

Unlocking Heavy Metal Remediation Potential: A Review of Cellulose–Silica Composites

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Abstract: This comprehensive review explores recent advancements in heavy metal remediation techniques, focusing on the utilization of cellulose–silica composites and tailored surface modification techniques. We examine the synthesis strategies and properties of cellulose–silica adsorbents, highlighting their enhanced adsorption capacities and structural robustness for removing heavy metal pollutants from aqueous environments. The review investigates various surface modification approaches, including thiol functionalization, amino acid grafting, and silane coupling agents, for optimizing the surface chemistry and morphology of cellulose–silica composites. Mechanistic insights into the adsorption processes and kinetics of modified adsorbents are discussed, along with considerations for optimizing adsorption performance under different environmental conditions. This review provides valuable perspectives on the development of effective adsorbent materials for sustainable heavy metal remediation applications.

Keywords: heavy metal remediation; cellulose–silica composites; surface modification; adsorption kinetics; environmental sustainability; surface chemistry

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1. Introduction

The term “heavy metals” encompasses a diverse group of elements with varied chemical compositions and significant biological roles. According to Ismanto, et al. [1], heavy metals are defined as metallic compounds with a relative density higher than water. Heavy metal ions often manifest as insoluble, poisonous, biohazardous, and persistent pollutants. These contaminants pose serious threats to human health, animal welfare, and ecosystem integrity, necessitating urgent remediation efforts. Moreover, the unchecked discharge of heavy metal ions into water bodies, stemming from industrial activities, mining operations, and agricultural practices, has led to widespread environmental degradation [2,3]. Soil and plants, in particular, accumulate heavy metals, compromising agricultural productivity and food safety [4,5]. Furthermore, heavy metal contamination in water sources, including sewage and stormwater, originates from diverse sources such as industrial runoff, vehicular emissions, and atmospheric deposition [6]. To mitigate the adverse impacts of heavy metal pollution, effective remediation strategies are urgently needed. There are many techniques used today to treat wastewater. A few common techniques for cleaning wastewater include precipitation, neutralization, membrane filtration, ion exchange, flotation, and adsorption. Additionally, technologies for treatment have been developed that integrate physical and chemical processes, such as the electrochemical process [7]. These are further elaborated below:

1.1. Chemical Precipitation

Chemical precipitation is a popular and cost-effective technique for removing heavy metals from wastewater due to its simplicity. This method involves adding chemicals to the wastewater to produce an insoluble precipitate. Variations such as heavy metal chelating precipitation, hydroxide precipitation, and sulfide precipitation are commonly used. Lime and limestone are frequently employed as precipitant agents due to their convenience and efficiency in treating inorganic effluents. However, challenges such as excessive chemical usage, sludge disposal, and overproduction of sludge need to be addressed [8].

1.2. Ion Exchange

Ion exchange relies on the ability of wastewater to exchange cations for metals. Various materials, both natural (such as alumina, carbon, and silicates) and man-made (like zeolites and resins), are used in this process. Zeolites are particularly common in ion exchange due to their effectiveness in aqueous media. However, ion exchange lacks selectivity and is highly sensitive to pH variations [9].

1.3. Membrane Process

Membrane filtration techniques, including ultrafiltration [10], nanofiltration [11], reverse osmosis [12], and electrodialysis [13], are used to filter out heavy metals from aqueous solutions. Each variation targets specific contaminants, such as oils, suspended particles, and heavy metals. These processes are effective but may require high-energy inputs and maintenance costs [14].

1.4. Flotation

Large-scale flotation is a method for removing toxic metal ions from wastewater. Additional flotation techniques include precipitate flotation, dissolved air flotation (DAF), and ion flotation. DAF is used more frequently for removing heavy metals from aqueous solutions as compared to other flotation techniques [15].

1.5. Coagulation Process

The coagulation process is used to produce colloids. Coagulate substances like aluminum, ferrous sulfate, and ferric chloride are used to neutralize contaminants in wastewater or water. Many researchers have shown that it is an important technique. Polyaluminum chloride (PAC) and ferric chloride solution are used as coagulants to remove heavy metals [16].

1.6. Electrochemical Process

In electrochemical processes, metal is removed from an electrolyte solution while being influenced by an external direct current. The coagulation process weakens colloidal particles and triggers the sedimentation process by adding a coagulant. An increase in the rate of coagulation requires the flocculation process, which quickens the conversion of weak particles into bulky flocs [17].

1.7. Adsorption Process

Adsorption is a reasonably affordable, useful, and simple technology. It has excellent metal removal efficiency and is utilized as a quick method for treating different types of wastewaters. According to reports, adsorption is the most popular technique for removing various contaminants, particularly metal ions [18,19]. This is likely due to adsorption's high efficacy, ease of use, lack of waste production, and low cost. This technique is gaining acceptance because to the possibility of recovering the metal and reusing the adsorbent [20]. Adsorption is a cost-effective method for efficiently removing heavy metals from wastewater by binding metal ions to solid surfaces. While activated

carbon (AC) remains a popular adsorbent due to its high surface area and microporous structure [21], there is increasing interest in low-cost bio-adsorbents [22]. Low-cost bio-adsorbents, including agricultural waste materials and bio-adsorbents like microbial biomass, have gained attention due to their affordability and effectiveness in metal removal [23,24]. These bio-adsorbents, derived from agricultural waste materials, industrial by-products, and natural waste materials, offer affordability and effectiveness in metal removal but typically exhibit low efficiency [25]. This is because their density may limit water permeability and the efficiency of heavy metal removal.

Therefore, chemical modification of cellulose with silica enhances adsorption and desorption performance due to silica's porous structure, high surface area, and surface chemistry.

1.8. Cellulose–Silica Composites

Among the various adsorption techniques, cellulose and silica-based materials have emerged as promising adsorbents for heavy metal removal [26]. Cellulose, a polysaccharide found in plant cell walls, offers excellent sorption capacity and biocompatibility. It comprises glucose units that are joined α -(1,4) together to make up a long linear polysaccharide with a molecular formula of $(C_5H_8O_4)_m$ (Figure 1). Materials with a high cellulose content include plant fibers, woods, stalks, stems, shells, straw, grasses, etc. [27]. Cellulose is a substance of interest for a variety of applications because of its amazing physicochemical characteristics, which include colorlessness, a lack of odor or taste, great mechanical strength, superior sorption capacity, hydrophilicity, and biocompatibility. Because of its low density and reactive surface with OH side groups, cellulose is able to graft chemical species onto its surface. Silica, on the other hand, offers chemical stability, surface reactivity, and the ability to modify surface properties.

When coupled with silica and different functional groups, these composites exhibit enhanced adsorption capacity and selectivity for heavy metals. While the understanding of heavy metal contaminants and their environmental implications has been extensively studied and reviewed in the scientific literature, previous reviews have often overlooked the potential synergistic effects of coupling cellulose and silica with different functional groups to enhance adsorption capacity and selectivity. While previous reviews have touched upon individual aspects of heavy metal remediation potential, there are notable gaps in the overall understanding of the field. For instance, while some reviews have examined the sources and environmental impacts of heavy metals [2,3], others have delved into the mechanisms of heavy metal adsorption by various materials [28]. Additionally, many reviews have failed to systematically compare the adsorption capacities and efficiency of different adsorbents, hindering the identification of optimal materials for real-world applications. Despite these efforts, there remains a need for a comprehensive review that synthesizes the latest advancements in heavy metal adsorption using cellulose and silica coupling agents, addressing the limitations of previous reviews and offering new insights into the field.

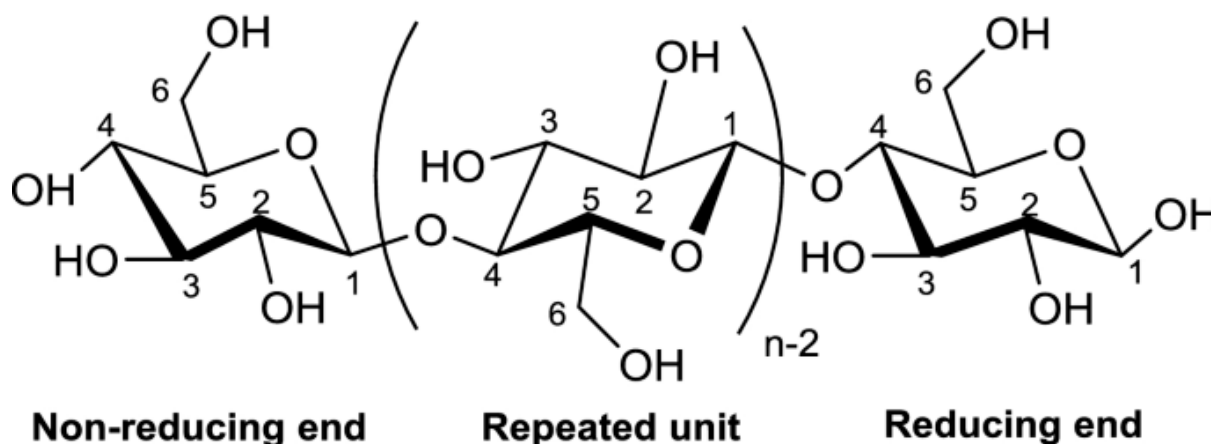


Figure 1. The structure of cellulose (Source [27]).

1.9. Purpose of the Review

This paper comprehensively reviews recent advancements in the field of heavy metal adsorption using cellulose and silica coupling agents. By synthesizing findings from a wide range of studies, we offer new insights into the potential applications of these materials for environmental remediation. Moreover, we systematically compare the adsorption capacities and efficiency of different cellulose and silica-based adsorbents, enabling researchers to identify the most promising materials for further investigation. Overall, our review aims to bridge the gap between theory and practice, offering practical guidance for researchers and policymakers working in the field of heavy metal remediation. The objectives of this review, therefore, include:

To review recent advancements in heavy metal adsorption using cellulose and silica coupling agents.

To compare the adsorption capacities and efficiency of different cellulose and silica-based adsorbents reported in recent literature.

To identify key research gaps and propose directions for future research in the field of heavy metal remediation.

2. Materials and Methods

The information in this study was sourced from published books and literature downloaded from websites and online journal hubs, including Google Scholar, PubMed, Science Direct, Sci Finder, and Scopus. We used appropriate keywords such as “heavy metal adsorption”, “cellulose”, “silica”, “coupling agents”, “removal efficiency”, and “adsorbent capacity” to narrow down the search results. We included studies published in the English language within the last five years to ensure relevance and currency of information. We included articles that focus on the adsorption of heavy metals (e.g., Pb, Cd, Cu, Zn) using cellulose and silica-based adsorbents. We extracted relevant data from selected articles, including the type of adsorbent (cellulose, silica, or their coupling agents), heavy metal ions studied, adsorption capacity (in mg/g or percentage removal), experimental conditions (pH, temperature, contact time), and key findings into EndNote software (version 21). Thereafter, we analyzed the extracted data to identify trends, patterns, and discrepancies in the adsorption capacities of cellulose, silica, and their coupling agents for different heavy metal ions.

3. Literature Review

This section provides a concise and precise description of the relevant literature on recent advancements in heavy metal remediation techniques, focusing on the utilization of cellulose–silica composites and tailored surface modification techniques.

3.1. Natural Fiber

The effects of toxic heavy metals on the environment and human health are big problems. The continued decrease in water quality and the degree of contamination have been noted by scientists, who are concerned about them. Many methods for removing heavy metals from water and waste have recently undergone extensive research. Because non-renewable resources are used, and costs are high, heavy metal removal and remediation are provided at a high price by current technology. A variety of materials have frequently been employed as adsorbents, and many researchers are now utilizing adsorption techniques for this purpose. Due to its many advantages, such as stability, usability, cheap cost, simplicity of use, and performance, adsorption has proven to be a viable method for purification [29].

Adsorption technology employs a range of inexpensive adsorbent materials, including metal oxides, biosorbents, clays, activated carbons, and zeolites, to drastically lower the concentrations of heavy metal ions. Because it depends on so many variables, the process of metal adsorption onto adsorbent material—especially on agricultural wastes—is extremely intricate. The phases of complexation, chemisorption, and adsorption–complexation on pores and surfaces, microprecipitation, and ion exchange are all included in this process. Metal ions from water are attached to certain functional groups, including amido, hydroxy, carboxyl, and sulphhydryl, when biological materials are employed in the adsorption process [29,30].

Due to their low density, high strength/weight ratio, and reduction, natural fibers are vital light-weight composite and reinforcement materials. The microstructure and chemical composition of fibers, with the fiber cross-sectional area having the largest degree of change, affect the mechanical properties of fibers. Natural fibers have hydrophilic properties because they include hemicellulose, which makes them easily absorb water. As a result, they are less suited to a matrix with hydrophobic characteristics [30]. Higher cellulose concentration and crystallinity frequently result in better fiber strength, whereas lignin has the reverse effect. Additionally, variations in fiber anatomical qualities between and within species have an impact on the density and mechanical characteristics of fibers.

Natural-fiber-reinforced composites have gained popularity recently because of their low-weight, non-abrasive, flammable, non-toxic, affordable, and biodegradable qualities. Of the various natural fibers, the fibers from flax, bamboo, sisal, hemp, ramie, jute, and wood are especially important [30]. The advancement and increase in industrial alternatives can be attributed to the study of replacing synthetic fiber in fiber-reinforced composites with natural fibers. Natural fibers have the benefits of being inexpensive, biodegradable, and low in density. However, due to their relatively high moisture sorption and low matrix compatibility, natural fibers in composites are primarily disadvantageous. As a result, chemical treatments are taken into consideration to change the fiber surface properties [31].

Lignocellulosic natural fibers, such as kenaf, sisal, coir, jute, ramie, and pineapple leaf (PALF), have the potential to replace glass or other conventional reinforcing components in composites. Many qualities of these fibers make them a desirable substitute for conventional materials. They have high particular properties like modulus and are rigid, impact-resistant, and flexible. They are also widely accessible, renewable, and biodegradable. Additional desirable characteristics include affordability, low density, decreased equipment abrasion, reduced skin and respiratory irritation, vibration damping, and enhanced energy recovery [32].

3.1.1. Natural Fiber and Heavy Metal Adsorption Capacity

The adsorption of heavy metals from wastewater has been performed using a variety of natural plant fibers. Natural plant fibers are composed primarily of cellulose, a few extractives, and amorphous polymers (hemicelluloses and lignin). Agricultural waste

(cellulosic and non-wood) from crops generates a lot of waste after processing. Waste frequently contains a lot of cellulose. As a result, heavy metal adsorbents made from agricultural waste are increasingly being used in research and development. Agricultural by-products are frequently utilized for adsorption, either modified or unmodified. The adsorption of heavy metal ions from contaminated water has been successfully applied using banana, orange, and lemon peels, rice husk, rice straw, peanut shell, bran, and sugar cane bagasse [33–35].

Because of hazardous heavy metals, environmental pollution is a major issue in many densely inhabited areas of the world. The health of people is negatively impacted by the household and industrial pollutants that lead to various environmental issues. Before disposing of aqueous waste in the environment, some metals from industrial discharges must be removed. In order to evaluate the effectiveness of uptakes, a monitor was used to compare the adsorption of zinc (Zn^{2+}) and lead (Pb^{2+}) ions on banana fiber. The fiber in the banana stem was extracted mechanically and then treated with an alkali (NaOH) to make it softer. Parallel-laid webs were used to create needle-punched fabrics. When heavy-phase adsorption was initially studied in its foundational forms, the findings demonstrated that the concentration of heavy metals, the amount of adsorbent utilized, and pH levels all had a substantial impact on the adsorption capacity of banana fiber. Banana fiber removed 98% of zinc and 95.5% of lead with remarkable efficiency in batch trials. The findings indicated that the ideal pH range was found to be between 6.5 and 7.0, and that the equilibrium time for adsorption was 60 min [36].

The optimization of several variables has been a major problem in wastewater treatment plants to reach the appropriate limits on effluent discharge. Banana peels were used in the optimization study Afolabi et al. conducted in 2021 to assess the removal of lead (II) from wastewater. Using batch adsorption tests, the central composite design was used to investigate the interactive effects of the operating parameters (initial concentration, solution pH, adsorbent dosage, and particle size). The response surface design yielded the greatest results, with a removal percentage of 98.146%, at an initial concentration of 100 mg/L, pH of 5, adsorbent dosage of 0.55 g, and particle size of 75 m.

In a comparable investigation, Cheah et al. [37] discovered that heat and chemical preparation of banana peels, aside from acid pretreatment, improved metal removal efficacy. The study found that pretreatment can improve the removal of metal by banana peels; chemical pretreatment was shown to be more successful than heat treatment, and detergent was found to be a practical and useful pretreatment agent. Bhagat, et al. [38] examined the effectiveness of banana peel strip (BP) in eliminating copper and zinc ions from water. A cheap source of biomass generated from agricultural waste, BP demonstrated good adsorption capabilities when absorbing Cu^{2+} and Zn^{2+} from wastewater effluent.

One study investigated the capacity of banana fiber needle-felted fabric to absorb heavy metal ions (Pb^{2+} and Zn^{2+}) across various conditions, including pH, contact duration, and concentration. Results revealed that the uptake of Pb^{2+} and Zn^{2+} varied depending on the initial solution's pH, the amount of adsorbent used, contact duration, and concentration. Higher pH, concentration, and contact duration correlated with increased absorption of Pb^{2+} and Zn^{2+} ions (measured in mg/g). Notably, lead and zinc exhibited significant absorption at pH 7 irrespective of time or concentration, while deviations from this pH level resulted in lower absorption rates, attributed to the use of chemicals (NaOH , HCl) to alter the solution's pH. Batch tests demonstrated that banana fiber effectively removed 95.5% of lead and 98% of zinc.

Heavy metal ion contamination of fresh water sources represents a serious risk to the safety of drinking water. Therefore, it is essential to treat water to remove specific contaminants, such as copper ions. Adsorbents or continuous membrane/filter procedures are frequently used to do this. For example, alternative combinations of these processes that could be applied as a treatment in this case include adsorption or ion-exchange membranes/filters. As a result, environmentally friendly alternatives to traditional

adsorption membrane/filter materials include those made from renewable resources. For instance, filters made of natural fibers and nanocellulose were coated with (2,2,6,6-Tetramethylpiperidin-1-yl)oxy (TEMPO) and made from flax and agave fibers as well as other kinds of CNF. Although it has been demonstrated that anionic TEMPO-oxidized cellulose nanofibrils (TCNF) have a considerable affinity for heavy metal ions, their usage in nanopaper membranes is limited by their low permeance. Additionally, pure nanopapers have not yet been employed to effectively and efficiently adsorb metal ions [39]. (See Figure 2).

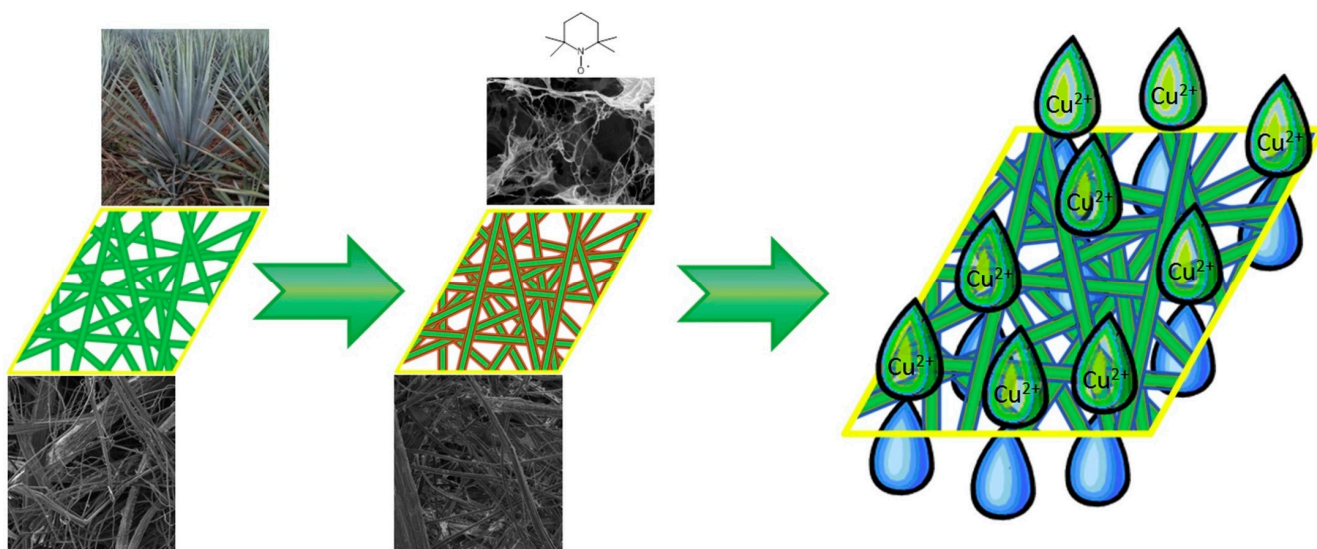


Figure 2. Natural fibre–nanocellulose composite filters for the removal of heavy metal ions from water (Source [39]).

Pure nanopapers have yet to be used successfully to adsorb metal ions with great permeance and efficiency. The permeance and copper adsorption capacity of these filters were used to evaluate how well they performed. This novel kind of filter made from industrial crop residue was demonstrated to have extremely high permeances, which allowed it to adsorb large amounts of Cu^{2+} ions during a continuous filtration process. For the active adsorption agent TEMPO-CNF, this translates to an adsorption capacity of more than 60 mg/g.

Due to the presence of hydroxyl functional groups, cellulosic biomaterials have strong adsorption potential. Banana fibers and other lignocellulosic fibers are made of cellulose, hemicellulose, lignin, pectin, wax, and water-soluble components. This fiber is readily available and easy to produce, which is an appealing quality that makes it an appropriate substitute for synthetic fibers that might be dangerous [40]. Sheng, et al. [41] modified banana pseudostem fiber using cellulose xanthogenation and steam explosion techniques to improve the capacity of the fiber to absorb heavy metal ions Pb^{2+} and Cd^{2+} . Steam explosion banana fiber cellulose xanthogenate s (SEBF-CX) adsorption kinetics fit in with the pseudo-second-order model. Pb^{2+} and Cd^{2+} adsorption in the pseudo-second-order model, however, were 99.0099 mg/g and 67.3401 mg/g, respectively. Compared to raw banana fiber (RBF), the metal ion adsorption capacities of SEBF-CX and SEBF were higher. The three fibers tested, among them SEBF-CX, were the best and might be employed as an effective absorbent to remove heavy metal ions from contaminated water.

Furthermore, Selambakkannu et al. [42] created a bio-adsorbent derived from banana trunk fibers, modified synthetically for potential application in heavy metal adsorption from wastewater. (See Figure 3). Initially, the fiber underwent grafting with a glycidyl methacrylate (GMA) polymer via electron beam irradiation. Subsequently, the GMA-grafted fiber was functionalized with an imidazole (IMI) group through an epoxide ring-opening process, yielding an amine density of 2.00 mmol/g.

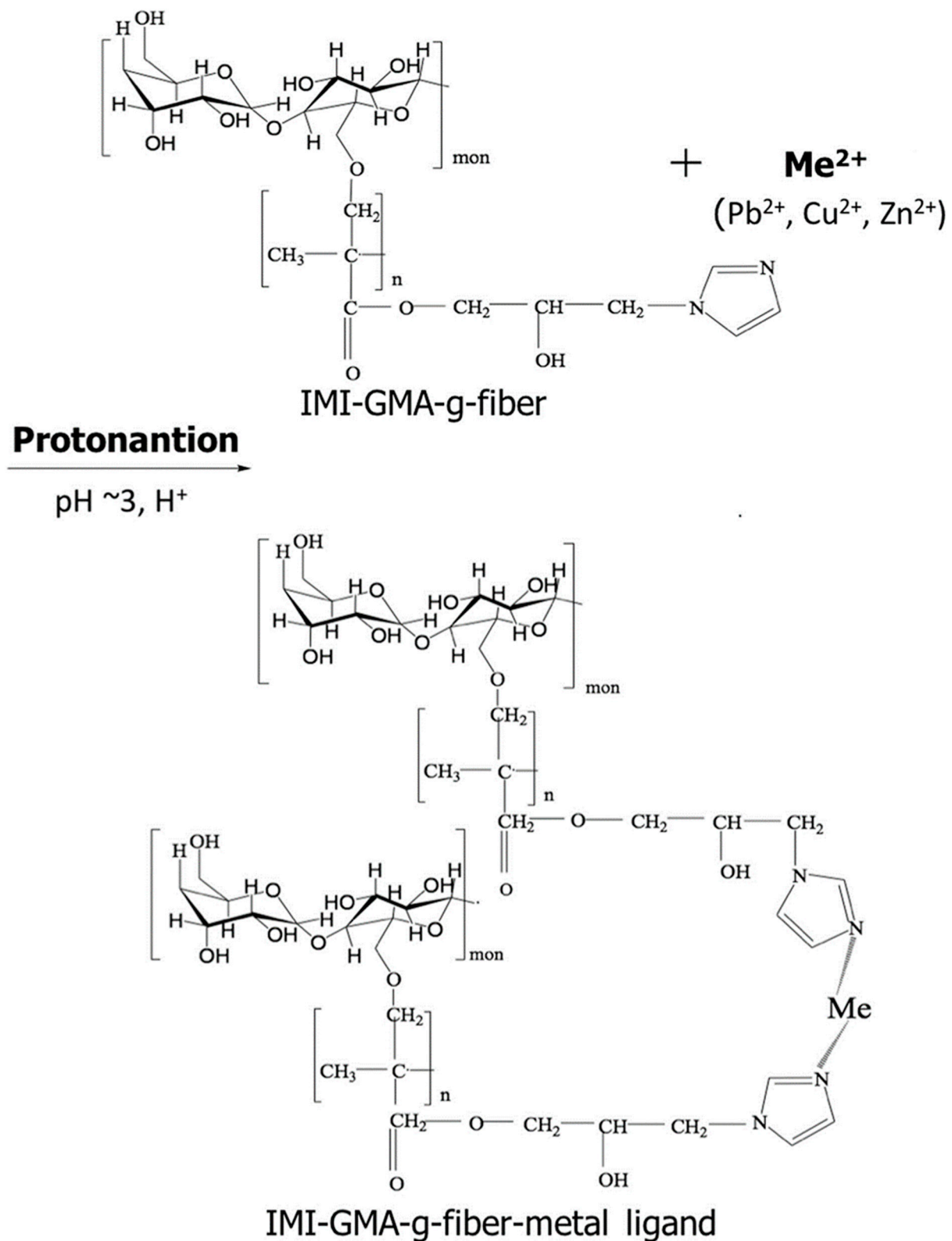


Figure 3. Metal ion adsorption mechanism by IMI-functionalized GMA-grafted banana fiber. (Source [42]).

The effective removal of metal ions from the aqueous solutions was carried out by the IMI functional group. This comprehensive kinetic and mechanistic study employs IMI-functionalized GMA-grafted banana fiber to remove metal ions (Cu²⁺, Pb²⁺, and Zn²⁺) via adsorptive removal. The saturation of the adsorbent, however, caused the removal %

to decline as the initial metal ion concentration rose. The adsorption capacities for the metal ions Cu^{2+} , Pb^{2+} , and Zn^{2+} were 71.6 mg/g, 84.2 mg/g, and 60.1 mg/g, respectively, using IMI-GMA-grafted fiber. On real sewage water that had been collected from a nearby household area, IMI-functionalized GMA-grafted fibers were tested as a metal ion adsorbent. Within one hour of contact time, a 100% removal of the target metal ions was accomplished. This test demonstrated that biosorbent made from fodder crops, in this case the banana trunk, may be adapted and used as a cost-efficient treatment for threatening environmental issues.

Polypropylene is also used because of its importance in producing strong composite materials for a variety of applications. The chitosan biopolymer is composed of a number of amino and hydroxyl groups and efficiently removes Cd ions from wastewater. For the adsorptive removal of cadmium (Cd) ions from wastewater, Alaswad, et al. [43] prepared polypropylene (PP)/sisal fiber, (SF)/banana fiber (BF), and chitosan-based hybrid (chitosan (CS)/SF)/BF) composite materials. (See Figure 4).

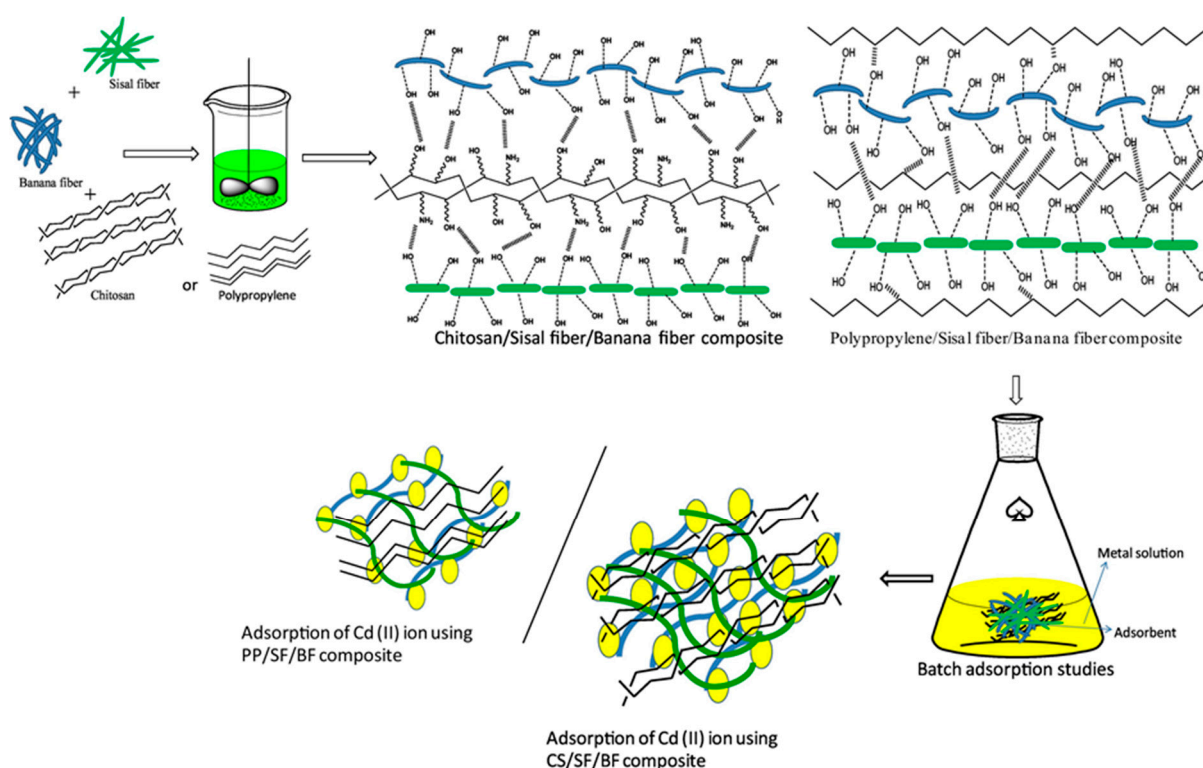


Figure 4. Schematic representation for the preparation of ternary chitosan/sisal fiber(SF)/banana fiber (BF) composite, polypropylene (PP)/SF/BF fiber composite (Source [43]).

The developed ternary hybrid composites were characterized, and the sample with the best amorphous/less crystalline nature was chosen for the adsorption tests. For PP/SF/BF composite and bio (CS/SF/BF) composite, the C_{max} value for the Cd (II) ion was determined to be 304 mg/g and 419 mg/g, respectively. Pseudo-first-order kinetics, pseudo-second-order kinetics, and intraparticle diffusion studies were used to analyze the kinetic adsorption data. For pseudo-second-order kinetics, PP/SF/BF and CS/SF/BF fiber composites both exhibited very high R^2 values. As a result, the biocomposite developed from chitosan, sisal, and banana fibers showed the greatest ability to adsorb and remove Cd (II) ions.

In the current work, the removal of lead ions from solid forms (as strips) by adsorption on green cellulosic fiber/polyacrylamide (GCFP) was investigated. Solid strips were developed in place of hydrogel to carry out the adsorption process without losing any water. The investigations included a number of operating parameters, including contact time, initial Pb concentration, adsorbent dosage, and pH value. The findings of the

kinetic investigation demonstrated that for the adsorption of Pb ions, the pseudo-second-order kinetic model offered improved correlation. The results showed that GCFP films are highly effective at removing lead ions from water. At pH = 7, an adsorbent dosage of 0.4 g, an initial Pb concentration of 50 ppm, and a contact time of 60 min, GCFP removed 98% (about 128 mg/g) of the Pb. These findings supported the GCFP film's strong attraction to Pb, which caused the metal to adsorb from the solution and fill the pores and active surface areas of the film [44].

3.1.2. Cellulose and Heavy Metal Adsorption Capacity

Numerous sources, including plants, animals, aquatic life, and microorganisms, can yield cellulose. Wood pulp is one of the most widely used sources of cellulose [45]. The ecosphere's most readily available and renewable source of organic polymers is cellulose [46]. An organic polymer called cellulose holds the anhydroglucose units of a long straight-chain molecule together. The α -(1,4)-glycosidic connections bind these anhydroglucose units together [45,47]. The abundance of OH groups in the cellulose structure allows for a number of processes to take place that can change the surface charge. This suggests that cellulose performance in various applications will be enhanced.

Cellulose has been derived from a variety of naturally occurring substances, including bacteria and plants, that are typically receptive and biodegradable. The fact that cellulose can be extracted from every portion of a fruit indicates that the fruit truly contains some cellulose and is therefore safe to eat. A new bacterial-cellulose composite has also been shown to be effective at adsorbing heavy metals like Pb^{2+} , Cu^{2+} , Ni^{2+} , and Cr(VI) . Su, et al. [48] developed a poly(hexamethylenediamine-tannic acid)-bacterial cellulose (HTA-BC) composite using abundant, inexpensive, and nontoxic natural material in a simple one-step technique for the decontamination of highly poisonous Cr(VI) . (See Figure 5). The as-synthesized HTA-BC had exhibited great capacity (534.8 mg/g) and good selectivity for Cr(VI) scavenging. It was functionalized with rich amino and phenolic hydroxyl groups.

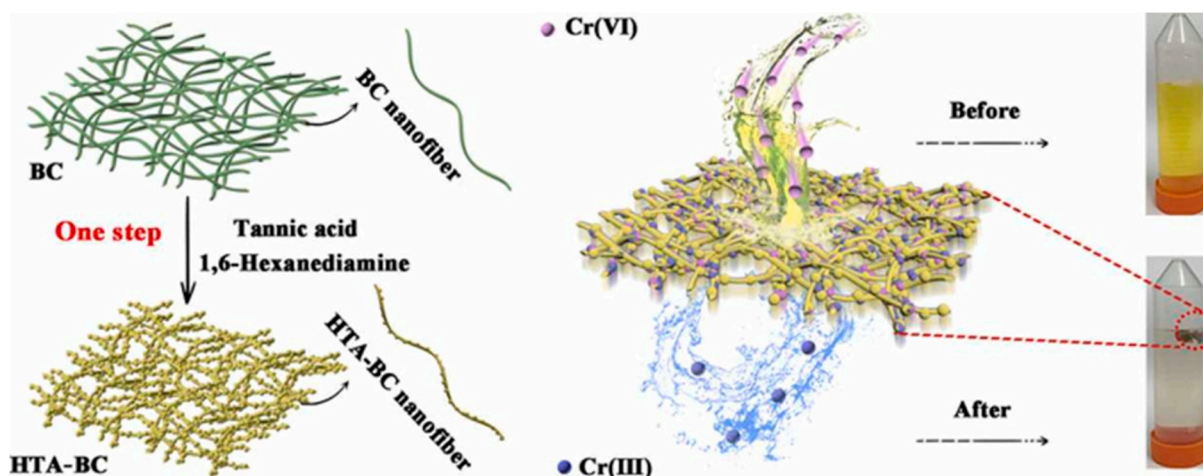


Figure 5. Schematic illustration of the possible polymerization mechanism of the HTA and the formation of HTA-BC (Source [48]).

The HTA-BC composite, as it developed, had a strong capacity for adsorption and great selectivity for the removal of Cr(VI) . The pseudo-second-order kinetic model had higher regression coefficients ($R^2 > 0.987$) for the adsorption kinetic parameters of Cr(VI) by HTA-BC. The findings also showed that HTA-BC's adsorption behavior toward Cr(VI) fitted in with the Langmuir model. The HTA-BC composite could effectively lower the content of the spiked Cr(VI) below the allowable levels for drinking water by treating real water samples.

The literature indicates that cellulose is a novel class of adsorbent substance that has demonstrated the ability to successfully extract heavy metals from aqueous solutions, the most well-known method of which is via adsorption membranes [49,50]. These nanopapers, however, are too dense to permit high water permeability, making the materials ineffective for removing heavy metals [39]. Therefore, modifying cellulose may greatly improve its capacity for adsorption and encourage adsorption processes such ion exchange, complexation, and electrostatic interaction. Very high adsorption capabilities have been obtained by functionalizing cellulose with amine groups, thiol groups, and other substances like nanobentonite and chitosan [51].

The heavy metals in wastewater and natural water bodies have significantly harmed ecosystems and reduced the quality of the water environment. A uniquely efficient activated carbon/carborundum microcrystalline cellulose core shell nanocomposite (AC/CB/MCC) was developed by Mubarak, et al. [52] to be used for the detoxification of As^{3+} and Cu^{2+} ions from aqueous solutions. The kinetic analyses showed that, among the models considered, the pseudo-second-order model is the most advantageous for ion adsorption. The maximal adsorption capabilities for the adsorption of Cu^{2+} and As^{2+} ions were 423.55 and 422.9 mg/g, respectively, at pH 7.0, 298 K, and 500 mg of the AC/CB/MCC adsorbent dose. It was indicated that the AC/CB/MCC nanocomposite can be employed as a substitute and effective nano-adsorbent for the removal of hazardous heavy metal ions from polluted effluents, such as Cu^{2+} and As^{3+} ions.

Numerous researchers have discussed the chemical modification of cellulose by esterification with EDTA for the recovery of metal ions, as well as the removal of metal ions from aqueous solutions by materials that link EDTA to cellulose derivatives [53,54]. In situ synthesized chelating (amino acetic acid groups) adsorbent grafted on cellulose and its heavy metal ion adsorption capabilities from aqueous solutions were developed by Hu, et al. [55]. (See Figure 6).

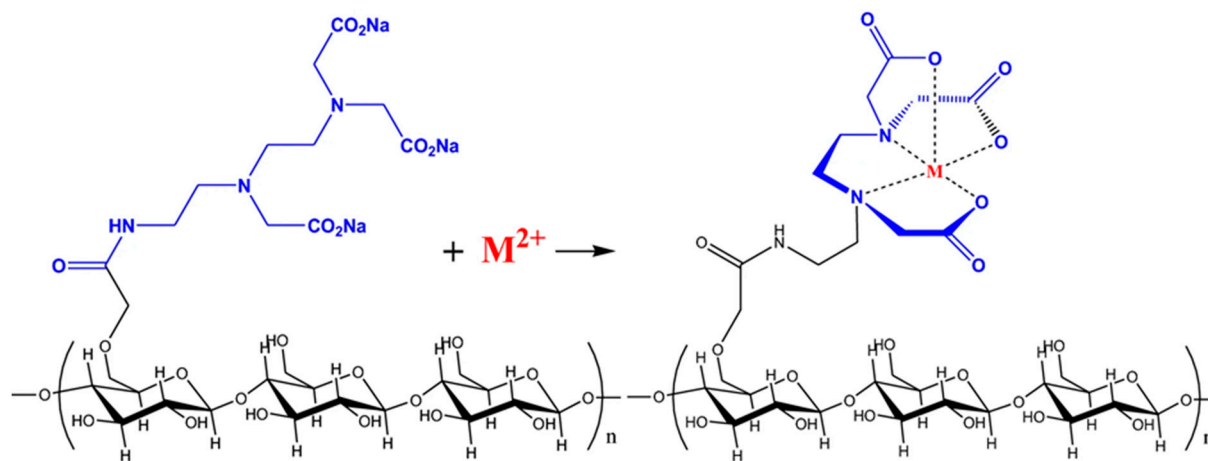


Figure 6. Proposed structure of the modified cellulose with amino acetic acid group and its chelating center with metal ions being adsorbed (Source [55]).

The findings showed that this modified cellulose had good adsorption capability for a variety of metal ions and displayed adsorption characteristics comparable to those of EDTA. The maximum adsorption capacity for Cu^{2+} on modified cellulose with an amino acetic acid group was 80.3 mg/g, while the maximum adsorption capacity for Pb^{2+} was 266.7 mg/g. By using the Freundlich and Langmuir models, the adsorption of Cu^{2+} and Pb^{2+} from single metal ion aqueous solutions onto this adsorbent was assessed and examined. The adsorption of both Cu^{2+} and Pb^{2+} ions was found to best fit the Langmuir isotherm model. The adsorbent saw a maximum quantity of Cu^{2+} and Pb^{2+} adsorption at pH 5.

3.2. Silica and Heavy Metal Adsorption Capacity

Due to their distinctive characteristics, such as a larger surface area, tunable pore diameters, excellent chemical and thermal stability, selectivity towards heavy metal ions, and ease of surface modification, silica nanoparticles from renewable sources have emerged as a leader in the various groups of nanoparticles. Studies [56,57] reported that silica nanoparticles can be synthesized from a variety of agricultural by-products and plants, including rice husk, maize cob, sugarcane bagasse, and bamboo residues.

Traditional mesoporous silica adsorbents have limited capacities or slow kinetics [58]. Mesoporous silica is thought to be an effective substrate for capturing pollutants as well as an excellent catalyst carrier because of its large surface area, rapid mass transfer inside nanostructures, excellent hydrothermal stability, tunable pore sizes, and ease of organic modification. Particularly, the organic modification and inorganic hybridization can be approached under relatively mild preparation conditions [59,60]. However, due to its capacity to remove heavy metal ions, silica has been used in adsorption techniques as a heavy metals remover in aqueous solutions. Due to its high efficiency, simplicity, and ease of use, adsorption has been widely used as a successful approach for removing a lot of heavy metal ions [61–63].

The testing of synthetic sorbents (SHNPs), developed by mixing colloidal hydrophilic nanoparticles (HNPs) with silica for useful water treatment applications, is described in Di Natale, Gargiulo, and Alfè [58]. (See Figure 7). Silica improves both the functionality and ease of removal of the used sorbent from the HNPs. The supported HNPs (SHNPs) show remarkable removal efficiency, particularly at neutral pH and low temperature (10 °C), which are typical conditions for natural-water remediation and some types of industrial wastewater. At a reference value of 0.2 mM, the SHNPs highest adsorption capacity for Cd^{2+} , Pb^{2+} , and Ni^{2+} ions are 0.042 mmol g, 0.027 mmol g, and 0.055 mmol g, respectively.

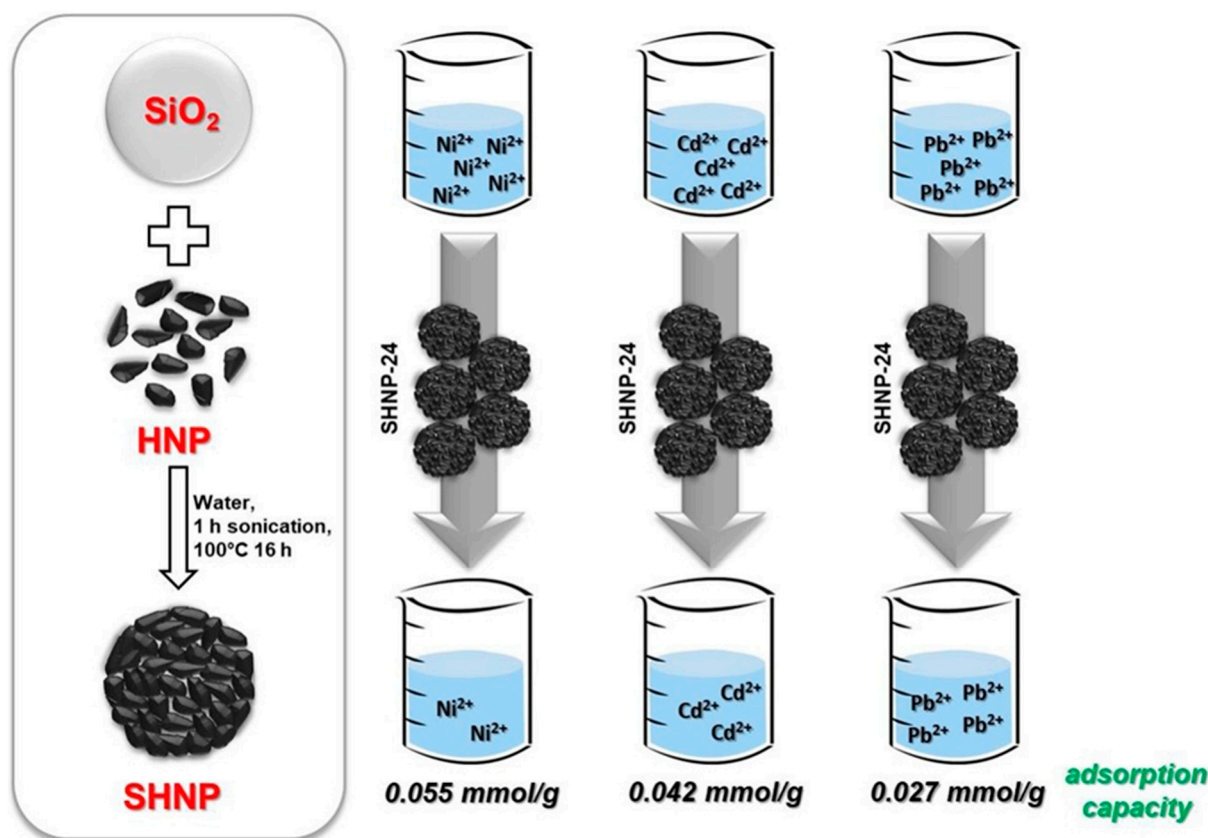


Figure 7. Adsorption of heavy metals on silica-supported hydrophilic carbonaceous nanoparticles (SHNPs) (Source [58]).

The sorbents demonstrate significant adsorption capabilities per gram of active phase (0.54 mg/g for Cd^{2+} ions, 13.48 mg/g for Ni^{2+} ions, and 8.87 mg/g for Pb^{2+} ions) at the corresponding quality level accepted by Italian legislation on wastewater, indicating a potential application for them in water treatment operations.

As a possible absorbent for heavy metal ions, Sachan, Ramesh, and Das [28] produced silicon nanoparticles (SNPs) from the dried leaf biomass of *Saccharum ravannae* (SRL), *Saccharum officinarum* (SOL), and *Oryza sativa* (OSL). SNPs were also used to remove copper (Cu^{2+}) and lead (Pb^{2+}) from wastewater as suitable adsorbent materials. (See Figure 8).

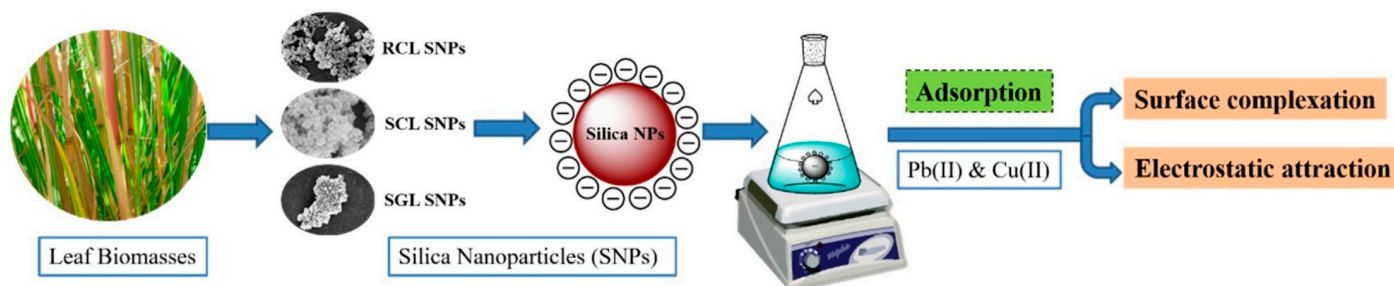


Figure 8. Green synthesis of silica nanoparticles from leaf biomass and its application to remove heavy metals from synthetic wastewater: a comparative analysis. (Source [28]).

The adsorption outcomes demonstrated significant capacity in removing heavy metal ions (Pb^{2+} and Cu^{2+}) with varying values for different types of nanoparticles: 140.06 mg/g and 149.25 mg/g for SRL SNPs, 338.55 mg/g and 179.45 mg/g for SOL SNPs, and 334.7 mg/g and 274.02 mg/g for OSL SNPs. These synthesized nanoparticles exhibited notable adsorption capabilities along with high reusability for eliminating heavy metal ions from synthetic wastewater, achieving over 95% removal efficiency. The adsorption behavior aligned well with the Freundlich isotherm model and followed pseudo-second-order kinetics, elucidating the adsorption mechanism for Pb^{2+} and Cu^{2+} using SRL, SOL, and OSL SNPs.

Al-Wasidi, et al. [64] synthesized a unique composite based on Schiff base synthesis on silica nanoparticles. (See Figure 9). First, 3-aminopropyltrimethoxysilane was used to modify silica nanoparticles, which contain silanol groups (Si-OH). A new Schiff base/silica composite developed after the modified silica reacted with 1-hydroxy-2-acetonaphthone.

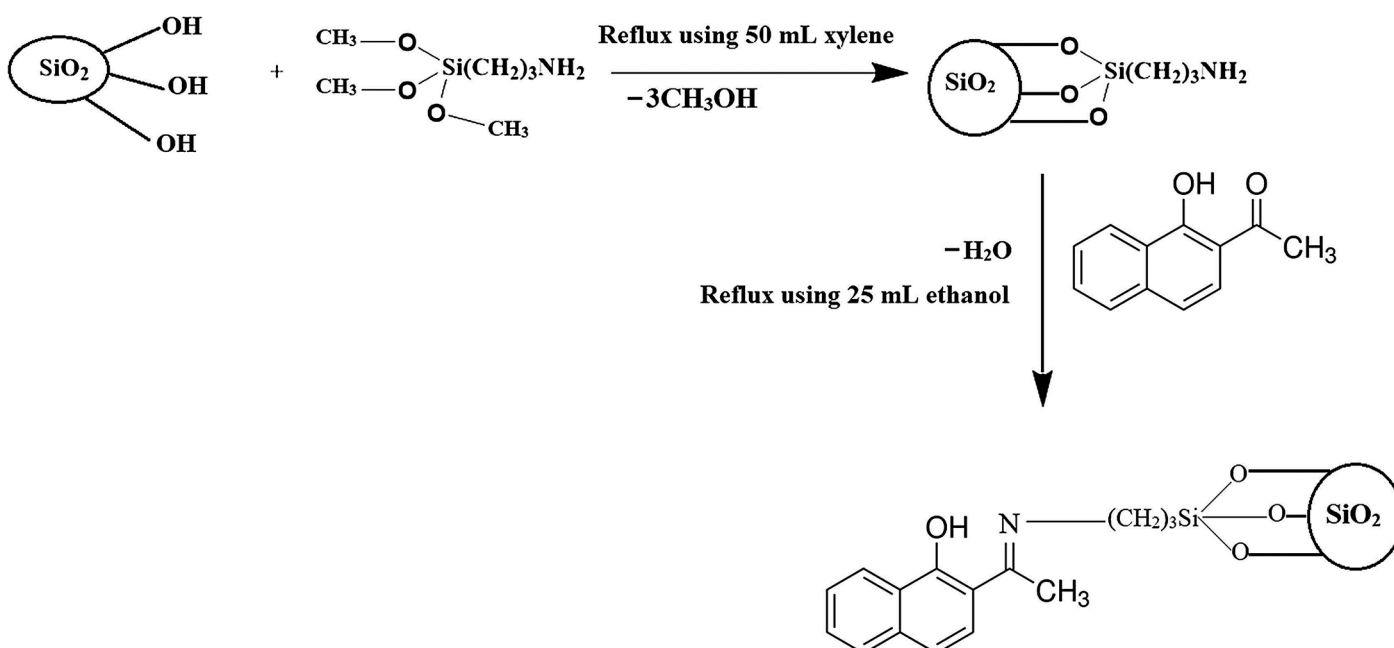


Figure 9. The synthetic steps of the composite (Source [64]).

For the effective removal of Ni^{2+} , Cu^{2+} , Zn^{2+} , and Hg^{2+} ions from aqueous solutions, the synthesized composite was used. The composite has a maximal absorption capacity of 68.630, 50.942, 45.126, and 40.420 mg/g for Cu^{2+} , Hg^{2+} , Zn^{2+} , and Ni^{2+} ions, respectively. The findings demonstrated that at pH = 6.5, contact time = 90 min, and adsorption temperature = 298 K, the greatest percentage removal of the examined metal ions was accomplished. Bifunctional magnetic mesoporous silica (NZVI-SH-HMS) was successfully synthesized by Li, et al. [65] for the efficient removal of Pb^{2+} and Cd^{2+} ions from aqueous solutions. First, a bifunctionalized magnetic mesoporous silica (NZVI-SH-HMS) material was manufactured at room temperature using the sol-gel and wet impregnation processes, with thiol and nanoscale zero-valent iron bound on the surface. (See Figure 10).

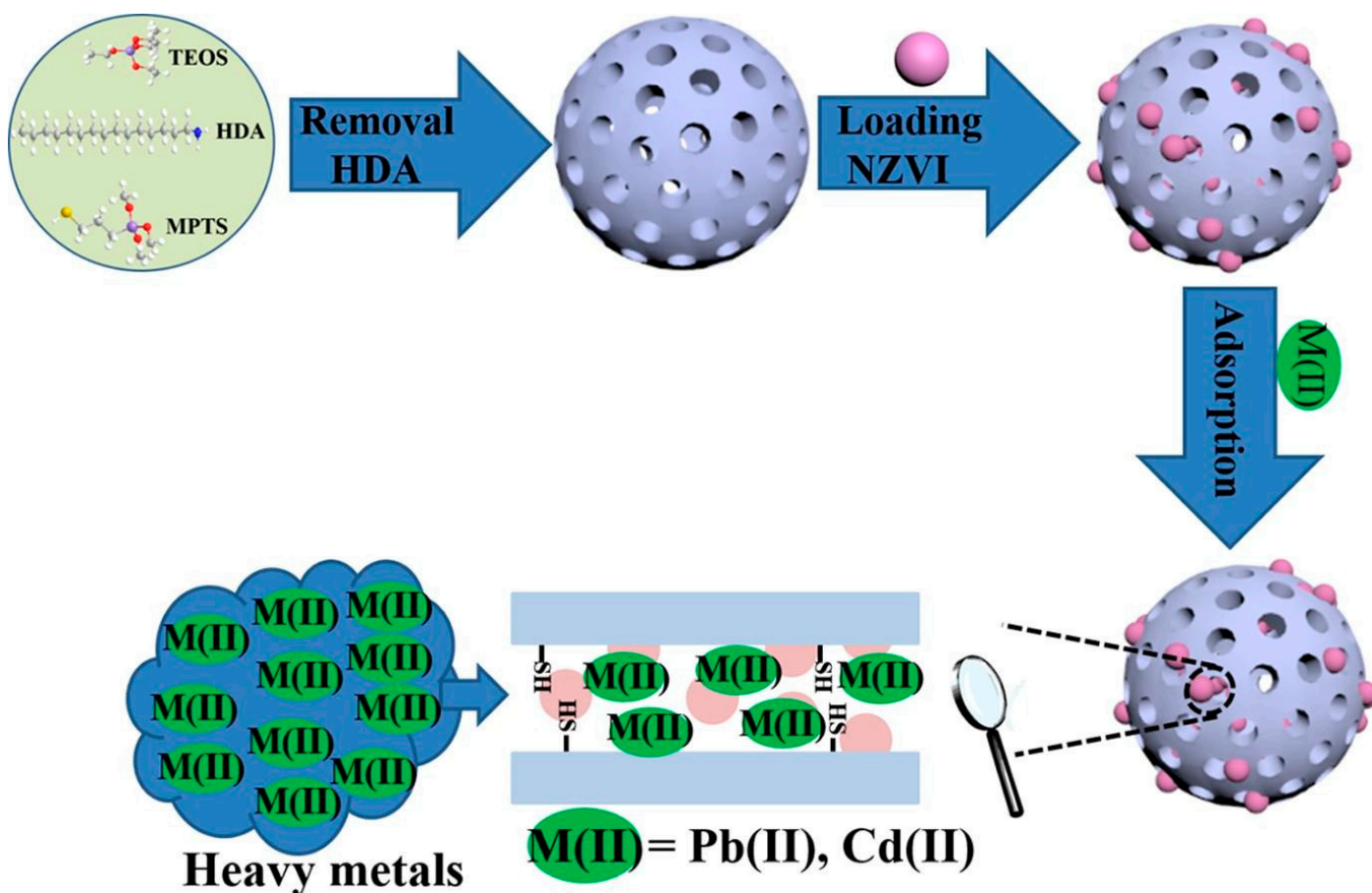


Figure 10. Highly effective removal of lead and cadmium ions from wastewater by bifunctional magnetic mesoporous silica (Source [65]).

NZVI-SH-HMS had maximal adsorption capabilities of 487.8 mg/g for Pb^{2+} and 330.0 mg/g for Cd^{2+} , respectively. Data on the pseudo-second-order kinetics and isotherm of adsorption were well fitted to the Langmuir isotherm model. The reusability and regeneration studies showed NZVI-SH-HMS had a large capability for removing heavy metals from the actual water environment and retained outstanding adsorption performance.

To increase the mechanical strength and heavy metal ion adsorption of silica aerogel, Parale, et al. [66] developed a novel in situ sulfur-doping manufacturing process. Three-dimensional monolithic silica aerogels were initially developed by polymerizing (3-glycidioxypropyl) trimethoxysilane and (3-mercaptopropyl)trimethoxysilane using an adjustable one-pot epoxy-thiol reaction, then by using the sol-gel method and supercritical drying. (See Figure 11).

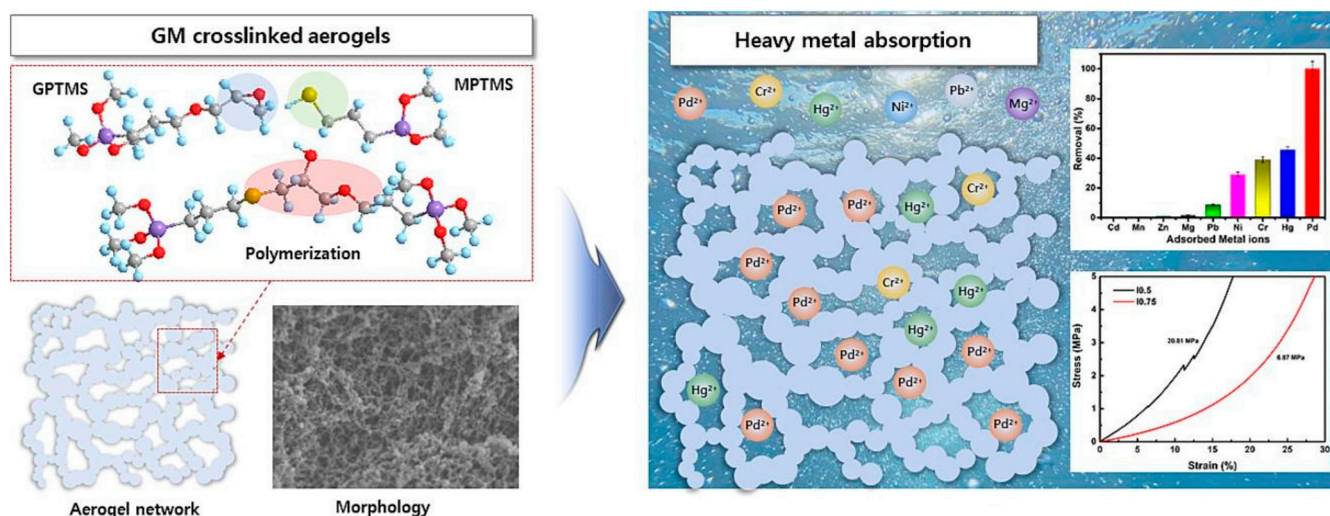


Figure 11. Cross-linked silica aerogels were synthesized using one-pot epoxy-thiol polymerization and a sol-gel process and heavy metal adsorption (Source [66]).

The heavy metals were eventually removed using the produced aerogels, with Pd^{2+} being adsorbed nearly 100% of the time. The Langmuir adsorption model was able to fit an adsorption capacity of up to 689.65 mg/g. The suggested technique is a novel approach for the in situ synthesis of sulfur-doped silica aerogels with improved mechanical properties for heavy metal removal.

Groundwater contamination by heavy metals in the environment has grown to be a major threat to the health of living things. In order to reduce the hazards involved, heavy metals in contaminated water must be removed. Amin, et al. [67] investigated mesoporous silica and chitosan nanoparticles that had been synthesized and coated with magnetite to absorb heavy metals from wastewater. (See Figure 12). First, due to the monodispersity offered by this approach, magnetite nanoparticles (MNPs) developed via the thermal degradation of the iron oleate precursor. The particles were given a mesoporous silica layer coating using the surfactant cetyltrimethylammonium bromide (CTAB). By stirring in chitosan solution, the coated particles were subjected to chitosan coating.

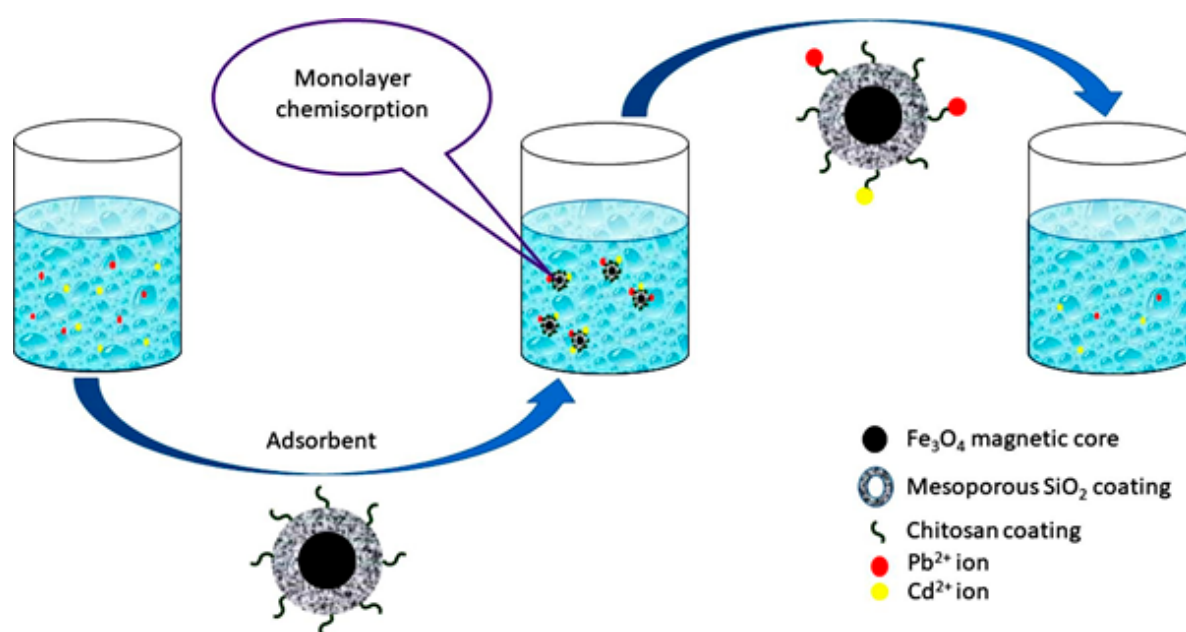


Figure 12. Heavy metal adsorption from wastewater by mesoporous silica and chitosan-coated magnetite nanoparticles (Source [67]).

In known concentrations of heavy metal salt solutions, the particles were utilized as an adsorbent. It is a favorable sign for future investigation and analysis because the produced adsorbent showed a reasonable adsorption capacity of 150.33 mg/g and 126.26 mg/g for Pb^{2+} and Cd^{2+} , respectively. The pseudo-second-order kinetic model and the Langmuir isotherm model are superior fits for the adsorption data of Pb^{2+} and Cd^{2+} based on the value of R^2 ($R^2 \geq 0.99$).

A new composite was developed in this study by Al-Wasidi, Naglah, Saad, and Abdelrahman [64], based on the production of a Schiff base on silica nanoparticles. A silanol group (Si-OH) was added to silica nanoparticles using (3-aminopropyl) trimethoxysilane. A novel Schiff base/silica composite was made by mixing the modified silica with 4,6-diacetylresorcinol. (See Figure 9).

Pb^{2+} , Cu^{2+} , Co^{2+} , and Ni^{2+} ions were efficiently removed from aqueous solutions using the produced composite. The composite had a maximal absorption capacity of 107.066, 89.767, 80.580, or 70.972 mg/g for Pb^{2+} , Cu^{2+} , Co^{2+} , and Ni^{2+} ions, respectively. The examined metal ions adsorption processes were chemical, spontaneous, and well-matched with the pseudo-second-order kinetic model and Langmuir equilibrium isotherm.

3.3. Cellulose with Silica Nanoparticles and Heavy Metal Adsorption (Cd, Pb, Cr)

Recent research has shown that nanotechnology has enormous potential for improving the efficiency of water prevention and purification while reducing costs. In this field, nanocellulose has attracted attention for two applications where it has effectively eliminated pollutants as a membrane and an adsorbent. This potential stems from its elevated aspect ratio, expansive specific surface area, outstanding water retention, and environmental inertness. Beyond these merits, the existence of active sites facilitates the integration of chemical groups, potentially enhancing the surface's efficacy in binding pollutants [68].

Heavy metals such as Cd^{2+} , Pb^{2+} , Mn^{2+} , and others pose a serious threat to the environment since they are nonbiodegradable. Using environmentally acceptable nanomaterials, heavy metal pollution can be minimized thanks to the development of nanobiotechnology. Specially designed bio-nanomaterials usually exhibit properties like a longer shelf life, self-healing nature, adaptability in varied environments, and cost-effectiveness in comparison to nanoparticles generated using physicochemical procedures. Due to their excellent selectivity and adsorption capacity, bio-nanomaterials can effectively remove heavy metals from wastewater, even when they are present in incredibly low quantities. In order to reduce expenses and create a way for environmental sustainability, bio-nanotechnology is applied in their cleanup [69].

The characteristics of nanoparticles have been extensively investigated by their restricted capacity to adsorb some heavy metal ions. According to Rajendran, et al. [70] there has been research on the effects of experimental conditions on the uptake of metal ions, including the dose of the adsorbent, pH, substrate concentration, response time, temperature, and electrostatic force. Furthermore, the use of polymeric membranes for the adsorption of dangerous particles may lead to the development of next-generation reusable and portable water filtration systems. Because they conduct both membrane filtration and adsorption, membranes for membrane adsorption (MA) are very effective at eliminating trace quantities of contaminants such as cationic heavy metals, anionic phosphates, and nitrates [71].

Utilizing carbohydrate biopolymers, several nanocomposite adsorbents for wastewater treatment have been developed. The effectiveness of extracting inorganic pollutants from aqueous solutions was investigated using these adsorbents. Toxic metals may be efficiently absorbed by cross-linkers, which dissolve in aqueous solutions of divalent heavy metal ions to assess their polymer absorption capacity. These nanocomposites were used to remove Cd^{2+} , Pb^{2+} , and Zn^{2+} , three very dangerous elements, from water. To improve the effectiveness of heavy metal ion absorption, various functionalization techniques have been applied, such as grafting, blending, or mixing,

with other nanomaterials that have an extra functional group. The ability of an adsorbent to be recycled depends in part on its mechanical efficiency, which is raised by integrating the second component into the primary polymer chain. The method for removing metal ions from wastewater is inexpensive as long as the adsorbent is recycled [72].

To recover heavy metal ions and benzene fumes, Yarkulov et al., 2022 [73] developed diacetate cellulose–silicon bio-nanocomposite adsorbent (DACSBNC). The observed findings validated the following: (i) the DACSBNC's adsorption capacitance for Cd^{2+} , Hg^{2+} , and Pb^{2+} ions was proven to be 12.23, 13.87, and 31.40 mg/g, respectively; and (ii) the DACSBNC's sorption capacitance for benzene vapors was 0.5618 mmol/g. For the extraction of heavy hazardous metal ions such as Cd^{2+} , Hg^{2+} , and Pb^{2+} from galvanic aqueous solutions, the researched DACSBNC materials have been suggested as potential sorbents.

To develop a porous matrix with balanced surface characteristics, silica from rice husks was treated using the sol-gel method, and cellulose from Nata de Coco was added in the gelling process. Hazardous waste is laboratory waste that pollutes the environment and contains heavy metals such as cadmium, chromium, nickel, and zinc. Adsorption is an efficient and inexpensive method to handle heavy metal waste. The material silica–cellulose was developed and used in this study by Royanudin, et al. [74] as an adsorbent for heavy metals, including cadmium, chromium, nickel, and zinc, in laboratory waste. The percentages of remediation for the metals cadmium, chromium, nickel, and zinc were 95.09%, 58.77%, 94.56%, 94.56%, and 97.50%, respectively.

In the study by Yang, et al. [75], the researchers created ferrocene-incorporated mesoporous organosilica nanoparticles, which is a novel inorganic–organic hybrid nanomaterial (MONs). Organoalkoxysilanes containing ferrocene were synthesized as shown in Figure 13a, and the raw material was used directly to synthesize MONs without any purification because 1,10-ferrocenedicarboxylic acid was not involved in the process. The results of the reaction are shown below.

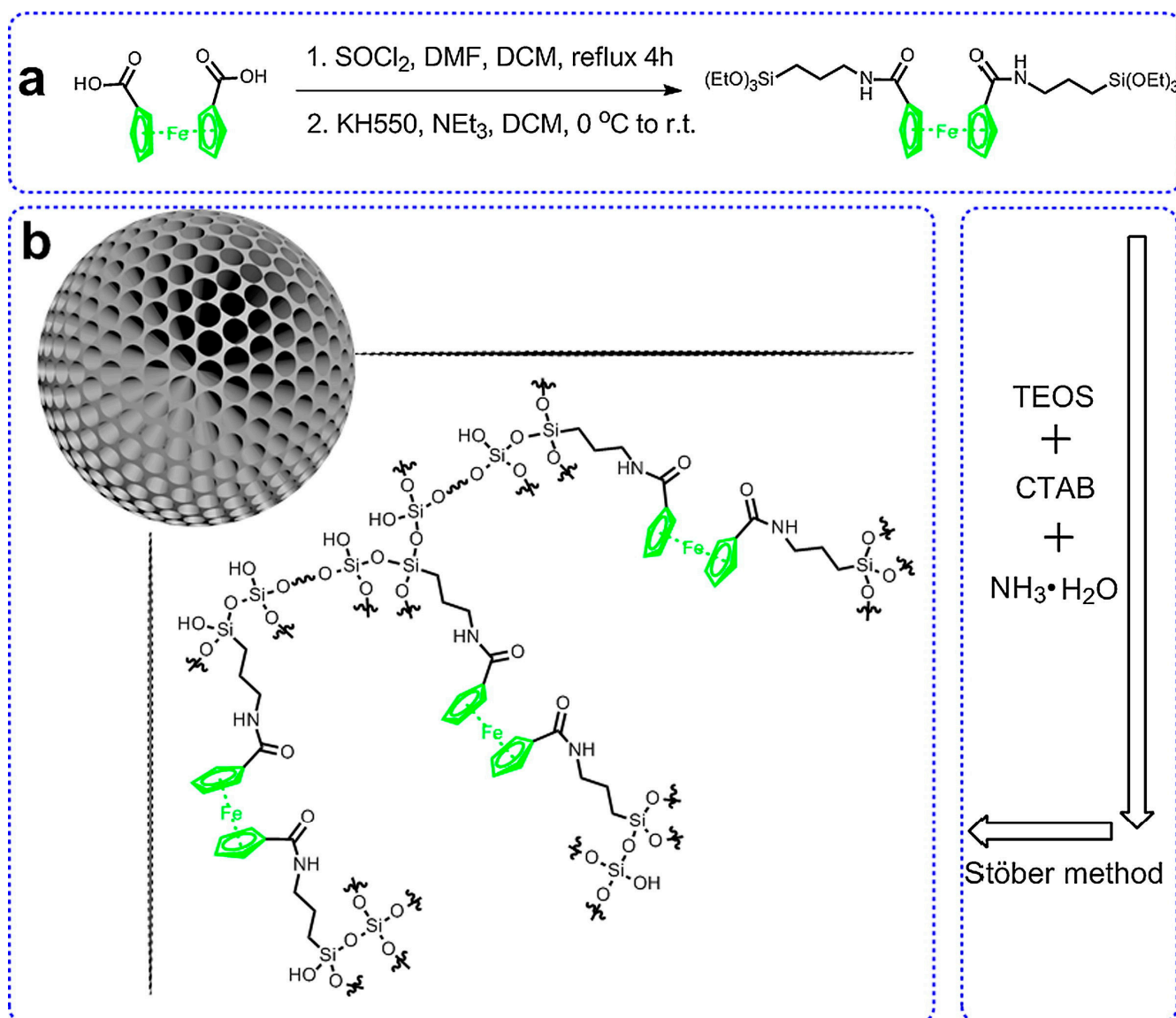


Figure 13. (a) Synthetic routes of ferrocene-containing organoalkoxysilanes and (b) schematic illustration of MONs (Source [75]).

The mesoporous structure, significant surface area, and incorporation of the ferrocene group within the framework enabled MONs to exhibit superior adsorption of phosphate anions compared to surface-modified MSNs ($\text{SiO}_2\text{-Fe}$) (488 mg/g). Comparative analysis revealed that MONs outperformed MSNs, with ferrocene surface modifications as a more effective absorbent. Additionally, Congo red (CR) and Pb^{2+} were employed as model pollutants. For the removal of heavy metals, titanium dioxide (TiO_2) and other inorganic nanoparticles were utilized. Nano TiO_2 demonstrated a higher adsorption rate compared to bulk particles [76]. To achieve multiple heavy metal adsorption, Wang, Zhan, Wu, Shi, Du, Luo, and Deng [46] fabricated titanium dioxide (TiO_2)/rectorite (REC)-trapped cellulose-composite nanofibrous mats using electrospinning. (See Figure 14). The interactions between inorganic adsorbents and cellulose molecules enhanced the mats thermal stability, surface area, tensile strength, and adsorption capacity.

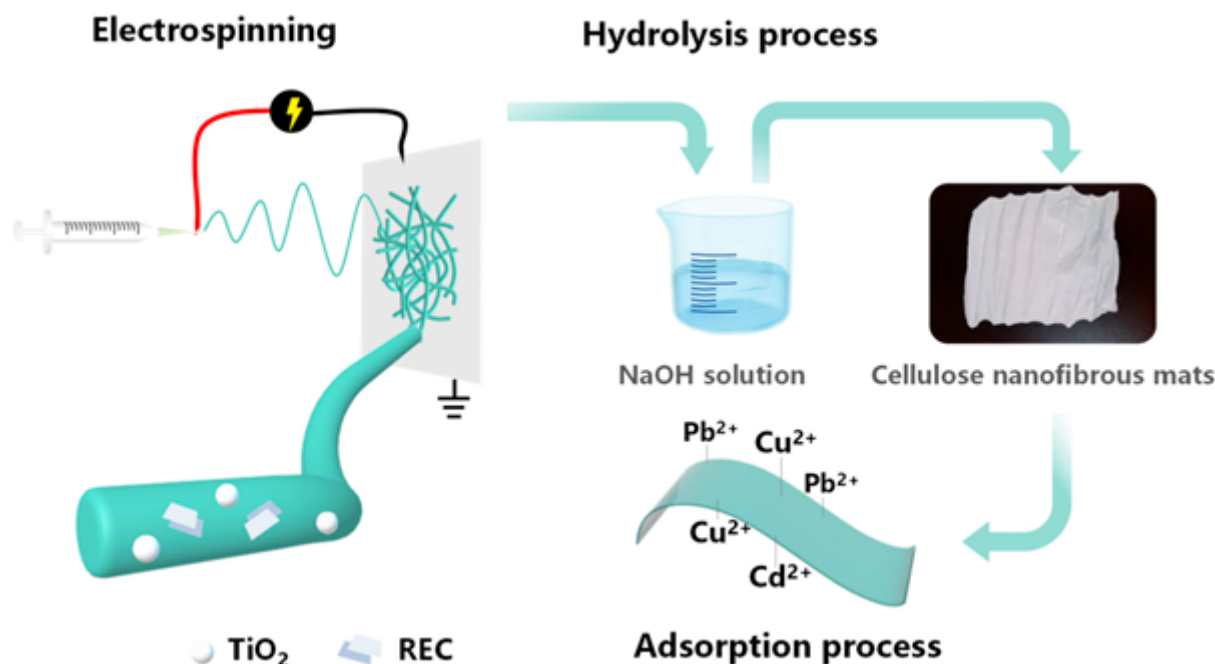


Figure 14. The schematic diagram illustrates the process of creating a cellulose membrane through electrospinning of cellulose acetate blended with TiO_2 nanoparticles and rectorite. Subsequently, deacetylation transforms it into pure cellulose, enhancing its absorption properties towards heavy metal ions such as Pb^{2+} , Cu^{2+} , and Cd^{2+} (Source [46]).

The pseudo-second-order model and Langmuir isotherm model were mostly used in the adsorption of Cd^{2+} onto cellulose– TiO_2 /REC nanofibrous mats. The pH of the solution influenced the multiple adsorptions of Pb^{2+} , Cu^{2+} , and Cd^{2+} onto composite nanofibrous mats. Cellulose– TiO_2 /REC2:1 nanofibrous mats at pH 6 had the highest total adsorption capacity of 69.81 mg/g. The produced cellulose– TiO_2 /REC nanofibrous mats might be employed to extract heavy metals from acidic wastewater. The composite nanofibrous mats successfully captured TiO_2 nanoparticles.

3.4. Cellulose–Silica and Amine–Silane Coupling Agents in Absorption of Heavy Metals

There are three common methods of surface modification for cellulose and silica coupling agents in absorption of heavy metals. Among these includes:

3.4.1. Silane Coupling Agents

The functionalization of cellulose through a reaction with organosilanes has frequently been utilized to enhance its characteristics. The impact of substitutions before coupling with silanes on improving the dispersions of the functional groups that act as the adsorption sites for aqueous arsenate has barely been explored [77,78]. Adsorbents with excellent adsorption performance toward heavy metal ions and other contaminants can be produced by adding coordination groups comprising coordination atoms, such as $-\text{OH}$, $-\text{COOH}$, $-\text{C}=\text{O}$, $-\text{C}=\text{N}$, $-\text{NH}_2$, $-\text{NH}$, $-\text{C}-\text{S}$, $-\text{C}=\text{S}$, $-\text{S}-\text{S}$, and $-\text{S}=\text{O}$, to cellulose-based adsorbents.

A novel cross-linked polymer known as cellulose acetate aminosilane (CAAS) was created by Bisla et al. [79] using acetylated microcrystalline cellulose and 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPTMS). (See Figure 15). The acetyl group probably encourages the formation of a polymer structure that facilitates aqueous ion diffusion during their adsorptions.

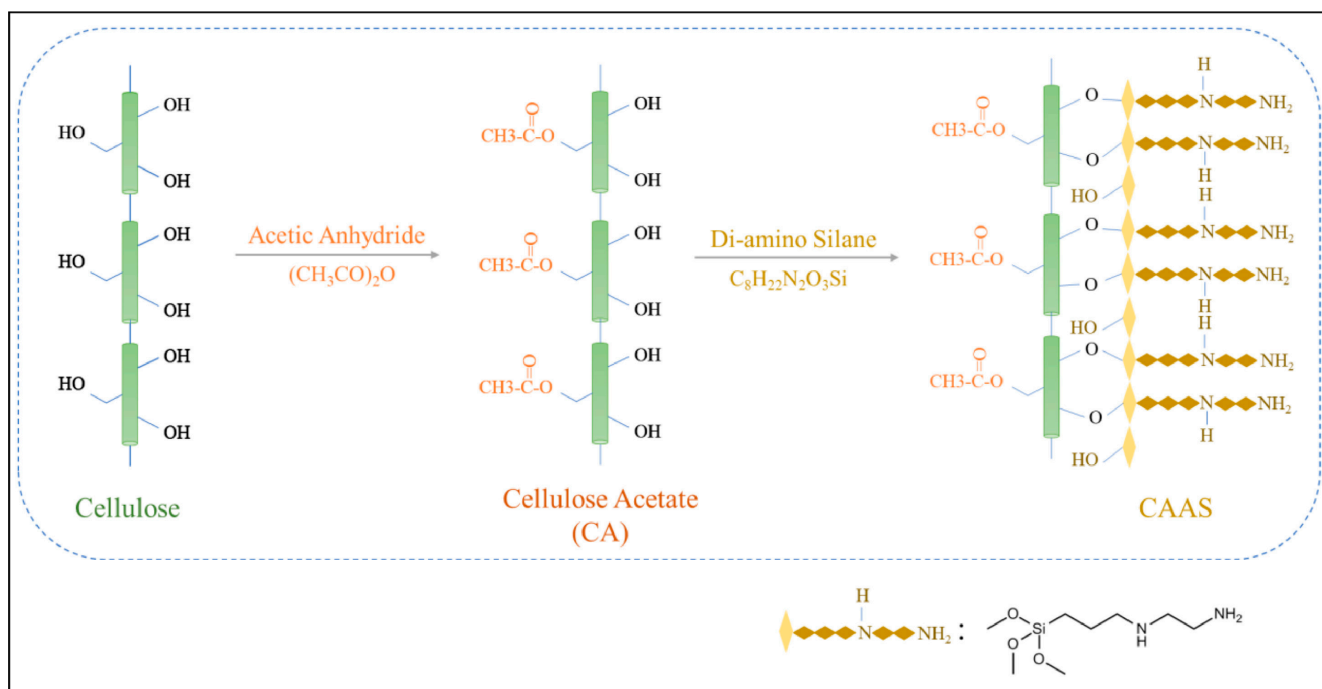


Figure 15. Schematic illustration for preparation of CAAS (Source [79]).

In a pH range of 2 to 10, a sizable amount of arsenate was adsorbed by CAAS, suggesting that the presence of both amine and acetyl groups broadens the adsorption pH range. The Langmuir isotherm and pseudo-second-order kinetic models fit the adsorption data well. The adsorption reached 455 mg/g, demonstrating a remarkable capability for the cellulose polymers treated with aminosilane.

Shaheen et al. [80] created a novel and cost-effective bio-based adsorbent capable of simultaneously removing an anionic dye and a hazardous metal. (See Figure 16). They utilized 3-aminopropyltriethoxysilane (APTES-CA) to modify porous cellulose acetate (CA) microspheres synthesized through a double emulsion (W/O/W)–solvent evaporation method.

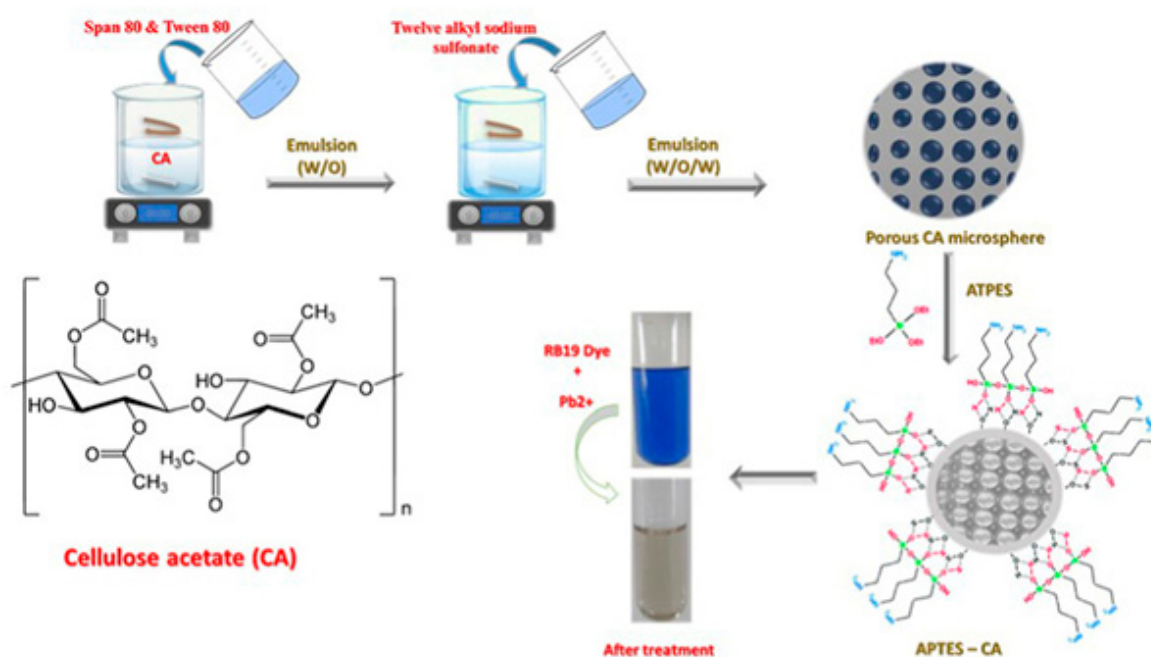


Figure 16. Schematic diagram for APTES-CA synthesis pathway and Reactive blue 19 (RB19) and Pb^{2+} adsorption (Source [80]).

According to the adsorption investigation, APTES modification increased the effectiveness of adsorption for RB19 and Pb^{2+} . According to the kinetic investigation, APTES-CA adsorbs RB19 and Pb^{2+} by several processes, specifically chemisorption for RB19 and physisorption for Pb^{2+} . A good efficiency of APTES-CA towards Pb^{2+} was demonstrated by the theoretical Langmuir monolayer saturation capacity (180 mg/g).

3.4.2. Thiol Functionalization

Through the addition of extra binding sites provided by functional groups containing sulfur, thiol functionalization increases the adsorption capacity for heavy metals. Because of their considerable affinity for metal ions, these groups make it easier to remove them from aqueous solutions. Dang-Bao, et al. [81] produced thiol-functionalized cellulose nanocrystals through chemical hydrolysis of cellulose followed by autocatalytic esterification with thioglycolic acid. Their study involved assessing the adsorption properties of these nanomaterials for divalent copper ions in water using isotherm and kinetic analyses. The thiol-functionalized cellulose nanocrystals demonstrated a notably enhanced adsorption capacity compared to unmodified cellulose, achieving 4.244 mg/g at pH 5 and room temperature.

A cellulose nanofiber membrane that has been thiol-functionalized and is capable of successfully adsorbing heavy metal ions is described by Choi, et al. [82]. (See Figure 17). As a result of the deacetylation of electrospun cellulose acetate nanofibers and subsequent esterification of a thiol precursor molecule, thiol was added to the surface of cellulose nanofibers.

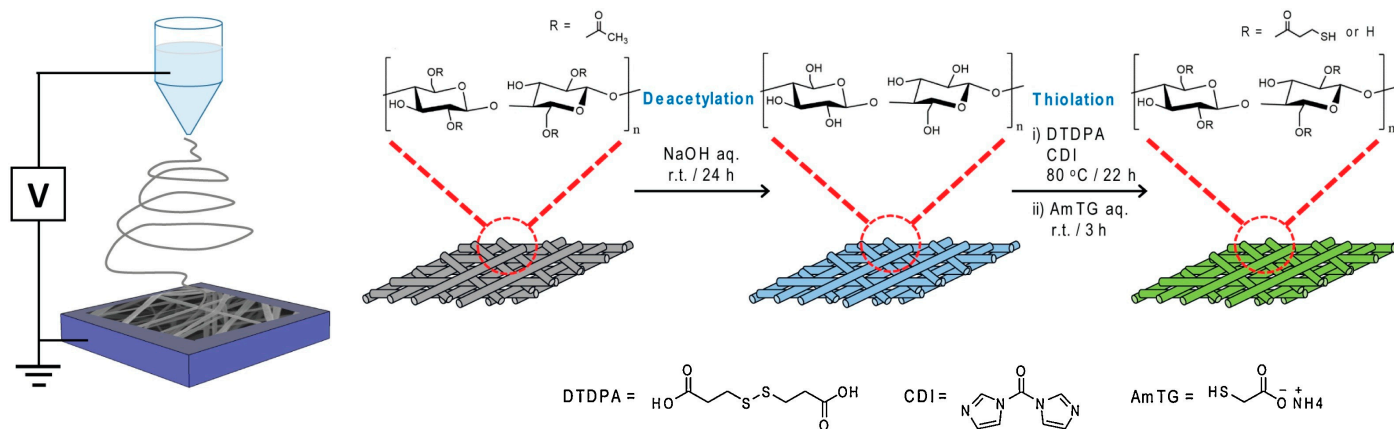


Figure 17. A schematic representation illustrating the fabrication process of a thiol-functionalized cellulose nanofiber membrane (Source [82]).

The Langmuir isotherm provided a good description of adsorption capacity as a function of adsorbate concentration, indicating that metal ions form a surface monolayer with a homogeneous distribution of adsorption energy. Cu^{2+} , Cd^{2+} , and Pb^{2+} ions have maximum adsorption capabilities of 49.0, 45.9, and 22.0 mg/g in the Langmuir isotherm, respectively. (See Figure 18). According to the time-dependent adsorption capacities, which were consistent with a pseudo-second-order kinetic model, chemisorption of each doubly charged metal ion takes place when there are two thiol groups present on the surface.

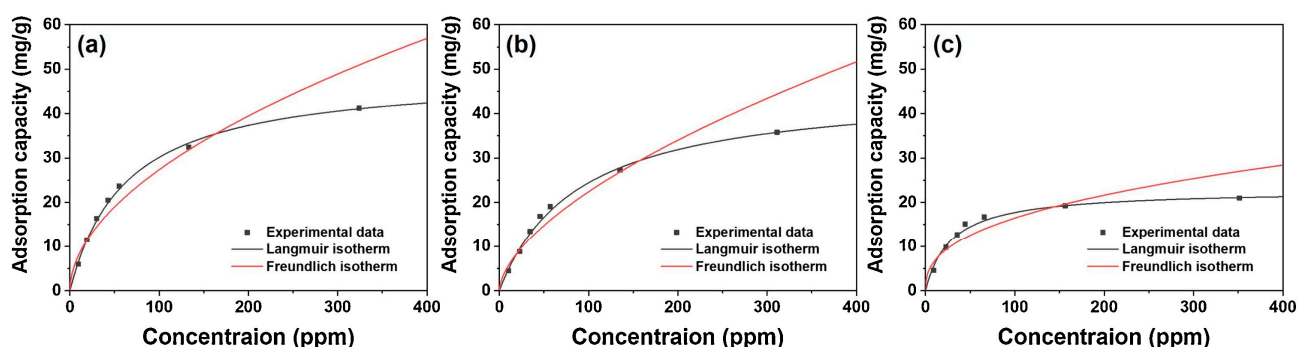


Figure 18. Isotherms displaying the adsorption of (a) Cu(II), (b) Cd(II), and (c) Pb(II) ions onto TC nanofibers, along with the fitting outcomes using Langmuir (represented by black solid line) and Freundlich (represented by red solid line) isotherm models (Source [82]).

3.4.3. Amino Acid Grafting

In this method, amino acid molecules are attached to the surfaces of cellulose and silica materials. Amino acids possess functional groups like amino ($-NH_2$) and carboxyl ($-COOH$) groups, which can engage heavy metal ions through coordination and complexation reactions. The grafting of amino acids enhances the selectivity and effectiveness of adsorption by modifying the surface chemistry of the materials. In order to improve the adsorptive removal of Cd^{2+} and Pb^{2+} from aqueous solutions, chelating celluloses functionalized with the four amino acids cysteine, histidine, aspartic acid, and methionine (as named Cys-CL, His-CL, Asp-CL, and Met-CL) were prepared by Chen, et al. [83] through a Schiff base reaction. (See Figure 19). These materials were then investigated by various means of characterization. Because it has a large number of active binding sites and uses complexation of its thiol, imine, and carboxyl groups with both metal ions as the adsorption mechanism, the Cys-CL stood out among the others for its excellent adsorptive capabilities for the improved adsorption of the Cd^{2+} and Pb^{2+} ions.

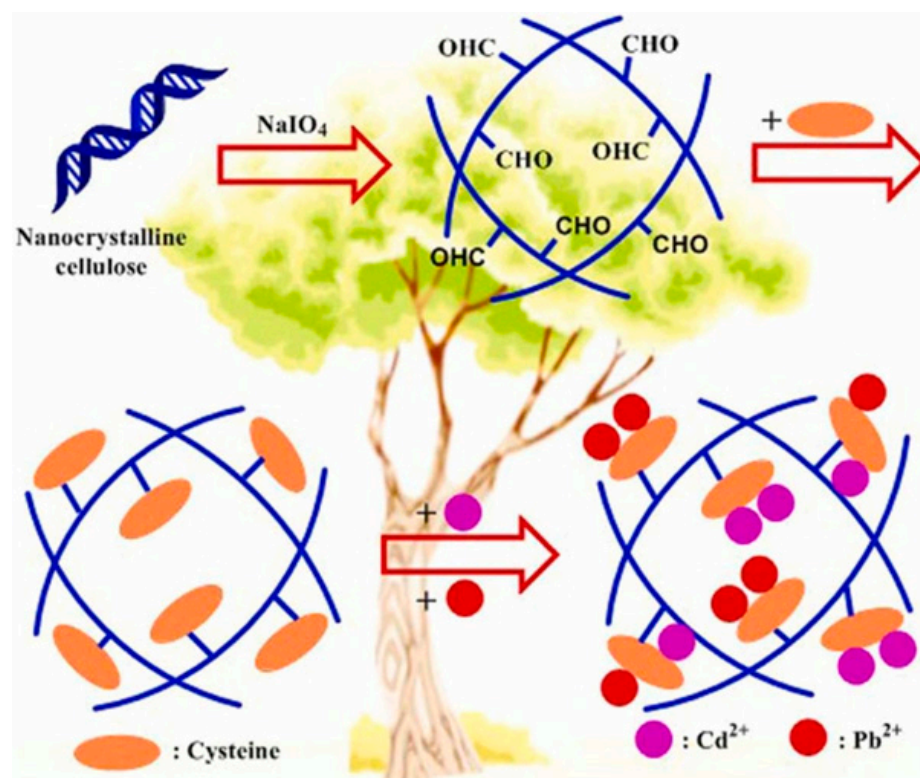


Figure 19. Synthesis of chelating celluloses functionalized with amino acid (cysteine) and heavy metals adsorption (Source [83]).

Using the radiation approach for Pd(II) capture, four environmentally friendly amino acids (arginine, histidine, methionine, and cysteine) were used to change cellulose microspheres (designated as ArgR, HisR, MetR, and CysR). Their excellent specificity for Pd(II) was demonstrated by batch studies, which were in good agreement with the pseudo-second-order kinetic and Langmuir models. Notably, at 143.47 mg/g, CysR showed the highest maximal adsorption capacity. Moreover, CysR demonstrated remarkable resilience to high salt concentrations, while MetR demonstrated strong resistance to acidic environments. These altered microspheres successfully removed traces of Pd from PCB leachate in real-world applications [84]. (See Figure 20).

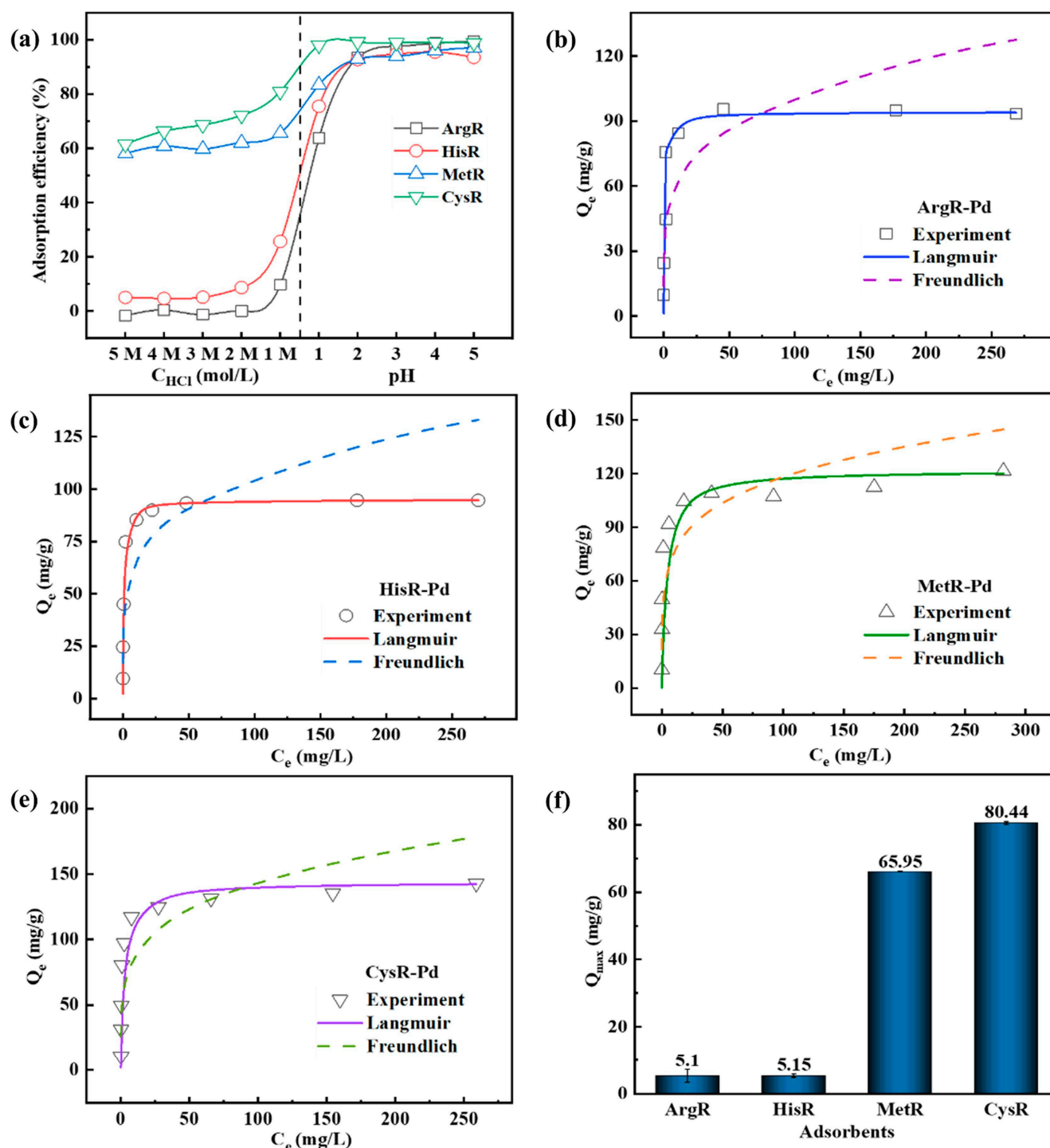


Figure 20. Effect of pH on adsorption efficiency of Pd(II) (a) ($C_0 = 100$ mg/L, adsorbent mass = 10 mg, volume = 10 mL, $T = 30$ °C); Experimental isotherms of ArgR (b), HisR (c), MetR (d), and CysR (e)

(adsorbent mass = 10 mg, pH = 2, V = 10 mL, T = 30 °C, t = 24 h); The maximum adsorption capacity of Pd(II) on amino acid resins at 5 mol/L HCl concentration (f) ($C_0 = 100$ mg/L, adsorbent mass = 10 mg, volume = 10 mL, T = 30 °C) [84].

The study on the reaction of hydroxy groups with diethylenetriaminepentaacetic acid (DPTA)-modified aminosilane shows the usage of a silane containing both carboxy and amine for the chemical modification of cellulose [85]. (See Figure 21).

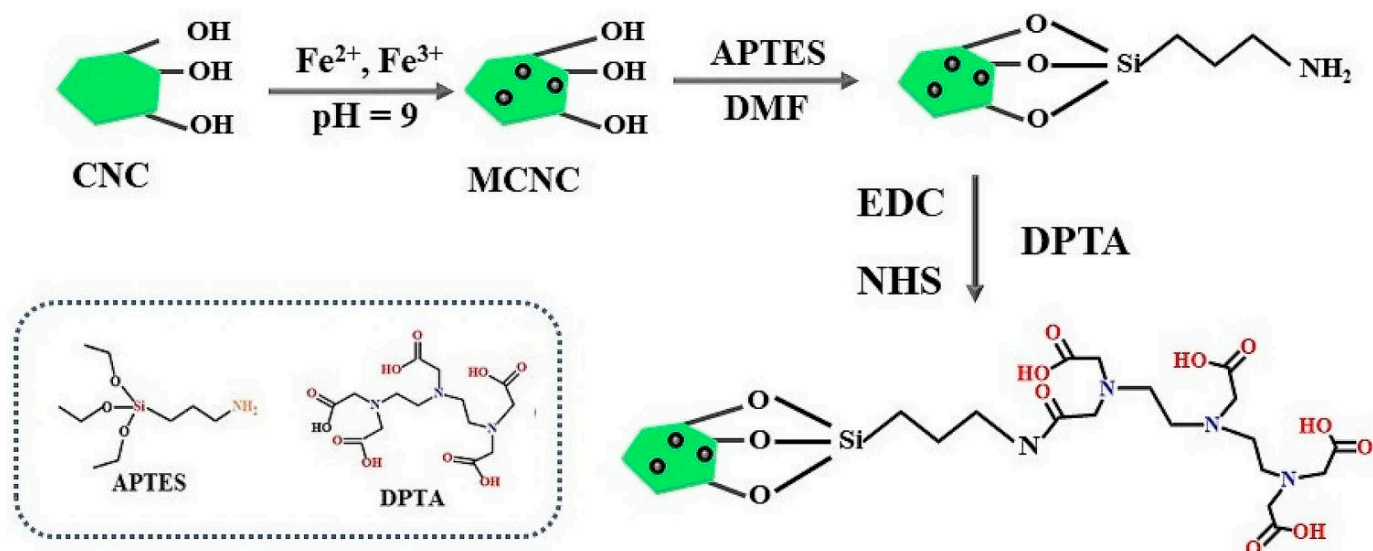


Figure 21. Schematic representation of the preparation of MCNC-DPTA (Source [85]).

Higher temperatures were discovered to facilitate adsorption, with maximum Pb^{2+} adsorption capacities of 424.78, 424.67, and 440.0 mg/g being obtained at 293.3, 298.3, and 303.3 K, respectively. This material's adsorption behavior was investigated, and the results show that the natural initial pH of the aqueous Pb^{2+} solution was optimal for the adsorption process. Investigations were made on the isotherm and kinetic parameters for Pb^{2+} adsorption by MCNC-DPTA. The Langmuir isotherm model and pseudo-second-order model were thought to better represent the adsorption process of Pb^{2+} by MCNC-DPTA due to the greater fitting coefficients.

One of the most serious environmental issues that has generated a great deal of worry in recent decades is copper contamination of water. For the purpose of removing Cu^{2+} from aqueous solutions, Gao, et al. [86] treated cellulose in two steps with N-[3-(trimethoxysilyl)propyl]ethylenediamine (KH-792) and diethylenetriaminepentaacetic acid (DTPA). (See Figure 22).

Enhanced adsorption of copper ions from aqueous solution by two-step DTPA-modified magnetic cellulose hydrogel beads

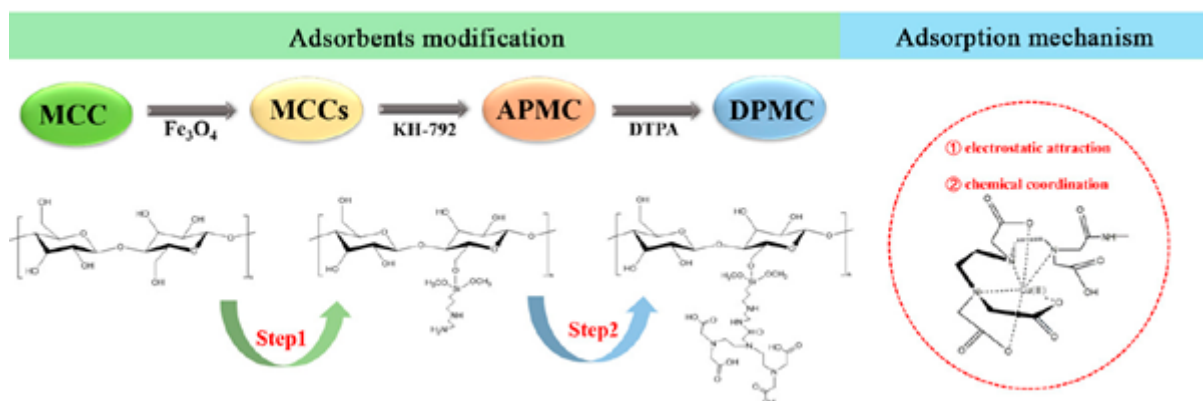


Figure 22. Cu(II) adsorption process and related mechanism ([86]).

DPMC had more Cu(II) adsorption capacity than MCCs and APMC, with a maximum adsorption capacity of 298.62 mg/g at pH 6. The equilibrium adsorption data were well represented by the Langmuir model, and the adsorption process was found to fit better with the pseudo-second-order kinetic model, indicating that monolayer chemical adsorption dominated the process. In order to remove Cu(II) from aqueous media, DPMC composite exhibits great potential as an adsorbent.

4. Results

Table 1 summarizes the type of heavy metal ions and the capacity removal in mg/g and/or percentage.

Table 1. Removal of metal ions using adsorbents.

Adsorbent Types	Heavy Metal Ions	Capacity Removal (mg/g) and/or Percentage Removal	Reference
Natural fiber and heavy metal adsorption capacity			
Banana fibre needle-felted fabric	Pb ²⁺ and Zn ²⁺	95.5% and 98%	Ariharasudhan, Chandrasekaran, Dhinakaran, Rameshbabu, Sundaresan, Natarajan and Arunraj [36]
Banana peel	Cd ²⁺	98.146%	Afolabi, et al. [87]
TCNF	Cu ²⁺	>60 mg/g	Mautner, Kwaw, Weiland, Mvubu, Botha, John, Mtibe, Siqueira and Bismarck [39]
SEBF-CX	Pb ²⁺ and Cd ²⁺	99.0099 mg/g and 67.3401 mg/g	Sheng, Shen, Dai, Pan, Ai, Zheng, Zheng and Xu [41]
IMI-GMA	Cu ²⁺ , Pb ²⁺ and Zn ²⁺	71.6 mg/g, 84.2 mg/g and 60.1 mg/g.	Selambakkannu, Othman, Bakar, Shukor and Karim [42]
PP/SF/BF fibre and CS/SF/BF fibre	Cd ²⁺	304 mg/g and 419 mg/g	Alaswad, Lakshmi, Sudha, Gomathi and Arunachalam [43]
GCFP	Cd ²⁺	98% (approximately 128 mg/g)	Abdelkhalek, Ali, Sheng, Zheng and Hasanin [44]
AC/CB/MCC	Cu ²⁺ and As ²⁺	423.55 and 422.9 mg/g	Mubarak, Zayed and Ahmed [52]
HTA-BC	Cr(VI)	534.8 mg/g	Su, Zhao, Lu, Zhong, Shen and Ruan [48]
Modified cellulose with amino acetic acid group	Cu ²⁺ and Pb ²⁺	80.3 mg/g and 266.7 mg/g	Hu, Hu, Tang and Liu [55]
Silica and heavy metal adsorption capacity			
SHNPs	Cd ²⁺ , Ni ²⁺ and Pb ²⁺	0.54, 13.48 and 8.87 mg/g	Di Natale, Gargiulo and Alfè [58]
SRL SNPs; SOL SNPs; and OSL SNPs	Pb ²⁺ and Cu ²⁺	(140.06 and 149.25 mg/g); (338.55 and 179.45 mg/g); and (334.7 and 274.02 mg/g)	Sachan, Ramesh and Das [28]
Silica nanoparticles with 1-hydroxy-2-acetonaphthone	Cu ²⁺ , Hg ²⁺ , Zn ²⁺ , and Ni ²⁺	68.630, 50.942, 45.126, and 40.420 mg/g	Al-Wasidi, Naglah, Saad and Abdelrahman [64]
NZVI-SH-HMS	Pb ²⁺ and Cd ²⁺	487.8 and 330.0 mg/g	Li, Li, Wen, Wei and Zhang [65]
Silica aerogel	Pd ²⁺	689.65 mg/g	Parale, Choi, Kim, Phadtare, Dhavale, Lee, Panda and Park [66]
Mesoporous silica and chitosan-coated magnetite nanoparticles	Pb ²⁺ and Cd ²⁺	150.33 and 126.26 mg/g	Amin, Gulshan, Asrafuzzaman, Das, Rashid and Hoque [67]
Silica with 4,6-diacetylresorcinol	Pb ²⁺ , Cu ²⁺ , Co ²⁺ and Ni ²⁺	107.066, 89.767, 80.580, and 70.972 mg/g	[87]
Cellulose, silica nanoparticles, and heavy metal adsorption (Cd, Pb, Cr)			

DACSBNC	Cd ²⁺ , Hg ²⁺ , and Pb ²⁺	12.23, 13.87, and 31.40 mg/g	Yarkulov, et al. [73]
Silica-cellulose	cadmium metal, chromium metal, nickel metal, and zinc metal	95.09, 58.77, 94.56, and 97.50%	Royanudin, Utomo and Wonorahardjo [74]
cellulose-TiO ₂ /REC nanofibrous	multiple adsorptions of Pb ²⁺ , Cu ²⁺ and Cd ²⁺	total adsorption capacity of 69.81 mg/g	Wang, Zhan, Wu, Shi, Du, Luo and Deng [46]
Cellulose and silica coupling agents in absorption of heavy metals			
CAAS	As ⁴⁺	455 mg/g	Bisla, Kawamura and Yoshitake [79]
APTES-CA	Pb ²⁺	180 mg/g	Shaheen, Radwan and El-Wakeel [80]
Thiol-functionalized cellulose nanocrystals	Cu ²⁺	4.244 mg/g	Dang-Bao, Nguyen, Hoang, Lam, Phan, and Tran [81]
Thiol-functionalized cellulose nanofiber	Cu ²⁺ , Cd ²⁺ , and Pb ²⁺	49.0, 45.9, and 22.0 mg/g	Choi, Bae, Hasegawa, An, Kim, Lee and Kim [82]
Cys-CL	Cd ²⁺ and Pb ²⁺	130.7 and 180.9 mg/g	Chen, Wang, Hao, Ding and Fan [83]
CysR	Pb ²⁺	143.47 mg/g	Peng, Zhang, Dong, Qi, Zhai, and Zhao [84]
MCNC-DPTA	Pb ²⁺	440.0 mg/g	Shen, Jiang, Wang, Ouyang and Jin [85]
DPMC	Cu ²⁺	298.62 mg/g	Gao, Zhang, Liu and Liu [86]

5. Discussion

The effectiveness of adsorbents in heavy metal removal is a crucial aspect of environmental remediation, with natural-fiber-based, silica-based, and cellulose–silica coupling agents demonstrating notable performance in various studies (Table 1). The Cd²⁺ and Pb²⁺ ions were shown to be adsorbed at 130.7 and 180.9 mg/g by the Cys-CL, respectively. All of these studies demonstrated the Cys-CL's potential to remove Cd²⁺ and Pb²⁺ ions from water as an effective adsorbent. The Langmuir and pseudo-second-order models accurately predicted the spontaneous and endothermic character of the adsorption of both metal ions by the Cys-CL. The Cys-CL has a high potential for the adsorptive removal of Cd²⁺ and Pb²⁺ from aqueous solutions due to its good adsorptive properties and recyclability.

Banana fiber needle-felted fabric and banana peel have shown high removal percentages for heavy metal ions such as Pb²⁺, Zn²⁺, and Cd²⁺ (Ariharasudhan et al., 2022 [36]; Afolabi et al., 2021 [87]). These natural-fiber-based materials offer several advantages, including their biodegradability, abundance, and low cost. The fibrous structure of these materials provides ample surface area for adsorption, while their inherent properties make them environmentally friendly options for heavy metal remediation in soil and water bodies (Sharma and Agrawal, 2005) [4].

Silica nanoparticles and silica aerogels have exhibited remarkable adsorption capacities for a wide range of heavy metal ions, including Pb²⁺, Cu²⁺, and Pd²⁺ (Al-Wasidi et al., 2022a [88]; Parale et al., 2023 [66]). The high surface area and porous structure of silica-based materials contribute to their excellent adsorption properties, making them suitable for applications in industrial wastewater treatment and groundwater purification. Additionally, the stability of silica-based adsorbents under varying environmental conditions enhances their potential for long-term use in heavy metal removal processes.

Furthermore, coupling cellulose and silica with different functional groups, such as thiol-functionalized cellulose nanofiber and MCNC-DPTA, has demonstrated promising adsorption capacities for various heavy metal ions (Choi et al., 2020 [82]; Shen et al., 2022 [85]). These hybrid materials combine the advantages of both cellulose and silica, including abundant availability, low cost, and favorable adsorption properties. The synergistic effects resulting from the combination of cellulose and silica further enhance

the adsorption capacity and selectivity of these materials, making them suitable for tailored solutions in diverse environmental remediation scenarios.

5.1. Potential Applications in Real-World Scenarios

The diverse range of adsorbents offers opportunities for their application in real-world scenarios, including industrial wastewater treatment, agricultural runoff remediation, and groundwater purification. Natural-fiber-based adsorbents can be utilized in agricultural settings to mitigate heavy metal contamination in soil and water bodies, thereby promoting sustainable agriculture practices (Sharma and Agrawal, 2005) [4]. Silica-based materials hold promise for industrial applications due to their high adsorption capacities and stability under varying environmental conditions, making them suitable for large-scale heavy metal removal processes (Parale et al., 2023) [66]. Cellulose and silica coupling agents offer customizable adsorption properties, allowing for tailored solutions to specific environmental remediation challenges, including point-source and non-point-source pollution (Choi et al., 2020) [82].

5.2. Implications for Future Research Directions

Further research is needed to optimize the synthesis methods and functionalization techniques of adsorbents to enhance their adsorption capacities and selectivity for specific heavy metal ions. Exploring novel hybrid materials and surface modification strategies could lead to the development of more efficient adsorbents with improved performance and stability. Long-term studies evaluating the ecological impacts and sustainability of adsorbent-based remediation strategies are essential for assessing their viability in large-scale applications. Collaborative efforts between researchers, industry stakeholders, and policymakers are necessary to translate laboratory findings into practical solutions for addressing heavy metal pollution on a global scale.

6. Conclusions

Due to their characteristics, cellulose membranes could be used to lower the high cost of efficient application methods for water treatment. Due to its low cost, high removal efficiency, adaptable working conditions, selectivity, and good stability to remove heavy metal ions, adsorption is a promising approach that has attracted interest. Cellulose has a great affinity for substances with hydroxyl functional groups and is highly reactive with water. Additionally, cellulose contains hydroxyl groups (-OH), which are polar and hydrophilic (like water). The surface-located hydroxyl functional groups (-OH) of cellulose are essential for the adsorption of heavy metals. The ratio of metal/binding sites determines the adsorbent's capacity for adsorption, which explains how much adsorbent to use. The positively charged heavy metal ions and the OH functional groups of the cellulose adsorbents form hydrogen bonds, which lead to the establishment of adsorption. However, the lack of reactive functional groups and poor thermal and chemical resistance are disadvantages for cellulose. The most effective method of action for enhancing the performance of composites is the introduction of silica (SiO₂) into cellulose membranes, which provides design flexibility, permeation performance, durability enhancement, thermal stability, and increases its surface hydrophilicity.

A previous research investigation found that a silica–cellulose composite outperformed cellulose alone and silica alone in terms of hydrophilicity, water content and permeability, thermal stability, and the removal of heavy metal ions. Due to the presence of silanols (Si-OH), which are hydrophilic and have numerous reactive sites, on the surface of silica particles, the researchers found that adding silica to cellulose did not sufficiently modify it to bind to heavy metal ions. As a result, silane coupling agents (Si(OR)₃) are mainly utilized for silica surface modification. They have the capacity to combine an organic polymer (cellulose) with inorganic substances like silica nanoparticles. In order to improve the structure of nanomaterials for the removal of heavy

metals, the previous work showed that surface modification was performed on amines (-NH₂), thiols (-SH), carboxylic (-COOH), and methyl (-CH₃) groups. Previous studies have mostly shown that the adsorption process is best described by a pseudo-second-order kinetic model.

Overall, the findings from this comprehensive review shed light on the critical role of adsorbents in mitigating heavy metal pollution, a pressing environmental issue with far-reaching implications. The significance of this review lies in its synthesis of current research, which offers a holistic understanding of the strengths and limitations of different adsorbents. By highlighting the promising performance of natural-fiber-based materials, silica-based compounds, and hybrid cellulose-silica agents, this review presents a roadmap for the development of effective and sustainable solutions for heavy metal remediation.

Moreover, this review underscores the importance of continued research efforts to optimize adsorbent synthesis methods, assess their environmental impact, and explore novel hybrid materials. Such endeavors are essential for translating laboratory findings into practical applications, ultimately contributing to the preservation of water quality, protection of ecosystems, and safeguarding of public health. In essence, this review serves as a valuable resource for advancing the field of heavy metal remediation, guiding future research directions, and facilitating the development of innovative adsorption technologies with real-world applications. Through collaborative efforts and interdisciplinary approaches, the insights gleaned from this review can pave the way for effective strategies to address heavy metal pollution and create a more sustainable future for generations to come.

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