed to exceptional adsorption performance, with removal rates reaching 96.4% for Cr(VI) alongside impressive dye adsorption capacities, while maintaining strong antibacterial activity. Crucially, the stable encapsulation within the biopolymeric matrix prevented AgNP leaching, ensuring the environmental safety of the system.

However, the transition from laboratory success to practical application requires careful consideration of potential limitations. As highlighted by Perumal et al. [151], despite the remarkable removal efficiencies demonstrated by various nano adsorbents, including metal oxides (99.3% ibuprofen removal), activated carbon (99.9% tetracycline removal), and novel MXenes (99.4% ceftriaxone removal), significant challenges remain regarding material instability, toxicity concerns, and scalable production. The very properties that make nanoparticles effective for adsorption also raise concerns about their potential environmental impact if released. This highlights the paramount importance of the immobilisation strategies described, particularly chemical grafting through covalent bonds and in situ synthesis within support matrices, which provide the robust anchoring necessary to prevent secondary contamination. The rigorous leaching assessment using ICP spectrometry becomes not merely an analytical procedure but an essential validation step to ensure that the nanotechnology solution does not become part of the problem it aims to solve, thereby fulfilling the promise of sustainable environmental remediation.

## 8. Challenges, Knowledge Gaps, and Future Directions

There is a lack of standardised testing protocols for evaluating the removal efficiency of ECs using adsorbent-based water treatment technologies, which limits the comparability and reliability of experimental results. According to Kumar et al. [152], ECs, including pharmaceuticals, personal care products, pesticides, and nanomaterials, are increasingly detected in surface water, wastewater, and groundwater, posing significant risks to human health and the environment. While various physical, chemical, and biological techniques have been explored for EC degradation and removal, the absence of consistent methodologies makes it difficult to predict treatment performance across different systems. In the study by Samadi et al. [153], polyaniline-based adsorbents were evaluated using a proposed standardised methodology that accurately determines adsorption equilibrium, kinetic rates, equilibrium time, and adsorption capacity. This approach demonstrates that adopting robust and uniform testing protocols is essential for reliably assessing removal efficiencies, understanding adsorption mechanisms, and enabling the scaling of laboratory findings to practical applications in sustainable water treatment.

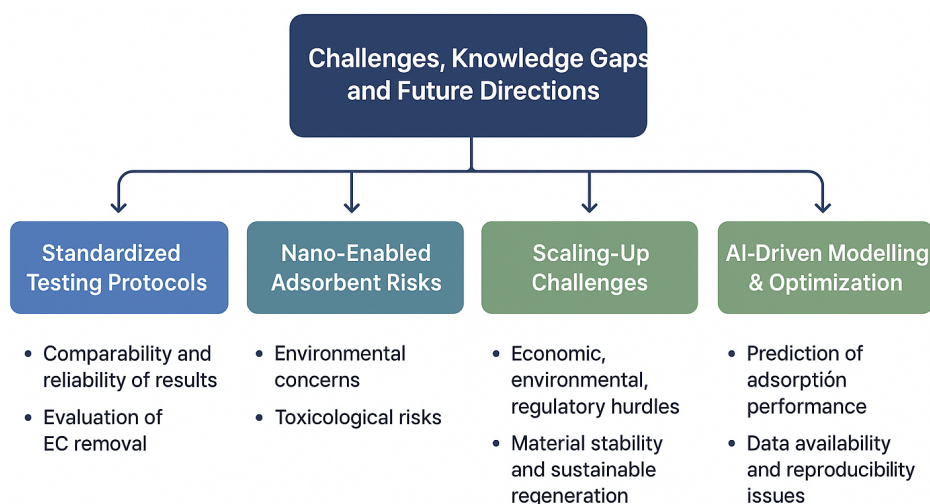
The use of nano-enabled bio-adsorbents in water treatment raises significant environmental concerns due to nanoparticle leaching and associated ecological toxicity. According to Mahlangu et al. [154], the incorporation of nanoparticles into polymeric membranes, while effective for enhancing water purification performance, can result in leaching if the nanoparticles are poorly supported or insufficiently immobilised. This leaching may cause secondary pollution, posing toxicological risks to aquatic organisms and potentially affecting other water consumers. Falinski et al. [155] further emphasise that although nanotechnology-enabled water treatment offers unprecedented advantages, such as enhanced catalysis, energy utilisation, and access to unconventional water sources, these benefits must be balanced with sustainability and safety considerations. They argue that all stages of the nano-enabled water treatment life cycle, including extraction, production, use, and end-of-life, require careful evaluation to prevent adverse ecological and human health impacts. Both studies highlight that addressing nanoparticle stability, optimising device design, and integrating eco-friendly frameworks early in development are crucial to ensuring that nano-enabled water treatment technologies provide safe, effective, and environmentally responsible solutions.

Scaling up adsorbent-based water treatment technologies from laboratory research to real-world field applications remains a significant challenge, particularly in resource-limited contexts. According to Satyam and Patra [156], while advances in adsorption materials, including high-performance nanostructured and functionalized adsorbents, offer promising efficiency and selectivity for contaminant removal, practical deployment is constrained by economic, environmental, and regulatory hurdles. Akhtar et al. [157] further highlight that although innovative materials such as nanocellulose, metal–organic frameworks, graphene-based composites, and biochar demonstrate exceptional pollutant removal in laboratory and pilot studies, scaling production, ensuring material stability, and implementing sustainable regeneration techniques remain key obstacles. Both studies underscore the need for multidisciplinary approaches, integrating material science, engineering, and policy frameworks, to bridge the gap between experimental research and practical, large-scale water treatment solutions.

Integrating AI-driven modelling techniques is increasingly recognised as essential for predicting adsorption performance and optimising adsorbent design for emerging contaminant removal. According to Mansour et al. [158], traditional trial-and-error approaches in wastewater treatment are often inefficient, whereas AI methods, including machine learning and neural networks, provide accurate predictions of adsorption efficiency, reduce operational costs, and improve resource utilisation. Similarly, Kumari et al. [159] emphasise that AI-enhanced adsorption modelling allows for precise assessment of different adsorbents' effectiveness in removing inorganic and organic contaminants, while also addressing challenges such as data availability, reproducibility, and real-world applicability. It is important to note that the critical application of artificial intelligence and machine learning represents a paradigm shift in the methodology of developing and optimising nature-based hybrid adsorbents, moving the field from empirical trial and error toward a predictive, data-driven science. Machine learning models, particularly supervised learning algorithms and genetic algorithms, can systematically analyse vast and complex datasets to establish nonlinear relationships between synthesis parameters such as precursor ratios, pyrolysis conditions, and functionalization protocols and the resulting adsorbent properties like surface area, functional group density, and ultimate adsorption capacity [160]. This capability allows for the *in silico* prediction of optimal material compositions tailored for specific contaminants, significantly accelerating the discovery process. Furthermore, AI-driven multi-objective optimisation can refine operational parameters in water treatment processes by modelling the intricate interplay between variables, including pH, temperature, adsorbent dosage, and the presence of competing ions to maximise removal efficiency and kinetic rates [161]. However, the efficacy of these models is fundamentally constrained by the quality, volume, and consistency of the experimental data used for training. The current lack of large, standardised datasets in adsorption science presents a significant challenge. To ensure reliability and provide genuine physicochemical insight, the implementation of explainable AI techniques is crucial to interpret model predictions and identify the dominant material characteristics governing performance, thereby transforming AI from a black box optimiser into a tool for mechanistic understanding and rational design [162].

There is an urgent need for cross-disciplinary collaboration between researchers, industries, and policymakers to advance sustainable water treatment technologies. According to Fan et al. [163], effective integration across energy, water, and waste management, coupled with supportive green policies, is essential to develop resilient and sustainable circular economy strategies that minimise environmental impacts and optimise resource efficiency. The study emphasises that environmental sustainability can only be achieved through case-based, real-world approaches that involve consensus-building among multiple stakeholders, supported by robust economic feasibility analyses. Likewise, Compagnucci and Spigarelli [164], highlight the critical role of university–industry–government interactions in fostering innovation in the water sector. Their work demonstrates that collaborative frameworks, such as the Triple Helix Model, can address pressing water challenges, including

facility upgrades, energy-efficient treatment technologies, denitrification, and desalination, while ensuring that innovations are locally relevant and practically implementable (Figure 6).



**Figure 6.** Development-to-deployment pipeline for hybrid adsorbents.

## 9. Conclusions

The escalating global challenge of water pollution, driven by persistent and emerging contaminants such as pharmaceuticals, heavy metals, and personal care products, underscores the critical limitations of conventional treatment technologies. This review has systematically addressed this problem by evaluating the transformative potential of nature-based hybrid adsorbents. The findings demonstrate that these materials, which synergistically integrate biopolymers like chitosan and alginate, agricultural wastes such as rice husk and banana peel, and advanced components like metal oxides or magnetic nanoparticles, achieve remarkable remediation efficacy. Their design leverages specific interactions, including complexation, ion exchange, and electrostatic attraction, to deliver exceptional removal efficiencies often exceeding 90% and record-breaking adsorption capacities, exemplified by values of 586 mg/g for lead and 394 mg/g for certain pharmaceuticals. The superiority of these hybrids stems from their multifunctional and tunable architectures, providing high surface areas, abundant active sites, and enhanced selectivity for target pollutants. Moreover, their foundation in renewable, low-cost resources and potential for regeneration align them with circular economy principles, offering a pathway to reduce operational costs by 30–80% compared to energy-intensive conventional methods. Despite these promising attributes, several limitations and pitfalls remain. The long-term structural and functional stability of these hybrid adsorbents under diverse water matrices is still insufficiently understood. The potential environmental risks associated with the leaching of nanoparticles or metal ions from nano-enhanced composites require thorough ecotoxicological evaluation. Scalability and reproducibility of the synthesis processes pose additional challenges, particularly for industrial-scale applications, where variability in agricultural feedstocks or synthesis conditions may impact performance. Furthermore, most studies focus on single or simplified pollutant systems, limiting insight into the complex interactions present in real wastewater streams. To fully harness the potential of nature-based hybrid adsorbents, future research directions should include: (i) rigorous long-term and multi-contaminant performance assessments under realistic conditions; (ii) the development of eco-friendly, scalable, and cost-effective synthesis methods; (iii) integration of predictive modeling and AI-assisted design to optimize adsorption efficiency and selectivity; and (iv) establishment of standardized testing protocols and regulatory guidelines to ensure safety, reproducibility, and field applicability. Collaborative efforts among academia, industry, and policymakers will be essential to bridge the gap between laboratory innovation and real-world implementation. Ultimately, addressing these challenges will accelerate the transition toward sustainable water treatment solutions, supporting resilient water security and environmental protection for future generations.

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## Data Availability Statement

Not applicable as the study did not generate new data.

## Conflicts of Interest

The author declares no conflict of interest.

## Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

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