

Review

Advancements in Adsorption Techniques for Sustainable Water Purification: A Focus on Lead Removal

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Abstract: The long-term sustainability of the global water supply, with a paramount emphasis on cleanliness and safety, stands as a formidable challenge in our modern era. In response to this pressing issue, adsorption techniques have emerged as pivotal and widely recognized solutions for the removal of hazardous pollutants, with a particular emphasis on lead adsorption from wastewater. This comprehensive review explores the relentless advancements made in the adsorption domain, highlighting innovations using separation and purification techniques that surpass traditional metal oxide-based adsorbents. Of particular note is the growing exploration of alternative materials, such as starch, chitosan, nanoscale structures like zeolites and metal-organic frameworks, magnetic materials, and carbon-based substances for the development of inorganic adsorbents. These materials, with their remarkable capacity for nanoscale structural adjustment, possess extraordinary capabilities for effective contaminant removal, facilitating swift water purification. The literature survey for this review was conducted using the Google Scholar engine, with “adsorbents for lead remediation” as the starting keywords, resulting in approximately 6000 papers. The search was refined to focus on the last three years and specifically targeted review papers which are most relevant to lead remediation. More than 100 papers were analysed to investigate various techniques, surface modifications, and adsorbent materials for managing inorganic pollutants in water. This review also illuminates research limitations, with a specific focus on starch-based adsorbents in lead remediation. As we progress towards practical commercial applications, this review identifies challenges associated with the development of inorganic adsorbents and provides invaluable insights into future prospects. Surface modification emerges as a promising path, with the potential to substantially enhance adsorption capacity, potentially doubling or even quadrupling it. Moreover, the adsorbents demonstrate impressive regenerative capabilities, maintaining up to 90% regeneration efficiency after multiple cycles. In conclusion, starch-based adsorbents show considerable potential as effective agents for lead purification from aquatic environments. Nevertheless, the need for further research persists, emphasizing the optimization of the adsorption process and exploring the long-term stability of starch-based adsorbents in real-world scenarios.

Keywords: adsorption; advanced separation technologies; lead; inorganic contaminant; starch-based adsorbents; nanoscale structures



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1. Introduction

Unfortunately, various contaminants can threaten the existence of life on planet Earth [1]. Approximately 1.7 million losses of life globally result from drinking polluted water, according to Dinka [2]. Over 40 per cent of the Earth’s inhabitants do not have safe water for drinking [3]. This is because of the accumulation of waste and toxins in the

surrounding atmosphere. Some of these include harmful chemicals found in automobiles and tanneries. Other chemicals can be introduced into water sources through various means including industrial discharges, agricultural runoff, or accidental spills. When these chemicals are present in water, they can alter its chemical composition and properties, including its solubility [3].

The accumulation of wastes and the presence of heavy metals can hinder the growth of algae and other aquatic life [3]. These chemicals can affect the organisms' photosynthesis. These pollutant chemicals are resistant to biological degradation. Also, they can bioaccumulate in the food chain [4]. These pollutants are either organic or inorganic compounds with different properties.

When compared to water, heavy metals (inorganic material) have a higher atomic weight [5]. Like most toxic compounds, they are toxic even at low concentrations. Due to their accumulation, they are considered the main ecological issue in water [5]. Various sources such as paper manufacturing units, electroplating businesses, and insecticides release heavy metal particles into the environment [5]. When hydrated, heavy metal ions can become more toxic, which can affect the life cycle of aquatic life. Removing these toxic substances from water bodies is necessary to prevent their negative effects on aquatic life [5]. There are four main types of heavy metals that significantly affect individual health: lead (Pb), mercury (Hg), cadmium (Cd), and inorganic arsenic (As) [5].

Hence, prior to discharging industrial wastewater into the oceanic ecosystem, it is crucial to separate the inorganic pollutants from the wastewater. Environmental studies have extensively concentrated on devising efficient techniques to achieve this objective. Various methods such as precipitation, coagulation–flocculation, advanced oxidation, solvent extraction, adsorption, ion exchange, membrane filtration, ozonation, and reverse osmosis have been investigated as potential approaches for treating wastewater [6].

Among the above-mentioned approaches, the use of a solid medium in adsorption techniques is the most effective in the separation of inorganic pollutants from wastewater. Adsorption methods have several advantages over other techniques, including cost-effectiveness in terms of both initial investment and ongoing operation, ease of implementation, the ability to use a wide range of naturally occurring solid media for adsorption, simple design, and exceptional efficacy in removing harmful contaminants even at low concentrations [7]. One of the main advantages of adsorbents is their specialization. Generally, most of the purification techniques focus on one type of pollutant, either organic or inorganic.

Currently, there are numerous conventional and emerging adsorbents applied in the treatment of heavy metals, particularly lead from water. A comprehensive review of the existing literature reveals that lead remediation research is multifaceted. While some studies exclusively explore specific lead remediation technologies [8], others address heavy metals broadly [9]. Advanced lead remediation strategies are the primary focus of certain research studies [10], whereas others delve into conventional remediation techniques [11]. A limited body of literature investigates the impact of modification strategies on remediation technologies, particularly their role in enhancing adsorption capacity [12]. Furthermore, several studies emphasize practical and feasible water treatment methods for heavy metal removal [13], with a notable emphasis on adsorption techniques such as the utilization of agricultural wastes [14] or nano adsorbents [15], and so on.

Yet, there is a need for a comprehensive study to evaluate their performance by focusing not only on treatment efficiency but also on the crucial aspect of surface modification of adsorbents to enhance their adsorption capabilities. Thus, this comprehensive review investigates the determined advancements made in the adsorption domain, highlighting innovations that mainly focus on separation and purification techniques which surpass traditional metal oxide-based sorbents. In addition, it seeks to bridge a significant research gap by delving into conventional and modern technologies employed for lead separation from wastewater. It examines the crucial aspect of surface modification of adsorbents to enhance their adsorption potential for the removal of inorganic pollutants, using lead as an

illustrative example of an inorganic heavy metal. Throughout this review, the factors that exert influence on adsorption performance are thoroughly explored and analysed. Moreover, the comparison between two distinct types of adsorbent materials, nanomaterials and carbon materials, is presented, shedding light on their respective merits and limitations. One notable aspect that sets this review apart is its extensive focus on starch-based adsorbents for tackling inorganic contaminants, specifically lead.

2. Lead (Pb^{2+}) Toxicity and Sources

Residues of heavy metals are distributed into the water from various manufacturing facilities. Before they are discharged into the environment, they should be reduced to a level that is safe for human consumption [16]. However, they can still harm aquatic life and animals. Due to their widespread use in the industry, lead Pb^{2+} ions are considered the most toxic target heavy metals. They can affect the health and well-being of humans and animals due to their binding to various components of living organisms [16]. The LD50 of lead acetate is around 100–200 mg/kg for oral ingestion in rats. In general, lead is a toxic compound that can cause a variety of health problems, including brain damage, neurological disorders, and reproductive problems. Even low levels of exposure to lead can be harmful, especially for children [17,18]. Figure 1 shows the potential health complications resulting from lead compounds for both children and adults.

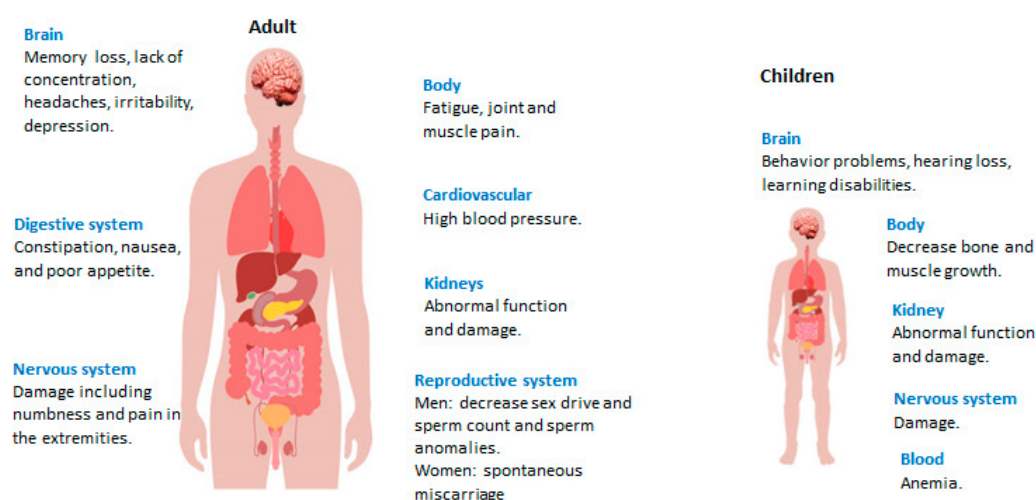


Figure 1. Health impact of lead exposure.

Lead Pb^{2+} is a metallic element that exists as *cerussite* (lead carbonate) and *galenite* (lead sulphide) [19]. Lead-acid batteries, electrical plating firms, electrical technology, steel construction companies, and explosive companies are the most significant sources of lead waste [19]. However, because of their single-atom-metal feature, Pb^{2+} ions seldom disintegrate in the ecosystem and must be controlled by a variety of means [20]. The United States Environmental Protection Agency (USEPA) has issued Temporary Potable Water Health Advisory limits of 0.015 mg/L for Pb^{2+} because they are damaging to human health [16]. Table 1 represents the main forms of lead Pb^{2+} in aqueous media, their generation source, industrial remediation, and whether they are easy or difficult to remove [21–25]. Natural Pb^{2+} waste has mainly been detected as a result of hill fires and volcanic explosions. Non-natural sources of Pb^{2+} pollution mainly refer to industrial emissions and transportation supplies [26]. The accumulated ions have serious consequences in humans. They have a destructive effect on the neurological system, haematology, cardiovascular disorders, and renal organs, especially in kids [20]. The incorporation of Pb^{2+} by marine organisms is reliant on various factors such as the pH value, dissolved inorganic carbon (DIC), temperature, and dead organic matter [20]. These factors can affect the speciation of Pb^{2+} , which can affect its toxicity, mobility, and bioaccessibility in aquatic systems [20]. In freshwater microalgae, a reduction in the internalization of Pb^{2+} was observed when DIC was present.

This finding suggests that the presence of DIC can facilitate lead ion uptake [20]. In fact, lead can be formed into complexes with anionic compounds in the environment. Multiple anionic varieties, like biota exudate, cell walls, and humic acid, can also contain ligands that are N-, S-, and P-. These can easily be used to form soluble and stable complexes in freshwater lakes with a pH range of 5 to 9 due to their affinity for Pb^{2+} . The most serious side effects of lead accumulation are renal and neurological system injury, mental abnormalities, and tumours in humans [5,27–29]. Many harmful metals are toxic after a short time, yet minimal amounts are critical for crucial functions [30]. In this context, permanently and successfully eliminating such contaminants remains a difficult challenge [3,31].

Table 1. Main common forms of lead (Pb^{2+}) in aqueous media, chemical formula, main characteristics, generation source, industrial remediation.

Form	Chemical Formula	Characteristics	Generation Source	Industrial Remediation	Reference
Lead nitrate	$(NO_3)_2$	A colourless crystal or white powder and is soluble in water	Used in pigments, as heat stabilizer in nylon and polyesters, in coatings of photo thermographic paper	Chemical precipitation, using lime, soda, or sodium sulphide precipitants	[21]
Lead chloride	$PbCl_2$	White crystals or powder, insoluble in cold water, soluble in hot water, low water solubility, odourless.	Occurs naturally as the mineral cotunnite, used in the synthesis of other lead compounds and is a precursor for many organometallic lead derivatives, lead-acid batteries, pigments. Used in making ceramics, infrared transmitting glass	Chemical precipitation using lime, soda, or sodium sulphide precipitants	[22]
Lead acetate	$Pb(CH_3COO)_2$	White crystalline powder or solid sweet taste, soluble in water and glycerine	Production of dyes and mordants, also used in hair dyes, and as a fixative for some photographic processes	Chemical precipitation	[23,24]
Lead carbonate	$PbCO_3$	White solid, occurs naturally as the mineral cerussite	Used in the production of pigments, glass, and ceramics.		[25]

3. Conventional and Emerging Methods for Lead treatment

There are various treatment methods that have been proposed to remove Pb^{2+} ions from aquatic media. These include chemical, physical, biosorption, and membrane filtration [20]. Precipitation and ion exchange are examples of chemical techniques. Membrane filtration adsorption and coagulation are part of the physical separation or purification approaches while bioleaching, biological stabilization, and biosorption are among the biological ones [5] (Figure 2). Although the above-mentioned techniques have some advantages, they have also encountered various limitations [5]. Chemical precipitation is widely used in industries to remove Pb^{2+} ions. This process can be performed by adjusting the water phase's pH [5]. It can also separate the compounds from the solution by separating them into carbonate, sulphide, or hydroxide. Despite its advantages, this method has its drawbacks [5]. Ion exchange is performed by using solid ion exchangers, which are commonly used in the recovery of Pb^{2+} ions from wastewater. This method has been implemented in the past to salvage metal plating effluents [5]. However, its practicality is often limited by the high cost of operation and secondary pollution [5]. Other than the high cost, the most common factors that prevent solid ion exchangers from being used effectively are secondary pollution and reusability issues [5].

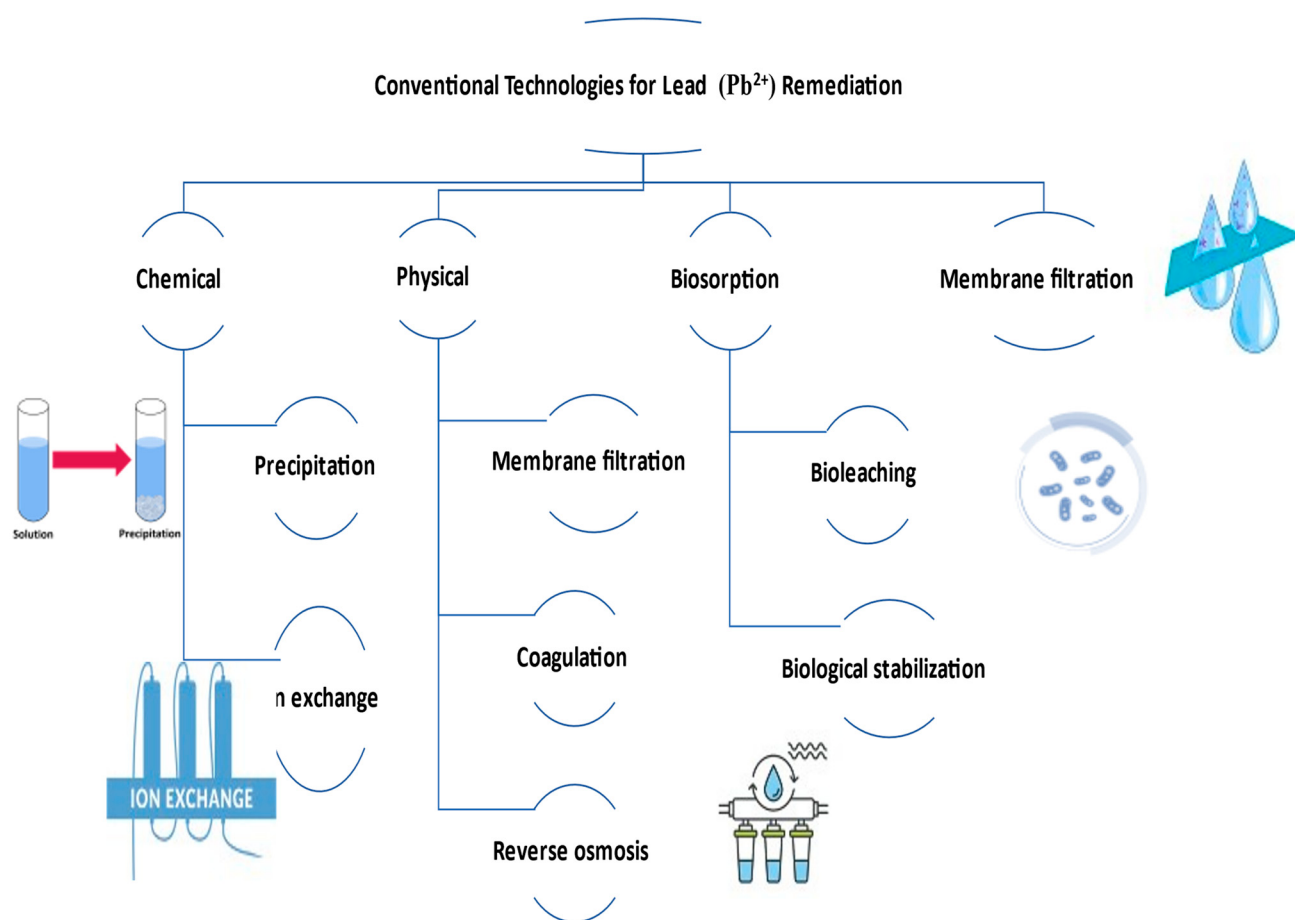


Figure 2. Conventional technologies for lead remediation.

Table 2 classifies types of conventional and emerging remediation technologies for aqueous solutions, showing methods, descriptions, examples, and references [5,32–36]. Physical approaches in the removal of contaminants offer numerous advantages such as low cost, minimal bi-product regeneration and high removal capacity [5]. Over the past two decades, the development of new technologies for the removal of heavy metals from aqueous discharge has been greatly supported by the use of economical materials such as agricultural, industrial (Figure 3), and urban residue [5]. Numerous studies have been carried out on various types of adsorbents such as chitosan, clay, lignin, activated carbons, and synthetic polymeric materials, as in Table 3. The widely used biopolymer known as chitosan is commonly used as an effective adsorbent for the removal of various heavy metals and hazardous substances such as proteins and dyes [37]. Chitosan is the only polycation found in nature, and its charge density varies according to the degree of acetylation and the pH of the medium [37]. The polymer's solubility is determined by its acetylation degree and molecular weight. Chitosan oligomers are soluble at all pH levels, from acidic to basic (physiological pH 7.4). It has good biodegradability and mechanical characteristics [37]. However, sometimes the dissolved sorbent can still be difficult to separate from the solution after the removal of the contaminants.

Table 2. Types of remediation technologies for aqueous solutions.

Conventional Technologies				
Category	Method	Description	Example	Ref.
Bioremediation	Bioremediation	Using microorganisms to break down contaminants	Bioremediation of petroleum hydrocarbon-contaminated groundwater using a mixed culture of microorganisms.	[32]
Chemical	Precipitation	Using (pH adjustment and flocculation)	Precipitation model is developed in the calcite precipitation via dynamic pH titration tests.	[33]
	Ion Exchange	Using an ion exchange resin to remove contaminants from water	Removal of heavy metals from wastewater using ion exchange.	[5,32]
Physical	Membrane Filtration	Using a membrane to remove contaminants from water.	Removal of microplastics from water using membrane filtration.	[32]
	Reverse Osmosis	Using pressure to remove contaminants from water through a semi-permeable membrane	Removal of fluoride from drinking water using reverse osmosis.	[32]
Emerging Technologies				
Nanoscale Materials	Nanoscale Materials	Using nanoscale materials to remediate contaminated water	Removal of arsenic from groundwater using iron oxide nanoparticles.	[36]
Phytoremediation	Phytoremediation	Using plants to remove contaminants from water	Removal of heavy metals from wastewater using water hyacinth.	[34]
Zero-Valent Iron	Zero-Valent Iron	Using zero-valent iron to remediate contaminated water	Removal of hexavalent chromium from groundwater using zero-valent iron.	[35]

Table 3. List of sorbent materials, their application, advantages, and disadvantages.

Material	Application Method	Advantages	Disadvantages	Pollutant	Reference
1. Activated Carbon	Adsorption column, batch mixing	High adsorption capacity, versatile, effective for a wide range of contaminants, commercially available	Expensive, can require regeneration or disposal after use, may require additional treatment for desorption of adsorbed contaminants	- Heavy Metals: Activated carbon can adsorb heavy metals like lead (Pb), mercury (Hg), cadmium (Cd), and chromium (Cr) from water and air - Chlorine and Chloramines - Ammonia (NH₃)	[38,39]
2. Silica Gel	Adsorption column, packed bed	High surface area, stable, commercially available,	Limited selectivity for specific contaminants, may require frequent replacement or regeneration, can release dust if mishandled	- Ammonia (NH₃) - Sulphur Dioxide (SO₂)	[20,40,41]
3. Zeolites	Fixed bed, packed columns	High selectivity for specific ions, ion exchange capabilities, stable, regenerable, commercially available	Limited capacity for certain contaminants, potential for clogging in fixed-bed systems, regeneration process may require additional chemicals.	- Ammonium (NH₄⁺) - Lead (Pb), cadmium (Cd)	[5,42–44]

Table 3. *Cont.*

Material	Application Method	Advantages	Disadvantages	Pollutant	Reference
4. Chitosan	Application Method: Batch mixing, filtration, membrane adsorption	Natural, biodegradable, versatile, high metal ion adsorption capacity, effective for heavy metals and dyes	Limited stability in acidic conditions, limited regeneration capabilities, potential for gel formation in aqueous systems.	- Lead (Pb), cadmium (Cd) - Chromium (Cr)	[5,45,46]
5. Polymeric Resins	Column, batch mixing	High selectivity for specific ions, excellent ion exchange capabilities, regenerable, commercially available	Limited selectivity for specific contaminants, variable quality depending on feedstock, may require pre-treatment for efficient adsorption.	- Lead (Pb), cadmium (Cd) - Arsenic	[47–49]
6. Biochar	Fixed bed, soil amendment, filtration	Fixed bed, soil amendment, filtration	Limited selectivity for specific contaminants, variable quality depending on feedstock, may require pre-treatment for efficient adsorption.	- Lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn) - Fluoride (F[−])	[50–52]
7. Natural Clays (e.g., Bentonite)	Mixing, packed bed, sedimentation	Abundant, cost-effective, natural, versatile, can remove various contaminants including heavy metals and organic compounds.	Limited adsorption capacity for some contaminants, potential for clogging, variable performance depending on clay type and composition.	- Lead (Pb²⁺), cadmium (Cd), copper (Cu), zinc (Zn), and nickel (Ni) - Nitrate (NO₃[−]) - Fluoride (F[−]) - Chloride (Cl[−])	[53,54]

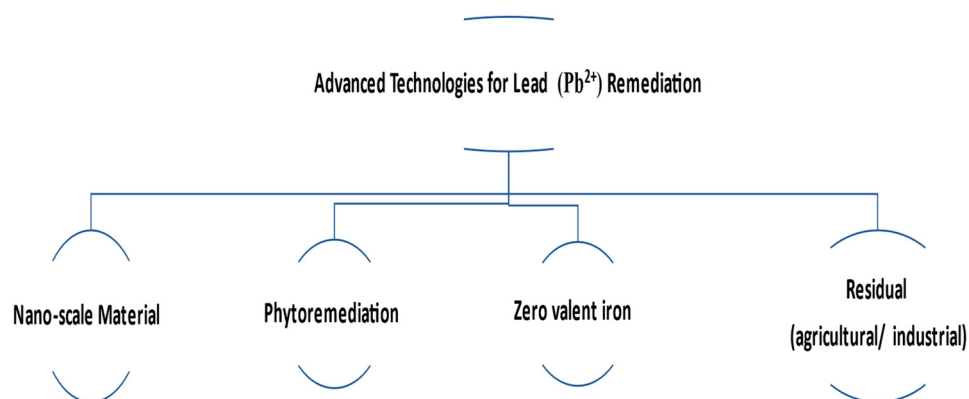


Figure 3. Advanced technologies for lead remediation.

The various kinds of adsorbent materials used to remove inorganic/heavy metal contaminants from effluent can be categorized into three main categories expressed by organic, inorganic, and by-products released from industry [55]. Others have classified them as natural, synthetic, and modified. The low price and great productivity of these materials are the main factors that determine their effectiveness in real-world wastewater systems [20]. The capacity of the adsorbent to remove contaminants depends on various factors, such as type of material, the size of the pore, and the structural characteristics of the adsorbent [55]. Large-sized surface areas of adsorbents provide many sites for the physical and chemical entrapment of contaminants in wastewater [55].

In terms of their industrial applications, various features such as mechanical integrity, recyclability, and adsorbent stability need to be addressed [55]. The flexibility of the adsorbent to be modified also can be an important factor in improving the adsorption performance. Hence, several adsorbent materials from carbon material are ideal choices. Carbonaceous adsorbents are the first choice for researchers who are looking to remove harmful metals and chemicals from water. These are made from various materials such

as graphite, activated carbon, charcoal, and activated sludge [56]. Their porous structure allows them to adsorb non-organic and organic chemicals in either gaseous or liquid phases. The primary source of activated carbon is usually coal, coconut shells, peat, and lignite. It can also be produced from various other precursor materials such as walnut wood, palm shell, coconut husk, wheat bran, and rice husk [56]. The physical and chemical characteristics of activated carbon can be affected by their preparation process and the precursor biomass [56]. Most of the known carbonaceous materials used to remove chemicals are either activated carbon or carbon nanotubes (CNTs). Carbon nanotubes can be categorized into multi-walled (MWCNT) and single-walled (SWCNT) types [56]. Activated carbon is usually less efficient due to its low porosity, while carbon nanotubes are usually used for comparison [56]. The high adsorption capacity of activated carbons can be attributed to their pore structures and porous nature. Compared to the average pore diameter of SWCNT and MWCNT, the average size of activated carbons was five times lower [38]. Table 4 demonstrates examples of adsorbents used for Pb²⁺ adsorption in an aqueous medium, and reports their adsorption capacity, regeneration, and equilibrium time [57–63].

Table 4. Model examples of adsorbents used for lead detoxification.

No.	Material	Adsorption Capacity mg/g	Regeneration %/No. Cycle	Equilibrium Time (min)	Ref.
1	Bio-adsorbent modified with carboxy methyl chitosan (BCCMC)	210	NA	60	[57]
2	Jujube pit biochar (JPB)	137.1	70%/5	30	[58]
3	Formaldehyde-polymerized peanut skins (FPPS)	217.6	NA	NA	[59]
4	Andean Sacha inchi shell biomass (SISB)	17.066	NA	NA	[60]
5	Improved lignin material (ILM)	17.5	NA	240	[61]
6	Carboxymethyl lignin nanoparticles (CMLN)	333.26	NA	NA	[62]
7	Poly Ethelene imine-grafted cellulose (PEI)	248.2	>86%/5	4800	[63]

As mentioned in Table 4, different materials have been used to adsorb lead ions from aqueous systems. Carboxymethyl lignin nanoparticles have the highest adsorption capacity while Andean Sacha inchi shell biomass has the lowest capacity. This is justified by the nature of the adsorbed material. Nanoparticles have the highest adsorption capacity among all adsorbents. They have nanosized particles with a high surface-to-volume ratio and thus enhance their adsorption capacity. There are a few aspects in the determination of high-quality adsorbent material such as equilibrium/adsorption time, regeneration capacity, bi-products, recyclability, dose of adsorbent, and many more. Equilibrium time is an important criterion to determine the efficiency of the adsorbents and their applicability. Based on this, Jujube pit biochar showed the least equilibrium time (30 min) compared to Poly Ethelene imine-grafted cellulose with 4800 min. Logically speaking, adsorption time is a crucial aspect when evaluating the activity of an adsorbent. This means adsorbents with the lowest equilibrium time are the best choice as a practical and applicable adsorbent. Additionally, the regeneration capacity is an important factor that determines adsorbent feasibility and reproducibility. In other words, regeneration or recyclability can decide the number of cycles that could be used by the same material with a good adsorption capacity. The regeneration cycle also determines the durability of the adsorbent, which can affect the cost of adsorbent maintenance. This limits the accumulation of such a material and allows for metal separation. Only two studies out of seven studied the regeneration of the adsorbents as in JPB and cellulose/PEI. On the other hand, a limited number discussed the time of equilibrium in spite of its importance in nominating the best-adsorbed material. Wood manufacturing units incorporate bark as a by-product. Tannin is an organic substance that can be used to remove heavy metal ions. It contains polyhydroxy compounds that can adsorb metal ions [5]. Masri et al. [64], for instance,

were the first to report that Douglas fir and black oak bark can remove mercury, lead, and cadmium [5]. The most commonly used in-process adsorbents for wastewater treatment are composed of metal oxides, layered double hydroxides (LDHs) [50], silica [65], clays [66], magnesium oxide (MgO), and zeolite [67]. They also adsorb metal–organic frameworks MOFs [68]. There are also various types of substances that can be utilized for water treatment. For instance, pre-treatment can be performed to improve the efficiency of the process [69]. In addition, chemically modified adsorbents made of metal/metal oxide are commonly used for wastewater treatment both in bulk and nanostructured [70]. They have various advantages such as their high mechanical stability, flexibility, and capacity to adsorb metal ions. Referring to adding porosity and adjusting morphology for these materials, nanostructured material with higher surface area can be created to improve the efficiency of the treatment process. Since nanoparticles are small, they can be prone to aggregation. This can be prevented by using porous supports such as silica [71], carbon [72], clays, or biochar [73]. For the removal of pollutants from wastewater, various kinds of metal oxides are commonly used, including iron oxide (Fe_2O_3 and Fe_3O_4), aluminium oxide (Al_2O_3), manganese oxide (MnO_2), titanium oxide (TiO_2), zinc oxide (ZnO), magnesium oxide (MgO), and zirconium oxide (ZrO_2) [3,74]. On the other hand, since heavy metal has a polarity, surface modification or chemically modified metal oxides (CMMOs) are ideal to be applied as adsorbents. Additionally, a superior surface must maximize the process's effectiveness to ensure high adsorption capacity. Numerous studies claim that the removal of heavy metals with sufficient surface resulted in better capacity. In a study by Saleh et al., a multi-wall carbon nanotube (MWCNT) composite coated with manganese dioxide (MnO_2) was used as an adsorbent for the removal of lead [75]. The researchers noted that the optimal removal rate was achieved between pH 6 and 7. They noted that the increase in the layer thickness of the nanocomposite led to the higher removal of Pb (II). They also found needles with a diameter of up to 30 nm and a length of up to 300 nm [3]. They could remove Pb (II) ions with 97% efficiency, and the optimal condition was found at pH-5.2 and $C_0 = 5 \text{ mg L}^{-1}$. The properties of lead ions have been fitted by Sips isotherm and Langmuir. The unique physical properties of iron and metal oxides, which enhance the removal capacity, are also responsible for this. The metal removal capacity of a superparamagnetic nanosphere was enhanced by its core–shell structure and the functionalization of the amino group. The improved capacity was observed when the structure was grafted with an amino group. The metal removal efficiency of various ions, such as cadmium (II), copper (II), and lead (II), were 99.96%, 199.9 mg g^{-1} , 88.05%, and 177.8 mg g^{-1} , 90.79% and 181.6 mg g^{-1} , respectively. The process was carried out according to Langmuir's model, and the kinetics exhibited pseudo-second-order characteristics [3].

Another study by Ignatius et al. 2014 investigated the rhizo-filtration of lead-containing wastewater using *Plectranthus amboinicus*, an aromatic medicinal plant [76]. This study was conducted due to the motivation of heavy metal contamination in water bodies and groundwater which leads to many aquatic and terrestrial plants accumulating heavy metals when grown hydroponically. The study suggests that the plant can be considered for the clean-up of contaminated wastewater along with biomass disposal alternatives [76]. However, mass production of such a phytoremediation method necessitates a deeper knowledge of plant–metal interactions, particularly the capacity of various plant species to accumulate metals in different regions of the plants, and that is essential for efficient remediation.

4. Multiple Modification Strategies for Conventional and Emerging Adsorbents

Adsorption is always considered a surface phenomenon; therefore, its efficacy is highly reliant mostly on the surface chemistry of both modified and natural materials. Surface functions are determined by the nature of the precursor and the mechanism applied for its modification. Abegunde et al. conducted a review discussing the influence of chemical changes on adsorbent performance [77]. Physicochemical alteration of the adsorbents seems like customizing a material's surface by manipulating its physical, chemical, or even biological properties as illustrated in Figure 2. These features distinguish the material

from the original and make it suitable for the targeted function. Adsorbents are commonly employed by scientists due to their high surface area, high adsorption capacity, and quick kinetics [3]. Moreover, a good adsorbent should be non-hazardous and not attach to pollution particles. It should be highly selective for contaminants even with trace amounts and easily regenerate [3]. Based on the previous features, as well as other different structural and morphological traits, scientists proved that nanomaterials (NMs) could perform as active adsorbents [3]. When converting from micrometre (m) to nanoscale (nm), the energy of the surface rises rapidly, ending with poor particle stability. In addition, higher agglomeration is caused by increased van der Waals bonding forces [3]. Therefore, surface modification would enhance stability in addition to increasing dispersity and thus will control agglomeration. Table 5 represents the capacity difference between modified and unmodified adsorbents used for different types of adsorbates (Figure 4).

As stated in the previous table, the comparison between the modified and unmodified form of the adsorbents shows clearly that the modified form of modified adsorbents is superior in adsorption capacity to the unmodified one. This shows that adsorption is a surface phenomenon, and once the surface of the adsorbent can be improved by choosing the ideal modification strategy, adsorption stability can be achieved perfectly. Among all the previous examples demonstrated in the table, cellulose has the highest adsorption capacity, which reached 976 mg/g for the modified one compared to 138 mg/g for the unmodified one. Cellulose was used for the adsorption of copper ions. It was the best applicable material with 85% regeneration. On the opposite side, chitosan had the lowest adsorption capacity with its modified state, which was around 60 mg/g, and it was used for the adsorption of lead ions. Both studies number three and seven investigate cellulose as the adsorbed material with different modification strategies. Additionally, the adsorbate in study three was for Cu while in the seventh study, it was used for the adsorption of metal ions Pb^{2+} and Cu. Both studies almost have the same percent of regeneration, 85 and 86, respectively. This obviously indicates that HPFC has maximized the surface area with multiple functional groups that guaranteed better adsorption capacity. Among the previous adsorbents, different materials are used for remediating lead ions including lignin, chitosan, biochar, and cellulose. Their adsorption capacity for Pb^{2+} was in the following order: biochar (594.17 mg/g), cellulose (184 mg/g), lignin (126 mg/g), and chitosan (59.85 mg/g). Through a microwave heating process, the nanoparticles of carboxymethyl-modified lignin were prepared. The two-stage antisolvent processes were utilized to decrease the adsorbent's solubility and improve its extraction ability. The adsorbent was able to remove lead ions with a maximum sorption value of 333.26 mg/g. The effect of pH value on the adsorbent's performance was studied in a range of 2.04 to 7.06 for lignin nanoparticle LNPs. It was shown that the former exhibited a higher adsorption capacity when the pH level increased to 6.03. On the other hand, the latter exhibited a lower sorption rate when the pH level was lowered to 2.04, which is related to more H^+ ions that combine with the $-COO^-$ group in the solution and form $-COOH$. The results of the study revealed that the carboxymethyl lignin particles exhibited better adsorption characteristics when compared to the lignin nanoparticles when it was at pH 6.03. They also showed better regeneration abilities [5].

Various investigations have been conducted on the modification of cellulose nanomaterials to improve their sorption properties. These modifications can be used to remove inorganic contaminants like copper ions for example [78]. The incorporation of both inorganic and organic groups can be achieved by placing titanium dioxide NPs on the surfaces of cellulose nanogels [34]. This allows for the creation of a low-energy surface that can act as a hydrophobic and oleophilic material. They can also absorb diverse organic solvents and oil from the water's surface, which has a capacity of up to 90% vol/vol [34].

Table 5. Comparison between modified and unmodified Adsorbents used for heavy metals (mainly Pb and Cu) source of WW, contaminants' initial concentration, and operational conditions.

No.	Adsorbent Material/Modification	Modified/Unmodified	Adsorption Capacity (mg/g)	Regeneration	Adsorbate	Source of Wastewater	Initial Concentration of Contaminants	Operational Conditions	Reference
1.	Lignin/eucalyptus lignin nanosphere	ECLNP's	126	After 3 cycles reached around 94	(Pb ²⁺) + Cu ²⁺	NA	Pb ²⁺ –20 mg/L Cu ²⁺ –20 mg/L	pH Pb = 6 pH Cu = 5.5 °C = 30	[62]
		LNP's	10						
2.	Chitosan/carboxymethyl nanoparticles	XCMCP	59.85	After 7 cycles it changed from 32.1 to 29.7	(Pb ²⁺)	Electroplating, Mine, and battery production wastewater	NA	pH = 6	[16]
		Unmodified form	NA						
3.	Cellulose/hyperbranched polyamide functionalized cellulose	HPFC	138 Cu (II)	85% of Cu (II) could be removed after 5 cycles.	Cu ²⁺ ions	Textile wastewater	NA	pH < 8.33 298 k	[78]
		Unmodified form	NA						
4.	Biochar/modified with carboxy methyl chitosan	BMCMC Unmodified BC	594.17 NA	Shows good reusability and stability	Pb ²⁺	Sewage sludge	25 ml	pH Pb ²⁺ = 5	[57]
5.	Cellulose/polyethylene imine	Cellulose/PEI Pure cellulose	184.0 25.6	86% after 5 cycles	Heavy metals (Pb ²⁺ , Cu)	Sewage	500 mg/L	pH Cu ²⁺ = 2 pH Pb = 5 room temperature	[63]

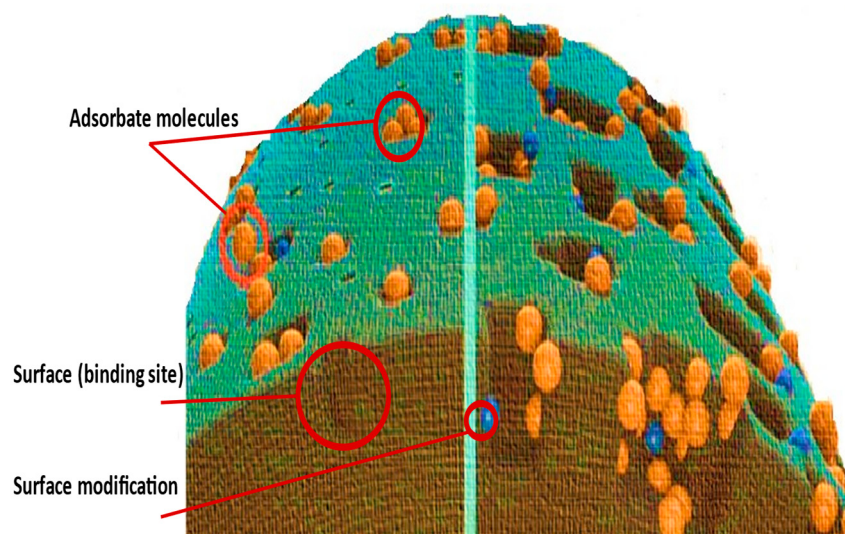


Figure 4. Surface modification of adsorbents.

A study conducted by Loganathan and colleagues analysed the various surface modification techniques that can be used to improve the sorption capacity (from 125 mg g^{-1} for amination to 363 mg g^{-1} for protonation) of adsorbent materials [79]. They found that the most effective modifications were the protonation and amine-grafted techniques [79]. However, the properties of metal oxides, such as titanium dioxide, manganese oxide, and iron oxide, are highly advantageous when it comes to reducing environmental risks. They can be used as sorbents that can eliminate various water pollutants, such as heavy metals and industrial chemicals. Due to their various characteristics, such as their size, crystal structure, surface area, and morphology, they have been studied extensively [79].

One paper shows how sewage sludge, which is waste from a polluted water treatment medium, can be reused as a solid support and then modified to form a bio-adsorption biochar. The modified biochar exhibited improved stability in water and was more beneficial for the environment. The bio-adsorption process was performed by reducing the pH level of the mixture. It exhibited better performance than that of conventional adsorbents, with a capacity of 594.17 mg g^{-1} for Hg (II) and Pb (II). Also, it unveils good reusability and stability. The results of the study demonstrate how waste valorization can be achieved through a simple and green approach. It involves turning the sewage sludge into a biochar adsorbent that can be used to remove heavy metal ions from the waste water [3].

5. Adsorption Mechanism and Alternative Remediator

The adsorption process is regarded as the most effective way to treat toxic compounds in wastewater [5]. However, the advantages of the adsorption process are numerous, such as reusability, besides its potential to remove toxic substances from wastewater successfully and effectively at a low cost. Furthermore, it is also more eco-friendly than traditional methods. A wide range of natural adsorbents were produced for the removal of metal ions from effluent [5]. Some of the characteristics that are required for the selection of an effective adsorbent include their cost efficiency, surface area, size, and distribution of pores in addition to their availability of functional moiety and polar properties for those sorbents [5].

Understanding the adsorption process is also important to ensure better performance. The process of adsorbing involves transferring a substance known as solutes onto a solid surface. The two kinds of forces that interact with adsorbate and are present in the solution are physical and chemical [5]. Physical ones are weak forces with no specificity in nature. Since the former is weak, adsorbed molecules can be easily attached to any surface. On the other hand, the chemical process is specific and involves the use of electrostatic or covalent

bonds to bind adsorbents while physical adsorption relies on van der Waals, hydrogen bonding, and dispersion interactions [5].

Due to the presence of different types of pollutants in wastewater, studies on the selective removal of these pollutants have become more important. One of the most important factors that can be considered when it comes to optimizing the performance of an adsorbent is the mechanism by which it interacts with the substance. The various parameters that affect the capacity of a particular adsorbent are also considered to ensure that they are effective. These include the pH level of the solution, the concentration of the adsorbates, the contact time, and the coexistence of other components [55,80]. The rate at which a particular adsorbent can remove a substance depends on its chemical and physical properties. It starts fast and slows down steadily as it reaches equilibrium. This can be influenced by the various factors that affect the concentration of adsorbates and the solid phase's equilibrium (solution parameters) [5]. In addition, the importance of material design and engineering in achieving high performance and selectivity for environmental purification and energy conversion applications is evident [81,82].

5.1. Adsorption Isotherm

The concept of the adsorption isotherm is a useful tool for analysing the optimal performance of an adsorbent and determining the interactions between an adsorbent and a substrate. It shows the distribution of adsorbed materials between an adsorbent (homogeneous or heterogeneous) and an adsorbate. This distribution depends on the type of adsorbent, its composition, and the exposure type [5]. Different fitting models were used to describe the adsorption mechanism and the interaction between adsorbent–adsorbate, and adsorbate–adsorbate. Table 6 describes some of these models [83,84]. Adsorption kinetics describes mass transfer, diffusion, and surface reactions to determine the adsorption rate. External mass transfer over the boundary layer, diffusion within adsorbent particles into pores, and bond formation at active sites are all steps in the adsorption process. Lagergren's pseudo-first-order and Ho's pseudo-second-order kinetic models are commonly used, while interfacial and particle diffusion models are used to explain the adsorption mechanism [73].

Table 6. Kinetics and equilibrium modelling equations.

Model	Plot
Langmuir	$q_e = \frac{q_m a_L C_e}{1 + a_L C_e}$
Freundlich	$q_e = a_F C_e^{b_F}$
BET	$q_e = \left[\frac{q_m B C_e}{(C_s - C_e) [1 + (B - 1) (\frac{C_e}{C_s})]} \right]$
Sips (Freundlich–Langmuir)	$Q_e = \frac{K_s Q_{ms} C_e^{ns}}{1 + K_s C_e^{ns}}$

5.2. Factors Affecting Adsorption Mechanism

There are various types of adsorbents that could be used to get rid of pollutants from effluents. They were categorized into three categories: inorganic, industrial, and organic by-products. The efficiency and cost of these materials are the two main factors that determine their effectiveness in real-world wastewater systems. The capacity and efficiency of adsorbent materials are the most important factors that control their proficiency in removing contaminants from wastewater. Besides their physical properties, other factors such as their chemical stability and mechanical properties can also affect their capability [85].

Large surface areas of adsorbent materials can be used to afford additional sites for both physical and chemical catching of pollutants in wastewater. Furthermore, a large surface area can maximize interaction between contaminant particles and adsorbed material, which increases the adsorption capacity. In terms of their industrial applications,

certain features such as mechanical integrity, recyclability, and shear are required to be addressed. Due to the presence of various types of pollutants in wastewater, studies on the selective removal of certain contaminants need more focus. One of the most important factors that can be considered when it comes to optimizing the performance of adsorbent materials is their ability to adsorb certain contaminants [85].

The surface of an adsorbent material such as xanthate cross-linked with chitosan/PVA (XCMCP) exhibited a microporous structure and an irregular shape. Some of the particles that were adsorbed on this surface were cubic-shaped, which is attributed to Fe_3O_4 . Compared to other materials such as poly (alcohol), chitosan, and Fe_3O_4 , the XCMCP surface was more rugged. The regular surface of XCMCP enhanced its ability to adsorb Cu^{2+} adsorption. After the process, the morphology of the adsorbent material's surface changed, with some initial pores being filled in, hexagonal particles being produced, and crystal structures being observed. These structures were different from the ones that were seen after Pb^{2+} adsorption, but they were still similar in appearance [5].

5.2.1. Effect of Hydrogen Ion Concentration

The measure of hydrogen ion concentration in a solution is known as pH. It shows the degree to which the solution's acidity affects the metal ion's adsorbent. For instance, by altering the surface loads of the bio sorbents in addition to the ionizing degree in an aqueous solution of the metal ions, the pH effect can be observed. A pH level that is moderate can be used to remove heavy metal ions [86]. This is because the sorbent surface's deprotonation can increase the number of negatively charged sites, which results in better electrostatic attractions between the metal cations and the adsorbent surface, and thus increases the capacity of the adsorbent [86]. At a lower level of pH, the hydrogen ions will increase, and thereby the number of positively charged sites can increase, which positively increases the repulsive interactions between metal ions and the adsorbent surface. Thus, can lead to a reduction in the metal ion adsorbent's effectiveness [86].

A study conducted on the effects of different pH levels on the sorption of Pb^{2+} ions by modified polyglycyl methacrylates revealed that the sorption rate decreased significantly. In fact, the extraction of Pb^{2+} ions by the resins increases as the pH of the solution increases, particularly in the pH range of 1–4.8. Higher pH promotes electrostatic attraction between positively charged metal ions and negatively charged biosorbent surfaces, increasing adsorption efficiency. The presence of electrostatic repulsion between these positively charged species on the adsorption surface and metal ions may explain the delayed adsorption [5].

Adsorption of Pb (II) and Cu (II) on the surface of chitosan/ TiO_2 nanofibers, for example, was greatest at pH 6.0 and lowest at pH 2.0 to 4.0 [5]. According to similar research, raising the pH from 4.0 to 6.0 increased the percentage of Cd (II) adsorption, which subsequently remained constant (97%) at pH 9.0 while raising the pH to 11.0 reduced the adsorption percentage to 80% [5].

5.2.2. Adsorbate Concentration

Another important factor in determining sorbent removal effectiveness is the initial concentration of sorbent used. The proportion of metal extraction increases as the amount of sorbent increases. This might be because of the presence of sorption spaces that the adsorbate will connect to. The estimation of adsorbent concentration offers an indication of how much sorbent is required for the sorption process [5].

5.2.3. Time of Interaction

It was discovered that the rate of adsorption increased with increasing reaction time until an equilibrium was reached between the number of adsorbents adsorbed on the adsorbents and the number of sorbates remaining in the solution. In general, adsorption occurs fast in the preceding stages and gradually slows when the metal achieves equilibrium in the liquid and solid phases [5]. Metal ions with various concentrations reached equilibrium at different times, which relies on the concentration of metal ions, adsorbents, starting

concentration, and solution temperature. Gupta et al. investigated lead ion removal using three distinct amine adsorbents, PAN-EDA, PANTETA, and PAN-TEPA. It was discovered that removal efficiency increases with time up to a certain limit [5].

5.2.4. Coexisting Ion

Because industrial wastewater contains a variety of anions and cations, assessing the influence of coexisting ions is critical in adsorption research. The various ions may compete for the same sites in adsorption. It is desirable to create a multi-functional sorbent capable of extracting various metal ion types [5]. Kesenci et al. created a poly (ethylene glycol dimethacrylate-acrylamide) copolymer for the extraction of (lead, mercury, and cadmium) metal ions from an aqueous solution, and the order of metal absorption was discovered to be lead > cadmium > mercury. For a 1.0 mg/L concentration of every metal, cadmium adsorption was found to be greater in the mixture (0.52 mmol) than in the individual solution (0.37 mmol) [5].

5.2.5. Type of Adsorbent

The characteristics of the biomass material and its functional groups are also important when it comes to the design and application of adsorbent types. For instance, the efficiency of a natural adsorbent can vary depending on its type and surface charge. For example, when lignin is used for catching lead ions, the maximum loaded amount of metal on the surface of lignin equals 1865 mg/g, compared to 155.4 mg/g when zeolite is used (Figure 5) [5].

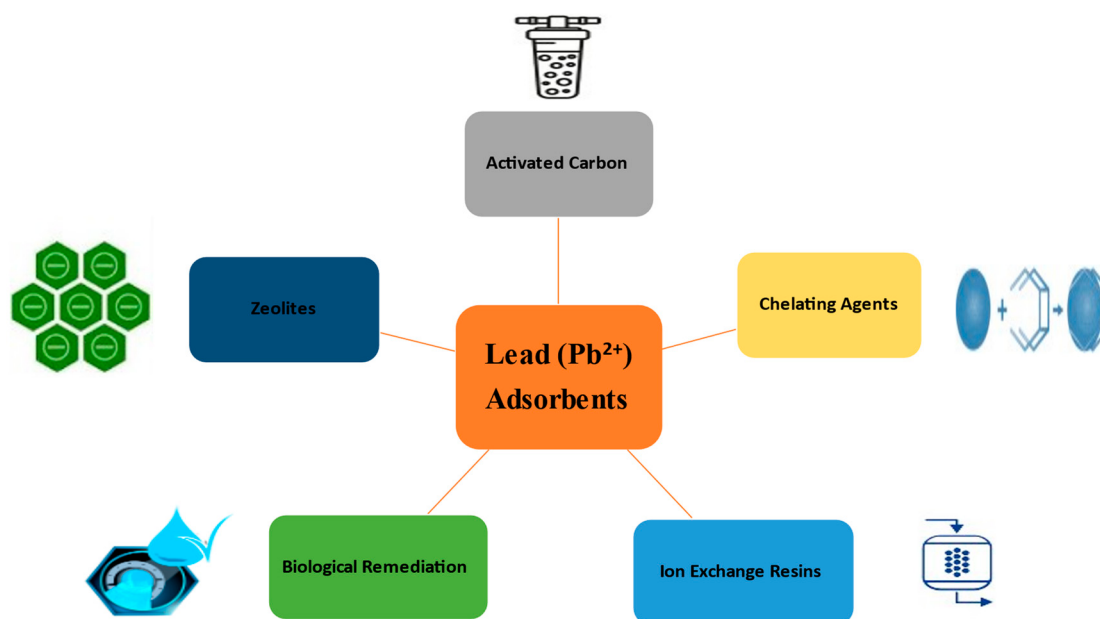


Figure 5. Different adsorbents for lead separation/purification.

The surface charge of HPFC (hyperbranched polyamide functionalized cellulose), which is a type of functionalized cellulose, was determined by analysing the pH range from 5.0 to 11.8. It was observed that increasing the pH level decreased the zeta potential. The isoelectric point (pHip) is the pH value at which a substrate has a zeta potential of zero. The (pHip) of HPFC was found to be 8.33. It indicates that the surface charge of the material is negative at pH more than 8.33 and positive at pH 8.33. The abundant HPFC amine groups interacted with H⁺ ions and formed cationic groups at pH 8.33 [78].

5.2.6. Temperature Effect

Temperature is a crucial parameter that significantly impacts the efficiency of the adsorption process for remediation purposes. The thermodynamic properties of the adsorp-

tion process were evaluated to ascertain whether the process is endothermic or exothermic. Thermodynamic parameters, namely Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), were determined using the following equation:

$$\Delta G^\circ = -RT \ln K_c \quad \text{-----} \quad K_c = C_{ad}/C_e$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

In these equations, R represents the ideal gas constant, T denotes the absolute temperature measured in Kelvin (K), K_c is the equilibrium constant, C_{ad} signifies the quantity of Pb (II) adsorbed onto the adsorbent per litre of solution (mg/L), and C_e indicates the equilibrium concentration of Pb (II) in the solution (mg/L). The changes in enthalpy and entropy were calculated from the slope and intercept, respectively, of the plot of $\ln K_c$ versus $1/T$. Nonetheless, for the process to be considered thermodynamically feasible, the value of ΔG° must consistently be negative [87].

5.3. Regeneration/Recycling

The process of adsorption is widely used to remove inorganic contaminants from water. However, it can be very challenging to manage the spent adsorbents after the treatment process has been completed [88], in terms of reusability and enhanced effectiveness. For instance, the recovery of those materials can be very costly. The economic reaction is the regeneration of adsorbents, which can be performed by using various solvents such as HNO_3 , NaOH, and EDTA [5]. Research studies on the regeneration of chitosan-based adsorbents have been conducted [5].

Current methods for recovering and regenerating adsorbent materials depend on the contaminant and the materials used, with regenerated samples often performing well compared to the original ones [89]. Managing spent materials after treatment has been a challenge, but they can potentially be reused in various applications like catalysts, soil amendments, or capacitors, reducing both waste and application costs. Chitosan, widely used in fields like wound healing and drug delivery, may also have potential applications in improving bioimaging and tissue repair using spent materials [90].

The rapid emergence and evolution of nanotechnology have led to the development of new materials and technologies. To meet the diverse requirements of these new applications, various efforts have been made to improve the surface properties of particles. These include the creation of multi-functional composite materials and the tuning of their bulk properties [86]. These new materials can be used to adsorb various types of particles and can recover them quickly and efficiently. They also have a high specific surface area-to-volume ratio and are not prone to internal diffusion. Polymeric shells can also be used to create magnetic nanoparticles that can be tailored to meet the diverse needs of different applications. These include drug delivery, high-density data storage, and magnetic resonance imaging (MRI) [86]. Table 7 demonstrates different nanomaterials utilized as adsorbents mainly for lead ions. These nanomaterials represent different magnitudes for their adsorption capacity and regeneration potential, in addition to equilibrium time. The presented materials are arranged and include nanoparticles [91–95], nanocomposites [34], nano magnetite [15,87,94,96–101], nano crystals [102], nanotubes [103], metal oxide [104–106], graphene [107], activated coconut waste [108], egg shell [109], grafted and cross-linked [110] nanoparticles. The adsorption capacity for the above-mentioned materials varies from 2.564 mg/g in the case of NM Full-IPN's ([Poly(Thiourea-Formaldehyde)—Epoxy resin]) Nanomagnetic [98] up to 1265.8 mg/g for SnO_2 [15,87,91–112].

Table 7. Different nanomaterials utilized as adsorbents mainly for lead ion Adsorbents (for lead).

		Ads. Capacity (mg/g)	Regeneration Percent/Cycle	pH Media	Initial Conc. Lead (Pb ²⁺)	Equilibrium Time (min)	Mechanism of Adsorption	Regeneration Method	Ref.
1.	efFe ₃ O ₄ /SiO ₂ (SiO ₂ /(3-Aminopropyl)triethoxysilane-Coated Magnetite Nanoparticles)	17.65	90%	pH 4	10 mg/L	NA	Chelation	Acid treatment	[91]
2.	Magnetite Fe ₃ O ₄ /Chitosan nanoparticles (Fe ₃ O ₄ /CSNPs)	79.29	NA	pH 6	15,20 mg/L	720	Ion exchange and complexation	Na ₂ EDTA	[92]
3.	Sulfonated magnetic NPs	108.93	99%	pH 7–10	10 mg/L	1440	Cation exchange	Acid treatment	[94]
4.	MgO	2614	NA	pH 6–8	NA	10,800	precipitation and adsorption MgO	NA	[104]
5.	Fe ₃ O ₄	53.11	NA	pH 5	25–100 mg/L	NA	Magnetic separation	Acid treatment	[105]
6.	MWCNT/SiO ₂ nanocomposite (f multi-wall carbon nanotubes and silica nanocomposite (CNT/SiO ₂))	13	NA	pH 6	5–30 ppm	NA	Chemisorption	NA	[112]
7.	NC@Co ₃ O ₄ (natural clay (NC) with Co ₃ O ₄ nanoparticles)	55.24	90%/5	pH 8.5	50–350 mg/L	140	Spontaneous adsorption	NaOH	[113]
8.	CNC/Fe ₃ O ₄ (cellulose nanocrystals (CNCs)/Fe ₃ O ₄)	241.6	NA	pH 5.5–6	200 ppm	50	Multilayer adsorption	NA	[102]
9.	NiO–CuO/Activated Carbon Nanocomposites	182.78	99.9%/4	pH 7	100 ppm	30	Multilayer adsorption	NA	[111]
10.	PS/AlOOH (Polystyrene/AlOOH)	23.61	NA	pH 6	20–100 mg/L	NA	Chemisorption and ion exchange	Acid treatment	[114]
11.	CNTs–PAMAM–Ag	18.7	99%	pH 8	40 mg/L	15	Intraparticle diffusion and the boundary layer effect.	4 cycles without losing adsorption capacity	[103]
12.	Ag nanoparticles (AgNO ₃)	25.65	96.6%/	pH 8	10 mg/L	60	Chemisorption	NA	[93]
13.	USMNs (ultrasmall superparamagnetic magnetite nanoparticles)	315.42	92%/5	pH > 4	50–500 mg/L	10	Spontaneous, feasible, and endothermic under the applied conditions	Ethanol and deionized water	[15]
14.	Fe–GAC (Iron-Doped Granular Activated Carbon)	11.9	96.3%	pH 6	100 mg/L	NA	Physical and chemical adsorption	Acid treatment	[115]
15.	amino silica-modified magnetic nanoparticles	35.45	90–100%	pH > 5	20 ppm	55–60	Chemisorption	NA	[97]
16.	Magnetic nanoparticles of iron oxide (Fe ₃ O ₄ NPs)	108.23	NA	pH 5	10–15 mg/L	NA	Intraparticle diffusion	NA	[87]
17.	ACW/Fe ₂ O ₃ (Activated Coconut Waste/Fe ₂ O ₃)	4.98	NA	NA	100 mg/L	30	Chemisorption	NA	[108]

Table 7. Cont.

		Ads. Capacity (mg/g)	Regeneration Percent/Cycle	pH Media	Initial Conc. Lead (Pb ²⁺)	Equilibrium Time (min)	Mechanism of Adsorption	Regeneration Method	Ref.
18.	ACW/Nio (Activated Coconut Waste)	4.98	NA	NA	100 mg/L	30	Chemisorption	NA	[108]
19.	ACW/Al ₂ O ₃ (Activated Coconut Waste)	4.96	NA	NA	100 mg/L	30	Chemisorption	NA	[108]
20.	NM Full-IPN's ([Poly (Thiourea-Formaldehyde)—Epoxy resin]) Nanomagnetic0	2.564	NA	pH 6	1, 10.20, 30 ppm	1500	Monolayer sorption	NA	[98]
21.	Bio-CaCO ₃ (Eggshell as a natural source of CaCO ₃)	108.5	NA	pH 6	1500 mg/L	20	Ion exchange	NA	[109]
22.	Eucommia ulmoides leaf extract (EUOL stabilized silver nanoparticles (EUOL@AgNPs)	370.37	49.4%/10	pH 7.2	250–450 mg/L	30	Chemical surface adsorption,	Acid treatment	[95]
23.	Fe ₃ O ₄ /RGO (Reduced Graphene Oxide)	107.52	81.1/5	pH 5	25–200 mg/L	60	cation– π interactions	Acid treatment	[107]
24.	CaO-NPs (Fe ₃ O ₄ sulfonated magnetic nanoparticle)	175.44	NA	pH 6.94	75.46 ppm	135	valence force or electron exchange	NA	[99]
25.	CMC@HAp (Hydroxyapatite and carboxymethyl cellulose)	625	NA	pH 5.5	2500–6000 ppm	90	Multilayer sorption	NA	[116]
26.	CTS@HAp (Hydroxyapatite and chitosan)	909	NA	pH 5.5	2500–60,000 ppm	45	Multilayer sorption	NA	[116]
27.	Mt@MH (amino magnetic nanoparticles coated montmorillonite)	38.15	7% decrease after 4	pH 6.5	NA	480	Electrostatic interaction		[100]
28.	MBCaAb (MNP-Biomass-calcium alginate) (MNP is magnetic nanoparticle)	197.02	NA	pH 5.5	1000–2900 mg/L	240	Intraparticle diffusion	External magnetic field	[101]
29.	SnO ₂	1265.8	30%/3	pH 7	100–400 ppm	90	Ionization	Acid treatment	[106]
30.	PAACS (Poly (acrylic acid) grafted and glutaraldehyde-crosslinked chitosan nano adsorbent)	734.3	72%/5	pH 5	0.015 mol/L	240	Physical and chemical adsorption	Acid treatment	[110]

6. Starch-Based Adsorbents

Starch, a plant-derived biopolymer, is widely available, and cost-effective, and there are numerous applications in both food and non-food industries. However, its native form has certain limitations that restrict its usage [55]. These drawbacks include low viscosity and thickening power after cooking and storage, retrogradation characteristics, and the absence of specific functional groups required for certain applications [55]. To overcome these limitations and enhance its potential usage, starch modification becomes essential. Various approaches, such as chemical modification, physical modification, and genetic modification, can be employed for this purpose. Among them, chemical modification is particularly crucial and impactful in improving the properties of starch. However, it may consume some chemicals, which are not eco-friendly. Furthermore, adsorbents with a starch backbone could integrate the starch nanoparticles' (SNPs) unique properties, such as availability, cost-effectiveness, size, form, crystallinity, stability, and adsorption capabilities, with exceptional surface functionality [55]. Starch is among the most prevalent, cost-effective, recyclable, and biodegradable natural materials. It is found in the roots, seeds, and leaves of many plants and algae [117]. As a polymeric material, starch is derived from D-glucose with a multiscale configuration that includes starch particles, semicrystalline growth rings, lamellar architectures (10 nm), crystal architectures, helical architectures, and exemplary molecule architectures (i.e., architectures of amylose and amylopectin) [118]. Bare starch occurs naturally in the form of semicrystalline granules composed of amylose and amylopectin. The linear polymer named amylose has 1–4 glycosidic linkages, whilst the branched one called amylopectin, with considerable short chains connected to the linear parts of the macromolecule via 1–6 linkage [119]. In spite of that, due to its limited surface area, bounded water solubility, low molecular weight, and absence of reaction functional groups, natural starch is hardly utilized directly as an adsorbent. As a result, efforts should be made to modify its sensitivity to pH and varying temperatures for adsorption [34,119].

Starch modification techniques, such as physical [120], chemical [121], and enzymatic alteration [122], have been developed to increase adsorption affinity against pollutants by tailoring structures and adding functional groups. As a matter of fact, several studies have proved the enormous potential of functionalized starch in water treatment [123]. A study revealed that the pseudo-second orders were better suited to the sorption of water than the Elovich, intraparticle diffusion, and first-order models. For the study, the researchers used a magnetic nanocomposite made of eggshell, starch, and Fe_3O_4 to eliminate heavy metal ions such as Pb^{2+} and Cd^{2+} from the water. They were able to achieve an effective adsorbent capacity of 57.143 mg/g for Pb^{2+} and 48.544 mg/g for Cd^{2+} using the nanocomposite. They noted that the process was carried out spontaneously, using the Langmuir and pseudo-second-order models [124].

Starch Nanomaterial as Adsorbents for Lead

As mentioned before, biodegradability, low cost, and high surface area are unique features that characterize starch nanoparticles [125]. It can be used to remove various metals from industrial effluents, wastewater, and drinking water. One study revealed that these particles could remove almost all lead ions from water samples. A study revealed that starch nanoparticles could adsorb copper ions three times more effectively than regular starch. These particles can also be modified to improve their performance by adding functional groups to their surface. For instance, the carboxymethylated starch particles can be used to adsorb mercury ions. Compared to other types of adsorbents, starch nanoparticles offer promising properties when it comes to metal removal [125–127]. Due to the high binding capacity of their functional groups, SNPs are already removing various inorganic contaminants like heavy metals, phosphates, and arsenic [128,129]. Accumulation of heavy metals in biological systems with detectable concentrations poses a risk to ecological systems, animals, and even people [130]. SNPs hold the key to properly addressing the issue of heavy metal contamination. The large specific area and the strong superficial

functional groups make metal binding by sorption an eco-friendly process without any harm residues [128,129].

7. Challenges and Future Research Direction

Most of the literature has investigated different adsorbents experimentally (either in a batch or column bed) without further investigation in a real application to examine their effectiveness in real effluents—concerning the adsorption mechanism, it is quietly controlled by a variable number of factors (ex. temperature, pH, initial concentration of both adsorbent and adsorbates, etc). Almost all researchers study the effect of one or two of those factors. However, there are not any studies that cover the initial concentration of adsorbent and adsorbate and the adsorption capacity of an adsorbent in the presence of other effluents or toxins at the same time as in real systems. Different modification attempts are discussed to maximize the adsorption capacity of the adsorbent, either chemically or by physical modification methods. Multiple researchers discussed the added value of modification without mentioning the side effects (if there are any) of these methods in terms of cost, environmental effects, or even human safety.

Scalability concerns in moving from laboratory-scale to industrial-scale applications are among the practical challenges of application for adsorption technology for hazardous pollutant removal, demanding careful design and optimization of adsorption systems for large-scale water treatment. Concerns about cost-effectiveness originate from the expense of adsorbent materials and operational expenses, necessitating efforts to improve economic viability, particularly in resource-limited environments. Adsorbent regeneration and disposal raise environmental and efficiency challenges, with several recovery strategies used to gather lead after regeneration. The problems of integration include assuring compatibility and flexibility with current water treatment systems, which may need system adjustments. Finally, regulatory compliance necessitates extensive testing and validation in order to achieve water quality and pollutant removal criteria.

8. Conclusions

In conclusion, this study has provided compelling evidence that adsorption is the best choice for treating toxin and pollutant removal either economically or environmentally. In this review, lots of alternatives are discussed as model adsorbents for different pollutants, and each material has its own properties and feasibility in addition to its limitations and constraints. Starch is one of the materials shortlisted as the most preferable adsorbent in terms of abundance and eco-friendliness, in addition to its applicability to various kinds of pollutants. However, there is still a demand to figure out the practical utility of the discussed adsorbents in real systems, which may lead to applied solutions in controlling pollution. Also, surface modification can substantially boost adsorption capacity, potentially multiplying it by two or fourfold. Additionally, the adsorbents can achieve impressive regeneration rates, with efficiency reaching up to 90% (as shown in much research), even after undergoing three or more cycles. Starch nanoparticles are the perfect solution as an adsorbent for toxic compounds in terms of low cost, high performance, efficient regeneration, and environmental protection. Concerning pH, the study explained clearly that raising pH to 6 will increase the adsorption capacity for lead and that it will be decreased by lowering to pH 2. Despite the growing interest in utilizing starch as sorbents for toxic compounds, there is limited knowledge of sorption mechanisms, which are not yet fully elucidated. Understanding the underlying mechanism is crucial for optimizing the sorption capacity and purification efficiency of starch-based materials. However, there is a need in future steps to concentrate on the scalability and reusability aspects of starch-based sorbents. Assessing these nanoparticles' performance over multiple sorption–desorption cycles and exploring regeneration techniques will be crucial to determine their long-term sustainability and cost-effectiveness.

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