



Polysaccharides and Composite Adsorbents in the Spotlight for Effective Agrochemical Residue Removal from Water

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Abstract: Agrochemical residues, including pesticides and herbicides, pose significant environmental and health risks when present in water sources. Conventional water treatment methods often fall short in effectively removing these persistent pollutants, necessitating innovative solutions. This review explores the use of polysaccharides and composite adsorbents as sustainable alternatives for agrochemical residue removal from water. Biopolymers such as chitosan, alginate, and cellulose are highlighted for their biodegradability, biocompatibility, and ability to be functionalized for enhanced adsorption performance. Recent advances in the development of composite materials incorporating nanomaterials, such as graphene, oxide, and metal oxides, have shown significant promise in enhancing the efficiency and selectivity of agrochemical adsorption. The review also addresses the fundamental mechanism of adsorption, such as electrostatic interactions, hydrogen bonding, and hydrophobic forces, that contribute to the effectiveness of these materials. Challenges associated with scalability, regeneration, and real-world applications are discussed, as well as future opportunities for integrating emerging technologies like 3D printing and machine learning into adsorbent design. Overall, polysaccharides and composites offer a promising pathway toward achieving efficient and sustainable agrochemical residue removal, with ongoing research needed to overcome current limitations and optimize their practical application in water treatment.

Keywords: polysaccharides; agrochemical residue removal; composite adsorbents; water treatment

1. Introduction

The paramount importance of removing agrochemical residues from water stems from the severe environmental and health risks associated with these pollutants. Agrochemicals, including pesticides and herbicides, pose a significant threat to aquatic ecosystems, human health, and agricultural sustainability when they contaminate water bodies [1]. Their presence can disrupt biodiversity, contaminate drinking water supplies, and contribute to the bioaccumulation of toxic substances within the food chain. These issues necessitate the development of effective strategies for removing agrochemicals from water systems. Previous reviews have explored bio-based adsorbents as environmentally friendly solutions for water treatment. These reviews highlight various materials, such as hydrogels, chitosan, nanocomposites, and bioflocculants, which offer high adsorption capacities and sustainability due to their biodegradable nature [2,3]. For instance, bio-based hydrogels have been shown to effectively remove heavy metal ions and organic micropollutants due to their unique structure and functionalization options, particularly when enhanced with nanoparticles for improved adsorption



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). efficiency [2]. Chitosan, another well-established biopolymer, has been used extensively in water treatment for removing organic contaminants, including pharmaceuticals, through functionalization techniques that enhance its adsorption capabilities [3]. Furthermore, recent research has focused on biomaterials like chitosan and nano-chitin composites, which provide greater surface areas for adsorption and improved interaction with pollutants, particularly in mitigating emerging contaminants like pharmaceuticals and personal care products [4]. Additionally, modified biopolymers and bio-based aerogels have shown promise in capturing microplastics and nanoplastics from water systems, addressing another critical environmental issue [5]. Our work builds upon these foundational reviews by providing a focus analysis of recent advances in polysaccharides and composite materials specifically for agrochemical residue removal.

Persistent organic pollutants, such as organochlorine pesticides, are particularly concerning due to their poor biodegradability and strong persistence in the environment [6]. These agrochemicals accumulate in groundwater, surface water, soil, and sediments, impacting ecosystems and non-target organisms. Furthermore, the misuse and over-application of pesticides have resulted in widespread contamination of water, air, and soil [7]. The contamination of water by agrochemical residues calls for innovative and sustainable approaches to manage their removal, as conventional water treatment technologies may not be fully effective in addressing these contaminants [8].

In response to the growing need for more efficient and sustainable decontamination methods, biopolymers have emerged as promising solutions. Derived from natural sources, such as plants, animals, and microbes, biopolymers are environmentally friendly, renewable, and biodegradable. Unlike synthetic polymers, biopolymers are eco-friendly and widely used in diverse applications, ranging from agriculture and food packaging to medical implants and environmental protection [9]. In water treatment, biopolymers can be used as adsorbents to remove agrochemical residues such as pesticides and herbicides. These materials act by attracting and capturing pollutants, minimizing their presence in water and mitigating associated environmental and health risks [10].

The focus of this review is to examine recent developments in the use of biopolymers and composite adsorbents for the removal of agrochemical residues from water. An overview of agrochemical residues are present to highlight the environmental and health risks posed by these contaminants. The review then delves into the properties and applications of biopolymers, including chitosan, alginate, and cellulose, and explores their capacity for agrochemical adsorption. Furthermore, the fundamental processes involved in the adsorption of agrochemicals by biopolymer-based materials are analyzed, providing insights into the molecular interactions that contribute to the effectiveness of these materials. The review also covers the synthesis and application of composite materials, emphasizing how the incorporation of elements such as nanoparticles into biopolymer matrices can synergistically enhance adsorption efficiency for comprehensive water decontamination.

Recent advances in polysaccharides and composite adsorbent technologies are discussed, offering an in-depth analysis of innovative studies and novel formulations. Finally, the challenges, limitations, and future perspectives surrounding the integration of polysaccharides and composites in water treatment are considered. This exploration provides insights into how these materials can contribute to the development of sustainable and efficient solutions for removing agrochemical residues from water sources.

2. Agrochemical Residues in Water: Environmental Impact and Challenges

Agrochemical residues, primarily originating from agricultural runoff, industrial effluents, and chemical spills, pose significant environmental risks due to their persistence and water solubility, allowing them to infiltrate diverse water ecosystems. These residues, including pesticides and herbicides, not only impact aquatic ecosystems but also present serious public health concerns through biomagnification and bioaccumulation [11]. As pesticides infiltrate water bodies, they partition among various components of the hydroThe dispersion of agrochemical residues occurs through multiple pathways (Figure 1), as listed below:



Figure 1. Some routes or ways through which pesticides move, spread, and enter different environmental compartments.

- Soil leaching: Pesticides penetrate soil layers, contaminating groundwater, particularly in regions with high irrigation or rainfall.
- Surface runoff: Rainfall or irrigation transports pesticides from agricultural lands into nearby rivers, lakes, and streams.
- Atmospheric deposition: Pesticides dispersed into the air are redeposited into water bodies and soil.
- Direct application: Pesticides directly applied to water bodies further contaminate aquatic ecosystems.
- Ecological transfer: These chemicals accumulate within organisms and magnify as they move up the food chain, with potential widespread ecological consequences.

These diverse pathways underscore the intricate ways in which pesticides move within the environment, posing risks to both ecosystems and human health [9].

In this sense, in a recent study, it was determined that 64% of global agricultural lands are exposed to contamination from more than one agrochemical, while 31% of these lands face elevated risk. Of the areas classified as high risk, approximately 34% are located in regions of high biodiversity, thereby increasing environmental damage and threatening endemic species [13]. For instance, excessive pesticide use has negatively impacted biodiversity in regions of Latin America, where the effects of both botanical and synthetic pesticides on pollinators like bees were evaluated, revealing a decrease in the frequency of visits to melon flowers. This reduction affects pollination, which is essential for agricultural production, and subsequently leads to lower crop yields [14,15].

Numerous experimental and epidemiological studies have emphasized the significant impact of various agrochemicals on neurological health. These investigations suggest that pesticide exposure may notably contribute to the development of neurological disorders, such as neurodegenerative diseases, cognitive impairments, and behavioral changes. As the understanding of how these chemical compounds interact with the nervous system deepens, the need for more thorough evaluation of the risks associated with their prolonged use, even at doses considered safe, becomes increasingly evident [16,17].

Among the most detected agrochemicals in water systems are herbicides (such as glyphosate, atrazine), insecticides (e.g., parathion, malathion, chlorpyrifos), and fungicides

(such as difenoconazole). These chemicals belong to various classes, including organochlorines, organophosphates, pyrethroids, and carbamates, each contributing differently to environmental toxicity and persistence [11,18,19]. Atrazine, in particular, stands out as a prevalent contamination across multiple water sources, further emphasizing the need for comprehensive monitoring. Table 1 shows some noteworthy chemicals, classes of pesticides, matrices, and concentrations across diverse studies.

Table 1. Some noteworthy chemicals, classes of pesticides, matrices, and concentrations across diverse studies.

Agrochemical Type	Noteworthy Chemicals	Classes of Pesticides	Detected in	Environmental Concerns	Reference
Herbicides	Atrazine, glyphosate sarosate, paraquat, clear weed, delsate, roundup.	Organochlorines, organophosphates, carbamates, carboxylic acid derivatives, urea, substitute triazines, pyrethroids, and others.	Water samples.	Persistence, biodiversity impact, health risks, exceeded drinking water standards.	[19]
Pesticides	DDT, DDE, parathion, malathion, chlordane, atrazine, glyphosate.	Organochlorines, organophosphates, carbamates, carboxylic acid derivatives, urea, substitute triazines, pyrethroids.	Water bodies, sediments, fish	Distribution patterns, ecological risks.	[11,19]
Organophosphorus	Permethrin, diazinon, chlorpyrifos, malathion, fenvalerate, pyrethroids.	Organophosphorus, pyrethroids.	Deep wells	Prevalence, elevated pyrethroid concentrations.	[20]
Various pesticides	Various pesticides p,p'-DDT, bifenthrin, aldrin, fenoxycarb.		Deep wells in Nuevo Leon, México	Risk assessment, exceeded European standards, potential health implications.	[20]
Various chemicals Atrazine, alachlor, metolachlor, metribuzin, simazine.		N/A	Diverse water sources	Variability in concentrations, alachlor, and atrazine predominantly detected.	[21]

The persistence of agrochemical residues in water, coupled with challenges in detection and regulation, highlights the complexity of managing this environmental issue. Many water samples reveal residue concentrations that exceed permissible limits established by regulatory bodies like the European Union and NESREA, signaling potential environmental and health risks. The widespread distribution and resilience of these chemicals in different geographic regions call for stricter regulatory oversight and the development of more effective decontamination strategies.

3. Mechanisms and Interactions to Remove Agrochemicals from Water

Various technologies have been developed for water treatment, which can be primarily classified into non-destructive techniques, such as adsorption, ion exchange, aeration, and precipitation, and destructive techniques, such as advanced oxidation processes, microwaves, and sonication, among others. One of the most widely used non-destructive methods is adsorption, which can be defined as a heterogeneous process in which a liquid phase, containing dissolved compounds called adsorbates, interacts with the surface of a solid material (adsorbent). This interaction can result in strong binding forces (chemisorption) or electrostatic interactions (physisorption). During adsorption, the adsorbates are attracted to the surface of the solid, reducing the surface's free energy. This transfer from the liquid phase to the solid continues until an equilibrium is reached between the amount of adsorbate adhered to the solid material and the amount remaining in the solution [22]. Ultimately, the distribution depends on the affinity between the adsorbate and the adsorbate.

Among the destructive methods for contaminant removal are advanced oxidation processes (AOPs) [23], which propose the treatment of contaminated water based on the in situ generation of highly effective oxidizing agents. This principle underlies photocatalytic technologies, which, under ultraviolet radiation, generate highly reactive oxygen species such as hydroxyl radicals (OH) and superoxide radicals (O_2^-) [24,25]. Both species, due to their unpaired electrons, are extremely efficient oxidizing agents, as demonstrated in the electronic configuration diagram of oxygen molecules (Figure 2).

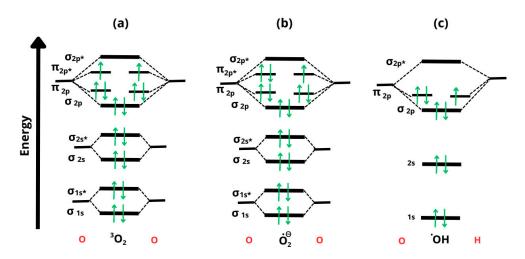


Figure 2. Electron configuration of molecular radical oxygens, molecular oxygen (**a**), superoxide anion radical (**b**), hydroxyl radical (**c**).

The removal of agrochemical residues from water through adsorption has gained increasing attention due to its simplicity, cost-effectiveness, and eco-friendliness [26,27]. Among various adsorbents, biopolymers have emerged as promising materials due to their biodegradability, renewability, and functional versatility [27,28]. The adsoption mechanism revolves around the interaction between the agrochemical molecules and the surface of the biopolymer, with multiple forces driving the process, including electrostatic interactions, hydrogen bonding, van der Waals forces, and hydrophobic interactions. These mechanisms are further influenced by the physicochemical properties of both the agrochemicals and the adsorbent surfaces.

Agrochemical residues exhibit diverse molecular structures and properties, affecting how they interact with adsorbents. The adsorption process depends on the chemical nature of the agrochemical, its solubility, charge, and molecular size. Biopolymers, due to their modifiable surface functionalities, can be tailored to optimize adsorption for specific agrochemical groups [26]. Figure 3 illustrates the different adsorption mechanisms occurring between biopolymer-based adsorbents and agrochemicals.

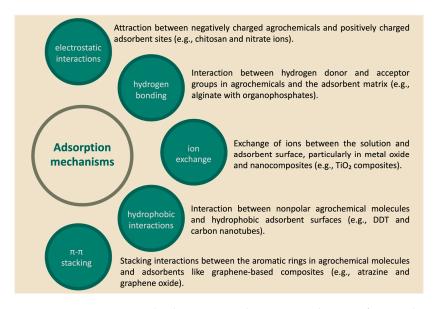


Figure 3. Interactions involved in various adsorption mechanisms for agrochemical removal.

Organochlorines such as DDT and DDE are highly hydrophobic and persistent in the environment [29–31]. Their removal via adsorption relies on hydrophobic interactions

and π - π stacking with polymer surface. Biopolymer surfaces modified with hydrophobic moieties or aromatic groups exhibit enhanced adsorption capacity for these nonpolar molecules [32–34].

Organophosphates, including malathion and parathion contain phosphate groups, making electrostatic interactions a dominant force in their adsorption. Negatively charged biopolymers, such as carboxylate derivatives of chitosan and alginate, exhibit strong affinity for these agrochemicals via ionic interactions. Additionally, hydrogen bonding plays a critical role due to the presence of polar functional groups in both adsorbent and agrochemicals molecules [35,36].

Herbicides like glyphosate are polar and exhibit high solubility in water, making their removal challenging. For these agrochemicals, surface-modified biopolymers incorporating amine or hydroxyl groups enhance adsorption by creating hydrogen bonding and electrostatic interactions with the agrochemical molecules. For instance, chitosan modified with amine groups has been shown to have high affinity to glyphosate due to its ability to form hydrogen bonds with the carboxyl and phosphate groups of the herbicide [37,38]. In contrast, atrazine often requires hydrophobic interaction-based adsorbents, such as functionalized cellulose or nanocomposites, to improve adsorption efficiency [39,40].

Additionally, urea-based herbicides, like diuron and linuron, exhibit a similar challenge in the removal due to their persistence in water systems [41–43]. Biopolymers functionalized with hydrophobic groups can improve adsorption efficiency for these herbicides through hydrophobic interactions.

Neonicotinoids, such as imidacloprid and acetamiprid, are widely used insecticides known for their water solubility and environmental persistence. Adsorption of neonicotinoids is driven by electrostatic interactions and hydrogen bonding, particularly when using biopolymers functionalized with carboxyl and amine groups [44–46]; therefore, there will be the same electrostatic interactions within the amine groups present in chitosan with these kinds of pesticides.

Carbamates, including carbaryl and aldicarb, interact with biopolymers via electrostatic interactions and hydrophobic forces. Functionalization of biopolymers with polar groups enhances adsorption by enabling stronger bonds with these polar agrochemicals [47]. Carbamates pose significant risks to aquatic environments, and their removal through biopolymer adsorption can be effective with tailored surface modifications [48].

Fungicides, such as tebuconzole and mancozeb, also contribute to water pollution. These agrochemicals interact with biopolymers primarily via hydrogen bonding and π - π stacking, particularly when functionalized with aromatic groups [49–51]. For example, functionalized chitosan or cellulose derivatives have shown promise in adsorbing fungicides by improving surface affinity for aromatic compounds [52].

Pyrethroids, like permethrin and fenvalerate, are hydrophobic and are adsorbed through van der Waals forces and hydrophobic interactions with biopolymers surfaces. Hydrophobically modified biopolymers significantly improve the affinity for these nonpolar agrochemicals, enhancing their removal from water systems [53–55].

To provide a compressive overview of the interactions between agrochemical residues and biopolymer adsorbents, Table 2 summarizes key agrochemical groups, their specific examples, the primary adsorption mechanism, the types of interactions involved and the necessary biopolymer modifications for enhanced adsorption efficiency.

Table 2. Overview of agrochemical groups, examples, adsorption mechanisms, interaction types, and biopolymer functionalization for effective agrochemical residue removal.

Agrochemical Group	Examples	Primary Adsorption Mechanism	Interaction Type	Biopolymer Functionalization	Reference
Organochlorines	DDT, DDE	Hydrophobic interactions, π - π stacking.	Aromatic interactions	Functionalization with hydrophobic/moieties (CMC, chitosan).	[29–31]
Organophosphates	osphates malathion, parathion Electrostatic inter-		Ionic bonds, hydrogen bonds	Carboxylated, chitosan, alginate.	[35,36]

Agrochemical Group Examples		Primary Adsorption Mechanism	Interaction Type	Biopolymer Functionalization	Reference
Herbicides	glyphosate, atrazine	Hydrogen bonding, electrostatic interactions.	Hydrogen bonding, ionic bonds	Amine- or hydroxyl-modified polysaccharides (chitosan).	[37-40]
Urea-based herbicides	diuron, linuron	Hydrophobic interactions.	Hydrophobic bonding	Hydrophobic groups (cellulose acetate).	[41-43]
Neonicotinoids	imidacloprid, acetamiprid	Electrostatic interactions, hydrogen bonding.	Ionic bonds, hydrogen bonding	Carboxyl- and amine-modified chitosan.	[44-46]
Carbamates	carbaryl, aldicarb	Electrostatic interactions, hydrophobic interactions.	Ionic bonds, hydrophobic bonding	Functionalization with polar groups (chitosan, silica).	[48]
Fungicides	Fungicides tebuconazole, mancozeb		Hydrogen bonding, π - π stacking	Aromatic functionalization with chitosan or cellulose.	[49-51]
Pyrethroids Permithrin, Fenvalerate		van der Waals forces, hydrophobic interactions.	Hydrophobic bonding	Hydrophobic modification of biopolymers (alginate, lignin, cellulose).	[55]

Table 2. Cont.

4. Polysaccharides as Adsorbents: Recent Developments

In recent years, polysaccharides have gained significant attention as effective adsorbents for removing agrochemical residues from water. Their inherent biodegradability, biocompatibility, and renewability make them attractive alternatives to synthetic adsorbents. Various modifications and innovations have further enhanced their adsorption capacity, selectivity, and stability. Polysaccharides are linearly structured or branched molecules, and the polysaccharides most used as adsorbents are chitosan, alginate, and cellulose. This section highlights the latest developments in the use of key polysaccharides, as well as other emerging biopolymers.

4.1. Chitosan

Chitosan, derived from chitin, is one of the most widely studied biopolymers for agrochemical adsorption due to its high amine group content, which provides abundant active sites for interactions with agrochemical molecules [56,57]. Recent research has focused on modifying chitosan's surface to improve its affinity for specific agrochemicals [53,58]. Additionally, chitosan has been combined with materials like graphene oxide and metal oxides to form nanocomposites. These nanocomposites exhibit increased surface area and improved adsorption capacity, particularly for pesticides such as atrazine and malathion [58,59]. Another area of development in chitosan is in its regeneration and reusability. Crosslinking techniques have led to the creation of crosslinked chitosan adsorbents, which maintain their adsorption efficiency over multiple cycles of adsorption and desorption, making them a suitable and cost-effective solution [60,61].

4.2. Alginate

Alginate, derived from brown seaweed, has gained attention for its biocompatibility and its carboxyl group functionality, which allows for strong ionic interactions with positively charged agrochemicals. Recent advancements have focused on the functionalization of alginate, particularly through carboxylation and crosslinking, to enhance its adsorption capacity for organophosphates and carbamates. These modifications improve alginate's ability to form ionic bonds with the phosphate and carbamate groups present in many agrochemicals, making it a highly effective adsorbent [62]. Furthermore, alginate-based nanocomposites, where metal oxide nanoparticles are embedded into alginate matrix, have shown a significant increase in adsorption capacity, particularly for complex agrochemical mixtures such as insecticides like imidacloprid [63]. Research continues to highlight not only the high adsorption capacity of alginate-based materials but also their environmental benefits, as these materials are biodegradable and easy to dispose of with minimal environmental impact.

4.3. Cellulose

Cellulose, derived primarily from wood sources, is recognized as the most abundant natural polymer on Earth. Its unique structural properties, coupled with its widespread availability, make it an efficient material for the adsorption of various contaminants from water. The inclusion of cellulose in the cadre of biopolymers used for adsorption processes highlights its versatility and significant potential for water treatment applications [63–66].

Both plant-based cellulose and microbial cellulose share a common composition of glucose monomers connected by β -1,4 glycosidic linkages, but they differ in their source and polymerization degree. Plant-derived cellulose typically features a polymerization degree ranging from approximately 2500 to 15,000 glucopyranose units, while microbial cellulose, synthesized by bacteria as a primary metabolite, exhibits different structural characteristics that enhance its potential in various applications [64]. An exciting aspect of cellulose-based materials is the ability to obtain them from vegetable waste sources, which presents a cost-efficient and sustainable method for production, further solidifying cellulose's role as an eco-friendly adsorbent for environmental remediation [63–66].

Modifications to cellulose, such as grafting amine and carboxyl groups, have improved its ability to adsorb polar agrochemicals, including glyphosate and atrazine. For example, cellulose nanofibers grafted with functional groups have demonstrated high efficiency in removing pyrethroids and organochlorines via hydrophobic interactions and π - π stacking [67]. Another development in this field is the use of nanocellulose, which refers to cellulose materials at the nanoscale.

In collective synergy, these biopolymers contribute significantly to the removal of various contaminants, including organic dyes, heavy metals, oil, solvents, and CO_2 from water [68,69]. The unique properties of polysaccharides like cellulose, chitin, and chitosan play a crucial role in advancing adsorption processes, aligning with the imperative goal of mitigating environmental pollution.

Table 3 summarizes the adsorption properties of different bio-based adsorbents in terms of contaminant type, initial concentration, adsorption time, capacity, and mechanism, and functionalization.

4.4. Other Unusual Polysaccharides as Adsorbents

In addition to the more established polysaccharides like chitosan, alginate, and cellulose, several other natural materials are being explored for their potential as adsorbents. Starch-based materials, for instance, have been functionalized with cationic groups to improve their adsorption capacity for anionic agrochemicals [71]. Similarly, pectin and lignin, which are naturally abundant, have also been studied. Recent modifications of these biopolymers have improved their ability to absorb complex agrochemical residues, such as fungicides and insecticides, by facilitating multiple interactions with agrochemical molecules [72]. Additionally, protein-based adsorbents, such as soy protein and casein, are gaining attraction as eco-friendly materials for agrochemical removal. When functionalized, these proteins exhibit promising results in removing a broad range of agrochemical residues, further expanding the scope of natural materials that can be utilized in water decontamination [73,74].

Adsorbent	Contaminant	Initial Concentration	Adsorption Time	Adsorption Capacity	Adsorption Mechanism	Regeneration Ability	Functionalization	Ref
Chitosan	Nitrate and phosphate ions.	100 mg/L for both nitrate and phosphate solutions	45 min for nitrate, 30 min for phosphate	90.09 mg g ⁻¹ for nitrate, 131.29 mg g ⁻¹ for phosphate	Electrostatic adsorption, ion exchange, hydrogen bonding.	Retains 75% efficiency over 5 cycles	Embedded Zr ⁴⁺ ions into chitosan and soybean husk biochar.	[57]
	Nitrate ions	100 mg/L	5 min	74% removal of nitrate at pH 11	Photocatalytic reduction using UV light, with Ag nanoparticles enhancing electron-hole separation.	Maintains 71% efficiency over 3 cycles, dropping to 50% by the fourth cycle.	Ag-doped TiO ₂ , γ -Al ₂ O ₃ , and chitosan hybrid structure.	[57]
	Nitrate ions	100–300 mg/L	Nano-CS/Clino:30 min; Nano-CS/Clino@H: 20 min; Nano- CS/Clino@PEHA:15 min	Nano-CS/Clino: 185.18 mg/g; Nano-CS/Clino@H: 227.27 mg/g; Nano- CS/Clino@PEHA: 277.77 mg/g	Electrostatic interaction between positively charged adsorbent sites (amine and hydroxyl groups) and nitrate anions.	Adsorption capacity maintained after three adsorption-desorption cycles with values of 77.93 mg/g for Nano-CS/Clino, 82.07 mg/g for Nano-CS/Clino@H, and 90.41 mg/g for Nano-CS/Clino@PEHA.	Nano-CS/Clino was modified with hydrochloric acid; Nano-CS/Clino@PEHA was functionalized with pentaethylenehexamine to increase the number of active adsorption sites.	[57]
	Atrazine	Maximum atrazine concentration of 5 mg/L	60 min	95% atrazine removal in the membrane bioreactor process	π - π interaction, hydrogen bonding, and electrostatic interaction between graphene oxide functional groups and atrazine molecules.	Membrane fouling and flux decline was reduced through pneumatic backpulsing techniques.	Graphene oxide was cross-linked with chitosan to form a stable, hydrophilic membrane on ceramic support	[58]
	Malathion	from 1 ng/mL to 20 μg/mL	Optimal inhibition achieved after 10 min of incubation	Detection limit of 0.39 ng/mL, with linear detection in the range of 1 ng/mL to 20 µg/mL	Inhibition of acetylcholinesterase activity by malathion, causing a decrease in current due to inhibition.	-	graphene oxide-tetraethylenepentamine (rGO-TEPA) and copper nanowires to enhance conductivity and loading of acetylcholinesterase.	[59]
Alginate	Potassium nitrate	solutions at 0.5%, 1%, and 2% concentrations	Swelling kinetics and water retention were studied over several h.	Maximum adsorption capacities of lead (Pb) and cadmium (Cd) ions were 628.93 mg/g and 456.62 mg/g, respectively	Chelating of heavy metal ions (Pb, Cd, Ni, Cu) through sulfonate and carboxylate groups in the hydrogel.	The hydrogel maintained 83% efficiency for Pb(II) and 90% for Cd(II) after three adsorption- desorption cycles.	The hydrogel was modified by graft copolymerizing poly(AMPS-co-AA-co-AM) onto sodium alginate (NaAlg)	[70]
	Nitrate	100 mg/L nitrate solutions	48 h for nitrate reduction.	4.3–9.6 mg NO ₃ [–] reduced to ammoniacal nitrogen per gram of immobilized NZVI	Chemical reduction of nitrate to ammonium by NZVI and immobilization of ammonium by powdered activated carbon.	-	Calcium-alginate beads impregnated with nano zero-valent iron (NZVI), magnetite nanoparticles (MNP), and powdered activated carbon (PAC).	[62]

Table 3. Adsorption performance of various polysaccharide adsorbents for agrochemical and pollutant removal.

Adsorbent	Contaminant	Initial Concentration	Adsorption Time	Adsorption Capacity	Adsorption Mechanism	Regeneration Ability	Functionalization	Ref
Cellulose	Industrial fertilizer effluents and Rhodamine B dye	10 mM RhB dye; unspecified for industrial fertilizer effluents	60 min	RhB dye: 96% degradation efficiency Fertilizer effluents: 52% degradation efficiency Mixture of RhB dye and fertilizer effluents: 86% degradation efficiency.	Photodegradation using visible light, where cellulose acts as a support to enhance the stability and charge separation in silver phosphate.	The catalyst retained 64% of its degradation efficiency after five cycles.	Silver phosphate nanoparticles were synthesized with cellulose extracted from agro-waste (fruit peels).	[5]
	Nitrate (NO ₃ ^{$-$}), nitrite (NO ₂ ^{$-$}), and phosphate (PO ₄ ³⁻)	100 mg/L for nitrate, nitrite, and phosphate	60 min	Nitrate: 79.65% Nitrite: 73.04% Phosphate: 98.18%	Electrostatic attraction between negatively charged nitrate, nitrite, and phosphate ions and the protonated surface of the aerogel in acidic conditions. Ion exchange also plays a role.	The aerogel maintained over 60% removal efficiency for nitrate, nitrite, and phosphate after three adsorption/ desorption cycles.	Cellulose nanofiber aerogel (CNF) crosslinked with carboxymethyl cellulose (CMC) and citric acid (CA).	[21]

Table 3. Cont.

5. Composite Adsorbents: Synergistic Approaches

In recent years, the development of composite adsorbents has emerged as a promising strategy to enhance the adsorption efficiency, selectivity, and regeneration capacity of biopolymer-based systems. Composite adsorbents combine biopolymers with materials such as graphene, metal oxides, and carbon nanotubes, leveraging the unique properties of each component to create synergistic effects. These composites address some of the limitations of pure biopolymer adsorbents, such as low surface area, limited adsorption capacity, and regenerations challenges. Furthermore, studies have highlighted the potential of pristine polysaccharides like cellulose, chitin, and chitosan in adsorption processes, showcasing their diverse adsorption capacities through rigorous laboratory tests that measure pollutant removal per unit weight of the adsorbent material [75].

5.1. Graphene-Based Composites

Graphene, known for its large surface area, excellent mechanical properties, and unique electronic characteristics, has been extensively studied for its adsorption potential. When combined with biopolymers like chitosan, alginate, or cellulose, graphene-based composites exhibit significantly enhanced adsorption capacities due to the increased number of active sites available for agrochemical interactions. For example, chitosan–graphene oxide composites have demonstrated high adsorption capacities for herbicides such as atrazine and glyphosate, as the interaction of the herbicide molecule and the composite is driven by hydrogen bonding, π - π stacking, and electrostatic interactions [76–78]. Additionally, the use of graphene not only increases the adsorption capacity but also enhances the mechanical strength and reusability of the adsorbent, making it suitable for multiple cycles of adsorption–desorption [79].

5.2. Carbon Nanotube Composites

Carbon nanotubes (CNTs) offer a high surface area and excellent chemical stability, making them ideal for use in composite adsorbents. When incorporated with biopolymers, CNT-based composites significantly improve the adsorption efficiency for both hydrophobic and hydrophilic agrochemicals. For example, cellulose–carbon nanotube composites have demonstrated high adsorption capacities for persistent organic pollutants like DDT and permethrin, where hydrophobic interactions between the agrochemicals and CNTs are maximized [60,80–82]. Moreover, the flexibility and strength of CNTs add to the durability of the composite, allowing it to be reused multiple times without significant loss in adsorption capacity. Studies on biosorbents such as banana peels also provide insight into cost-effective adsorption techniques, with Haq et al. reporting a maximum sorption capacity of 167 mg/g for metribuzin using banana peel-based adsorbents [83]. These findings indicate the potential for banana peels as a low-cost, effective adsorbent for pesticide removal.

5.3. Nanocomposites and Hybrid Materials

The development of nanocomposites and hybrid materials has further expanded the potential of biopolymer-based adsorbents. These materials combine nanoparticles, metalorganic frameworks (MOFs), and nanofibers with biopolymers to create adsorbents that exhibit enhanced selectivity and adsorption rates. For instance, chitosan–MOF composites have been studied for their ability to target specific agrochemicals through tailored pore sizes and surface functionality. These composites not only improve the adsorption capacity but also enhance the selectivity for agrochemicals like atrazine and malathion, making them ideal for complex water systems where multiple contaminants are present [84–86]. Furthermore, hybrid materials combining nanofibers with biopolymers have shown increased adsorption rates due to the large surface area provided by the nanofibers, allowing for more efficient interaction with agrochemical molecules [85–87]. Other innovations in biosorbents, such as the functionalization of cellulose materials with polyethyleneimine (PEI), have significantly improved the adsorption of organophosphorus pesticides due to the strong cationic characteristics of PEI [88,89].

Metal oxides, such as iron oxide (Fe ₃ O ₄), titanium dioxide (TiO ₂), and zinc oxide (ZnO),
are frequently integrated with biopolymers to form highly efficient composite adsorbents.
Metal oxide nanoparticles provide unique surface characteristics, such as high reactivity,
that complement the adsorption properties of biopolymers. For instance, chitosan-iron
oxide composites have been extensively studied for their ability to remove organophos-
phate pesticides such as malathion and parathion from water via electrostatic interactions
and surface complexation [90]. The magnetic properties of iron oxide also allow for easy
separation of the adsorbent from the water using an external magnetic field, simplifying
the recovery process. Similarly, Fe ₃ O ₄ nanoparticles grafted onto cellulosic materials have
demonstrated remarkable properties, including high specific area, biocompatibility, and
superparamagnetic nature, making them excellent candidates for long-term environmental
treatment, even after multiple cycles of use [91]. Additionally, cellulose nanocomposites,
particularly those incorporating graphene oxide, have shown enhanced adsorption capaci-
ties due to the synergy between cellulose and the high surface area and functional groups
of GO. These composites effectively remove various pesticides through interactions such as
hydrogen bonding and electrostatic forces [79].

Additionally, hybrid materials incorporating bioinspired and biomimetic technologies are gaining attention in agrochemical removal. For example, enzyme-immobilized biopolymers, where enzymes such as laccase are immobilized on cellulose or chitosan matrices, have shown promise in breaking down agrochemical residues through enzymatic reactions while simultaneously adsorbing the byproducts [92,93]. These enzyme-immobilized systems, along with MOF–biopolymer composites, offer enhanced selectivity and adsorption capacity, making them suitable for treating complex water systems with multiple contaminants [85,86].

Table 4 summarizes the key advantages and disadvantages for different composite adsorbents, each incorporating various fillers such as graphene, metal oxides, carbon nanotubes, and metal-organic frameworks.

Composite Adsorbent	Fillers	Advantages	Disadvantages	References
Graphene-based composites	Graphene	 high surface area enhanced adsorption capacity increased mechanical strength reusability 	 cost of graphene risk of aggregation without functionalization 	[60,76–79]
Metal oxide composites	Iron oxide (Fe ₃ 0 ₄) Titanium dioxide (TiO ₂) Zinc oxide (ZnO)	 high reactivity magnetic properties for easy separation enhanced adsorption through surface complexation long-term environmental treatment capability 	 limited reusability potential leaching of metal ions into water 	[80,90]
Carbon nanotube (CNT) composites	CNTs	 high surface area improved adsorption for hydrophobic agrochemicals like DDT and permethrin durability and mechanical strength reusability without significant capacity loss 	 high cost of production environmental concerns over CNT disposal 	[81,82]
Nanocomposites and hybrid materials	Metal-organic frameworks (MOFs), Nanofibers	 Enhanced selectivity and adsorption rates tailored pore sizes for specific agrochemical targeting increased adsorption efficiency with nanofibers versatile for complex water systems 	 complicated synthesis high cost of MOF materials 	[84–86]
Functionalized polymer composites	Polyethyleneimine (PEI), other functional groups	 strong cationic nature for enhanced adsorption of organophosphorus pesticides improved removal efficiency for agrochemicals 	 limited to specific types of agrochemicals functionalization can increase material cost 	[88,89]

Table 4. Advantages and disadvantages of composite adsorbents with various fillers.

6. Technological Advances and Innovations in Agrochemical Removal

In the quest to improve the efficiency and sustainability of agrochemical residue removal, significant technological advancements have been made in recent years. These innovations have focused on enhancing the adsorption capabilities of biopolymers and composite adsorbents, as well as integrating cutting-edge technologies such as nanotechnology, functionalization techniques, and 3D printing into the design of adsorbent materials. This section provides an overview of these advancements and their impact on agrochemical decontamination processes.

6.1. Nanotechnology in Adsorbent Development

Nanotechnology has revolutionized the field of water treatment by enabling the design of adsorbents with nanoscale precision. Nanomaterials, such as graphene oxide, carbon nanotubes, and metal oxide nanoparticles, are being increasingly incorporated into biopolymer-based adsorbents to create nanocomposites with enhanced surface area, selectivity, and adsorption capacity. The use of nanomaterials allows for the precise tailoring of adsorbent surfaces, optimizing them for specific agrochemical residues [94].

For instance, chitosan–graphene oxide nanocomposites have shown superior performance in the removal of herbicides like atrazine and glyphosate, as the large surface area of graphene oxide provides additional binding sites for the agrochemicals, while the chitosan matrix ensures stability and ease of recovery [77]. Additionally, the inclusion of magnetic nanoparticles, such as Fe₃O₄, in nanocomposites allows for easy separation of the adsorbent from water using an external magnetic field, simplifying the recovery process and making the technology more suitable for large-scale applications [80,91].

Nanotechnology has also enabled the creation of multi-functional adsorbents that not only adsorb agrochemicals but also degrade them through photocatalysis or other chemical reactions. For example, titanium dioxide (TiO₂) nanocomposites have been developed for both adsorption and photocatalytic degradation of persistent organic pollutants, providing a dual-function system for agrochemical removal [11,90].

6.2. Advanced Functionalization Techniques

The development of new functionalization techniques has significantly improved the performance of biopolymer-based adsorbents. Common functional groups used in agrochemical adsorption include amine, carboxyl, hydroxyl, and thiol groups. For instance, the amine-functionalization of biopolymers like chitosan has proven effective in increasing adsorption capacity for negatively charged agrochemicals, such as glyphosate and atrazine, by promoting electrostatic interactions and hydrogen bonding [61,95]. Similarly, carboxylate biopolymers, such as modified alginate, have demonstrated enhanced adsorption of positively charged agrochemical residues like organophosphates due to their strong ionic interactions with carboxyl groups [96–98].

One innovative approach in functionalization is the use of solvent-free green chemistry methods for grafting functional groups onto biopolymers. For example, Tursi et al. employed a green approach to graft 4,4'-diphenylmethane diisocyanate (MDI) onto cellulose fibers, creating an adsorbent with superior adsorption properties for organic pollutants such as gasoline and bisphenol A [95]. These advancements in functionalization not only improve the adsorption performance of biopolymers but also contribute to more environmentally friendly production processes.

6.3. Three-Dimensionally Printing Adsorbents

The advent of 3D printing technology has opened new possibilities for the design and production of highly efficient adsorbents with customizable properties. Three-dimensionally printed biopolymer composites allow for precise control over the structure, porosity, and surface area of the adsorbent material, enabling the creation of adsorbents tailored for specific agrochemical residues. This level of customization ensures optimal performance in terms of adsorption capacity, regeneration potential, and mechanical stability. For example, researchers have developed 3D-printed chitosan-based adsorbents with enhanced porosity, which allows for faster diffusion of agrochemical molecules into the adsorbent structure and increases the overall adsorption rate [99,100]. Furthermore, the ability to precisely design the adsorbent geometry enables the production of materials that can withstand multiple adsorption–desorption cycles without degradation, making them suitable for long-term use in water treatment applications.

6.4. Machine Learning and Computational Chemistry in Adsorbent Design

A significant recent innovation is the application of machine learning and computational chemistry in the design of adsorbent materials. These technologies allow researchers to predict the performance of adsorbents by simulating interactions between agrochemicals and the adsorbent surface, thus speeding up the development process and optimizing the design of new materials [101–103].

Machine learning models can analyze large datasets to identify the most effective adsorbent materials for specific agrochemical residues. For instance, these models can predict the optimal surface functionalization required for removing certain pesticides based on their molecular structure and physicochemical properties. Computational chemistry tools, such as density functional theory (DFT), are also being used to simulate the adsorption process at the molecular level, providing insights into the binding mechanisms between adsorbents and agrochemicals. These innovations not only enhance our understanding of adsorption processes but also accelerate the development of more efficient and targeted adsorbents.

7. Challenges and Opportunities for Future Development

Despite the significant progress made in developing biopolymer and composite adsorbents for agrochemical residue removal, several challenges remain. Addressing these issues presents both obstacles and opportunities for future advancements in the field. This section outlines the key challenges related to scalability, regeneration, real-world application, and cost, while also highlighting opportunities for innovation and interdisciplinary collaboration.

7.1. Scalability and Industrial Application

One of the primary challenges in the use of polysaccharides or biopolymer-based adsorbents is scalability. While many of the adsorbents developed in laboratory settings have demonstrated high adsorption capacities and efficiencies, scaling these materials for industrial use remains a major hurdle. For example, nanocomposites and hybrid materials, although promising, require sophisticated synthesis processes that can be difficult and costly to scale up for large-scale water treatment plants [104–106]. Moreover, achieving the same level of control over material properties (e.g., porosity, surface area, functional group distribution) at industrial scale remains a challenge.

To address scalability issues, future research should focus on developing simple and more cost-effective production methods of polysaccharides or biopolymer-based adsorbents. The use of abundant and renewable materials, such as agricultural waste or marine biomass, could provide a low-cost and sustainable source of biopolymers for large-scale applications [107–109]. Additionally, modular designs for adsorption units using 3D printing could offer a practical solution for scaling up production while maintaining control over material properties [100].

7.2. Regeneration and Reusability

Another critical challenge is the regeneration and reusability of biopolymer-based adsorbents. Over time, adsorption sites become saturated, leading to decreased efficiency, and requiring frequent replacement of the adsorbent material. Regeneration processes, such as chemical or thermal methods, are often costly, energy-intensive, and may lead to degradation of the biopolymer matrix, reducing the lifespan of the adsorbent [60,110].

Future developments could focus on developing low-energy regeneration techniques that maintain the structural integrity and adsorption capacity of the material over multiple cycles. For instance, magnetic nanocomposites, which allow for easy separation of the adsorbent form water, present an opportunity for easier recovery and reusability. Additionally, integrating photocatalytic materials, such as TiO_2 , into biopolymer composites could enable in situ degradation of adsorbed agrochemicals, reducing the need for external regeneration processes.

7.3. Real-World Applications and Environmental Conditions

Biopolymer adsorbents have been shown to be highly effective in controlled laboratory environments, but real-world water systems present a variety of additional challenges. Water contaminated with agrochemical residues often contains a complex mixture of pollutants, including organic matter, heavy metals, and microorganisms, which can interfere with the adsorption process. Additionally, environmental factors such as pH, temperature, ionic strength, and the presence of competing ions can significantly affect the adsorption efficiency of biopolymer-based materials [75].

To bridge the gap between laboratory performance and real-world application, there is a need for more comprehensive field studies that evaluate the performance of these materials under realistic environmental conditions. Moreover, the development of multi-functional adsorbents capable of simultaneously removing different types of pollutants (e.g., agrochemicals, heavy metals, and organic matter) represents a promising direction for future research [32,52,111]. This would involve creating hybrid materials that combine multiple adsorption mechanisms, such as electrostatic interactions, hydrophobic interactions, and surface complexation, within a single material.

7.4. Cost and Economic Viability

Cost remains a significant barrier to the widespread adoption of biopolymer-based adsorbents in agrochemical removal. Many of the advanced synthesis and functionalization techniques used to create high-performance adsorbents are expensive, limiting their commercial viability. Furthermore, some biopolymers, particularly those derived from microbial sources [64] or nanomaterials [57], may require costly extraction or production processes.

To overcome this challenge, future research should focus on economical and sustainable production methods that can make biopolymer adsorbents more cost-competitive with traditional water treatment technologies, such as activated carbon. Utilizing waste-derived biopolymers from agriculture, forestry, and food processing industries can provide low-cost feedstock for adsorbent production. Additionally, optimizing the use of natural enzymes and employing green chemistry principles in the synthesis and modification of biopolymers could reduce production costs and environmental impact [60,92].

7.5. Interdisciplinary Collaboration and Innovation

The future of agrochemical residue removal will depend on interdisciplinary collaborations across fields such as materials science, environmental engineering, chemistry, and biology. This will be especially important for the development of multi-functional adsorbents and next-generation composites that combine materials such as biopolymers, nanoparticles, and metal-organic frameworks (MOFs) for enhanced performance [85,112]

Additionally, integrating machine learning and computational modeling into the adsorbent design process represents a significant opportunity for accelerating the discovery of new materials. Machine learning algorithms can analyze large datasets to identify patterns and predict which combinations of materials and functional groups will yield the highest adsorption efficiency for specific agrochemical contaminants. Computational modeling can also simulate how adsorbents will perform under various environmental conditions, helping to optimize material properties for real-world applications [101–103].

While significant progress has been made in the development of biopolymer and composite adsorbents for agrochemical removal, several challenges remain. Scalability, regeneration, real-world performance, and cost are key issues that need to be addressed to enable widespread adoption of these technologies. However, these challenges also

present opportunities for innovation, particularly in the areas of sustainable production, multi-functional adsorbents, and interdisciplinary collaboration. By focusing on these areas, future research can pave the way for more efficient, cost-effective, and environmentally sustainable solutions for agrochemical residue removal.

8. Conclusions

In this review, we explored the significant advancements in the field of agrochemical residue removal using biopolymer and composite adsorbents. As agrochemical contamination continues to pose risks to environmental and human health, the development of effective and sustainable adsorbents has become a pressing need. Biopolymers such as chitosan, alginate, and cellulose have demonstrated high potential due to their biodegradability, biocompatibility, and surface modifiability, making them ideal candidates for environmental remediation. Moreover, innovations in functionalization techniques, nanotechnology, and composite formation have significantly enhanced their adsorption capacities and selectivity for a range of agrochemicals.

The integration of cutting-edge technologies, such as 3D printing and machine learning, has opened new avenues for optimizing the design of adsorbents, enabling the development of materials that are both highly efficient and tailored for specific contaminants. Furthermore, interdisciplinary approaches offer promising directions for the next generation of adsorption materials.

Despite these advancements, challenges remain, particularly in scaling up production, enhancing regeneration and reusability, and ensuring cost-effective implementation in realworld water treatment systems. Addressing these challenges will require ongoing research and innovation, particularly in the development of sustainable and economically viable production methods and the application of adsorbents under diverse environmental conditions.

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