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REVIEW

State-of-the-art modification, mechanistic insight and breakthrough curve analysis of chitosan scaffolds for sustainable heavy metal adsorbent

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Abstract

Heavy metals are toxic, non-biodegradable pollutants that can persist in the environment and pose serious threats to human health and aquatic ecosystems. Industrial discharge of heavy metal-containing effluents continues to degrade water quality, highlighting the urgent need for effective and sustainable remediation methods. Among various techniques, adsorption stands out for its high efficiency, low cost, and reusability. Chitosan, a biopolymer derived from renewable and abundant sources, has gained significant attention as a promising biosorbent for heavy metal removal. However, its poor acid stability and limited number of active adsorption sites can hinder its performance. This review discusses recent advancements aimed at enhancing chitosan's adsorption capacity and stability, focusing on three main strategies: (i) structural modification via crosslinking and grafting, (ii) selectivity improvement using the Hard and Soft Acid–Base (HSAB) theory, and (iii) optimization of operational parameters such as pH, contact time, and metal ion concentration. In addition, the adsorption mechanisms, including complexation, electrostatic interactions, and ion exchange, along with breakthrough curve analysis are explored to understand dynamic adsorption behavior. Importantly, this study also covers regeneration techniques, evaluating the reusability of modified chitosan across multiple cycles, cost analysis to assess economic feasibility, and findings from pilot-scale studies that demonstrate real-world applicability. Overall, this review provides a comprehensive guide for the development of efficient, cost-effective, and scalable chitosan-based adsorbents, contributing to the advancement of sustainable heavy metal remediation technologies.

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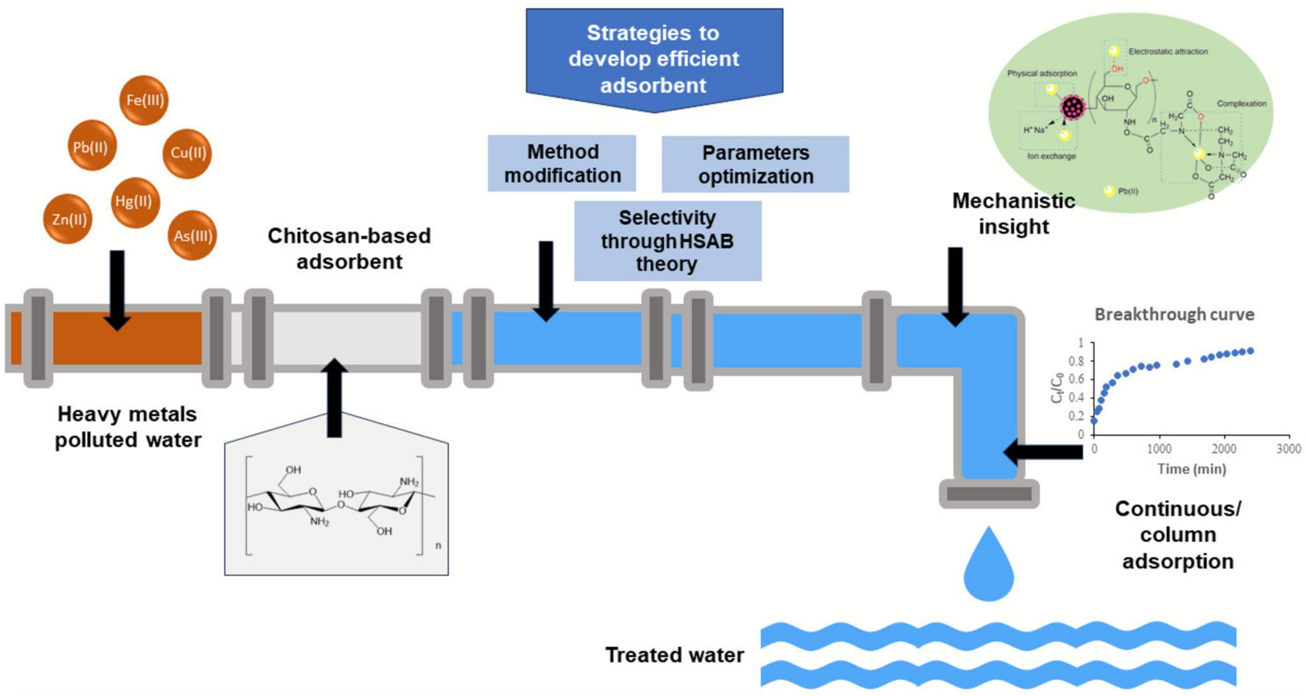
Graphical Abstract



Keywords Adsorption · Heavy metal removal · Modified chitosan · Sustainable development goals (SDGs) · Water treatment

Introduction

Nowadays, the demand for water has increased tremendously due to the growth in human population and the urbanization. Hence, a frontier and long-term initiatives need to be implemented to avoid the deprivation of clean water in the future. Therefore, the United Nation has established Sustainable Development Goals (SDGs) with vision to secure economic growth while mitigating climate change and protecting the environment (United Nation 2015). SDG 6 focuses on ensuring the availability and sustainable management of water and sanitation, in which by 2030, all populations are targeted to have equal access to safe drinking water. The access to clean water can be achieved through reducing water pollution using sustainable wastewater treatment and increasing recycling. However, the current rapid industrialization and anthropogenic activities lead to the discharge of pollutants in the water sources and causes contamination which affects the quality of access water. Qu et al. (2018) reported high heavy metal contents in the North America, South America, Asia and Europe mainly caused by the discharge from electroplating, leather tanning industries, mining and manufacturing activities. Untreated wastewater which contains hazardous heavy metals can possess health risks and limits the availability of safe drinking water towards the whole ecosystem (Zhou et al. 2020).

Heavy metals are known for their toxicity, even at low concentration (Vardhan et al. 2019). They are non-biodegradable and can bioaccumulate in nature, which can cause pollution as it will be persistent in the environment for a long time (Ali et al. 2019). Exposure towards these heavy metals at high amount may cause health issues such as cancers, respiratory, renal and nervous system issues (Sall et al. 2020). Heavy metals pollution in water sources also may give rise to various social and environmental issues, including unsafe drinking water, problem in food security and negatively impact the whole ecosystem. Food security is important for sustainability and the health of human population which was also addressed in SDG2 and SDG3 (United Nation, 2015). Food sources that are contaminated with heavy metals could hamper this attempt and affect the well-being of people (Anani et al. 2020).

Food safety has been identified as one of the highly placed sustainable goals because of its relevance to the sustainability and well-being of mankind. Over the years human being is faced with several adverse effects that normally result in uncountable impairment in their health. This might be linked to the high level of contamination and environmental pollution as a result of heavy metal due to various anthropogenic activities as well as several agricultural and environmental activities.

Various existing methods have been developed to remove these heavy metals from water sources which include chemical precipitation, coagulation, membrane filtration, ion-exchange, adsorption and electrochemical methods (Fu and Wang 2011). However, adsorption is considered as the most suitable method of heavy metals removal from water as it is inexpensive and possesses high efficiency. In the adsorption process, the heavy metals are separated from the water through mass transfer to a solid surface (adsorbent) and bonded through chemical or physical adsorption. The most commonly used adsorbent for heavy metal removal is activated carbon. However, it is not practicable for industrial application since it requires high cost and has limited regeneration (Vardhan et al. 2019).

Hence, efforts have been made to overcome these limitations, including developing adsorbents that are made from waste materials. One of the prominent sustainable management ideas is nature-based solutions which refers to the sustainable usage of nature to solve challenges related to socio-environment, including water pollution (Seddon et al. 2021). It is regarded as a comprehensive strategy that can minimise trade-offs and help bridge the gap between the SDGs (Seddon et al. 2020). Natural based adsorbents, as opposed to conventional designed solutions, have the ability to reduce the problem of environmental pollution at a low cost while also offering numerous advantages to the environment, society and economy. Aside from low cost, this alternative also produces adsorbent with high adsorption capacity, simple operation and does not cause secondary pollution through sludge production (Salari et al. 2019).

Chitosan is one of the biomaterials which has recently garnered attention and widely researched as an adsorbent for heavy metals. It is well known for being non-toxic and biocompatible in which it will not cause any harmful response when exposed to living organisms (Singh and Ray 2007). The hydroxyl and amine groups in chitosan's structure enable it to interact with the heavy metals and thus separating it from the polluted water source. These properties of chitosan lead to the efforts of developing it as an effective and safe adsorbent for water pollutant removal, including heavy metals. Derivation of adsorbent from this abundant, cost effective and renewable source can be a solution to the sustainable alternative in developing adsorbent for water treatment, aligned with United Nation's SDGs.

The application of modified chitosan adsorbents for heavy metal removal has garnered increasing attention in recent years due to their biocompatibility, environmental friendliness, and functional versatility. As illustrated in Fig. 1, the number of research publications on chitosan-based adsorbents for heavy metal removal has shown a steady increase from 2012 to 2022, highlighting the growing scientific interest in this field. The present review aims to compile and critically assess a selection of recent and up-to-date studies published between 2018 and 2025, focusing specifically on the modification and development of chitosan derivatives to enhance their performance in heavy metal adsorption. Several existing review articles have addressed the basic characteristics, modification techniques, and general applications of chitosan-based adsorbents. However, there remains a notable gap in the literature regarding their performance under real environmental conditions, particularly with respect to reusability, economic viability, and large-scale applicability. This review seeks to bridge that gap by not only summarizing the fundamental modification strategies

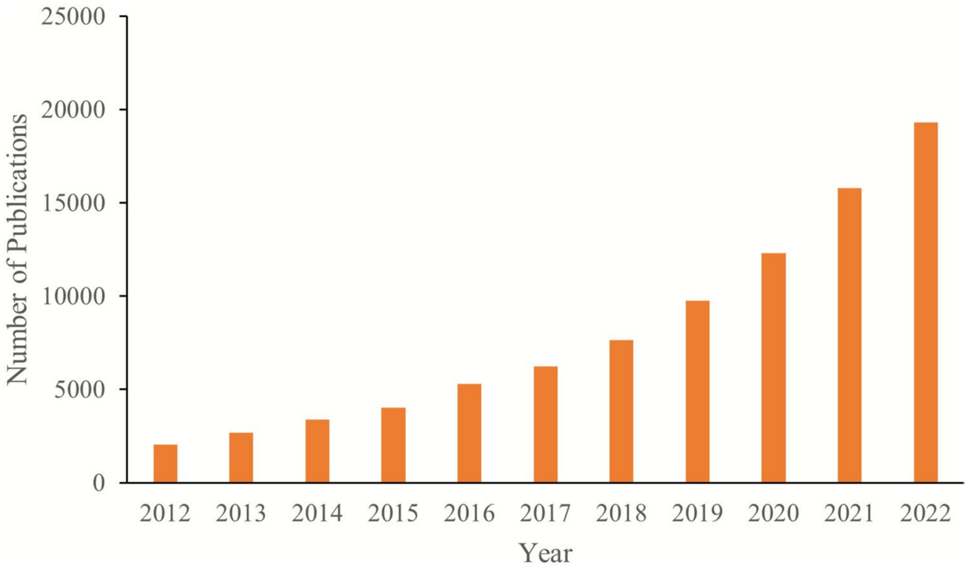


Fig. 1 Published research articles on "chitosan-based adsorbents for heavy metal removal" between year 2012 and 2022

but also providing a comprehensive guide for the development of efficient, cost-effective, and scalable chitosan-based sorbents. Special emphasis is placed on three key strategies: (i) structural modification to improve adsorption capacity and stability, (ii) selectivity enhancement through the application of the Hard and Soft Acid–Base (HSAB) theory, and (iii) optimization of operational parameters such as pH, contact time, temperature, and metal ion concentration.

In addition, this review incorporates recent advances in the regeneration and reuse of chitosan adsorbents, evaluating the effectiveness of different desorbing agents and regeneration protocols over multiple cycles. The inclusion of cost analysis provides insights into the economic feasibility of using chitosan, particularly when derived from low-cost or waste biomass sources. Furthermore, pilot-scale studies are reviewed to assess the real-world performance and scalability of modified chitosan systems, moving beyond laboratory conditions to practical applications. This review offers a comprehensive framework for researchers aiming to design next-generation chitosan-based sorbents by integrating insights from adsorption mechanisms, breakthrough curve analysis, and empirical data from regeneration and pilot-scale trials. To the best of our knowledge, this is the first review to systematically explore a multifaceted strategy that combines chemical engineering, environmental science, and materials design to maximize the adsorption potential of chitosan for heavy metal remediation.

Current issues of chitosan adsorbent

Chitosan has recently emerged as one of promising material to be developed as an environmentally friendly adsorbent for heavy metals removal as it is renewable and biodegradable. Aside from that, chitosan is also well known for being non-toxic and biocompatible in which it will not cause any harmful response when exposed to living organisms (Singh and Ray 2007). The hydroxyl and amine groups in chitosan's structure enable it to interact with the heavy metals and thus separating it from the polluted water source. However, the development of chitosan as an efficient adsorbent may be restricted due to several limitations that may affect their performance in adsorbing the pollutants.

Solubility in acidic medium

Chitosan is insoluble in the majority of solvents and dissolves only in aqueous acids (Bakshi et al. 2020). Acids initiate the protonation of the amino functional group in chitosan, forming cationic sites and increasing polarity, allowing chitosan to become soluble. This feature of chitosan has become a major impediment to its use as an adsorbent in an acidic aqueous medium. This is particularly pertinent for the water bodies near the mining site, where heavy metals in the sediments are likely to be discharged into the water at a low pH (Saalidong et al. 2022). The acid mine drainage may be resulted from the exposure of metal sulfide deposits and surrounding rocks to atmospheric oxygen, with an average pH value of 2.98, which is significantly lower than the surface water standard (Luo et al. 2022). As a result, the acidic water may increase the concentration of heavy metal ions in the water. This is because heavy metal ions are more prevalent in the water at low pH, as they have higher tendency to become soluble (Saalidong et al. 2022; Zhang et al. 2018). Hence, the instability of chitosan in acidic environments hinders its efficient application for removing heavy metals, particularly in acidic wastewater. Thus, modifications to the chitosan structure are usually performed to strengthen the adsorbent's acid resistance. Chitosan, for example, was crosslinked with glutaraldehyde to extract Au (III) from an acidic e-waste leaching solution at pH 2 (Bui et al. 2020). When the same adsorption test is performed on pure chitosan, it dissolves at low pH conditions.

Lack of selectivity

Generally, adsorbents with high selectivity are much preferred, not only for their enhanced adsorption efficiency towards the targeted pollutant but also to avoid competitive adsorption with other organic matter or ions present in the water (Wang and Zhuang 2018). Chitosan, however, does not show selectivity towards specific heavy metal ions (Yan et al. 2011; Guibal et al. 2000). Although chitosan has multiple potential adsorption sites, mostly through the amine functional group, it has been discovered that it has no selectivity for any heavy metal ions. As a result, alternative functional groups with a stronger affinity to the targeted metal may be introduced to the chitosan structure to tailor the adsorbent's affinity towards the heavy metal ion. In a study, chitosan with and without polyacrylamide modifications were compared for their ability to adsorb mercury and lead ions. It was discovered that polyacrylamide-modified chitosan shows greater selectivity for mercury ions over lead, but untreated chitosan has no obvious selectivity for either metal ion (Li et al. 2005)· It is thus inferred that the modified chitosan's affinity for the mercury ion is mostly due to its incorporation of an amide functional group.

Inadequate adsorption sites

As a biopolymer, chitosan may have the advantage of abundance potential adsorption sites, especially from its amine groups. However, the number of adsorption sites in pure chitosan might still be inadequate for some adsorption studies, resulting in fairly low adsorption efficiency (Xu et al. 2017; Mozaffari et al. 2019). Hence, to achieve higher adsorption efficiency, chitosan is often modified with other functional groups to increase its potential adsorption sites.

Strategies for development of effective chitosan adsorbent

Despite chitosan's additional benefits from its unique properties, it however has a few drawbacks that could limit the adsorption efficacy. Therefore, several strategies can be employed to overcome the problems and boost its effectiveness in adsorbing heavy metals. The three strategies that can be utilized to enhance the adsorption properties of chitosan as an effective heavy metal adsorbent are outlined in this review, which include the methods of chemical structure modification, the selectivity through hard soft acid base (HSAB) theory and optimization of the heavy metal removal.

Methods of chemical modification

Chitosan is rarely used in its original form due to some limitations, mainly for its solubility in acidic medium and the adsorption sites provided by chitosan is not abundant (Mozaffari et al. 2019). Hence, modifications are usually made towards chitosan to overcome these limitations or enhance its adsorbing performance. Chitosan can be modified through physical methods such as changing its form to beads, membranes, film or hydrogel, while chemical modifications of chitosan can be made through cross-linking, grafting and impregnation. However, this study focuses on chemical modification of chitosan through cross-linking and grafting methods as they are the most common method applied for the development of chitosan as an adsorbent. These modifications may enhance the properties of chitosan and form chitosan derivatives with improved adsorption sites and chemical stability in acidic environment (Kyzas and Bikiaris 2015). The presence -OH and -NH_2 functional groups in chitosan enable it to be chemically modified. Table 1 describes the general characteristic of the chemical modification methods.

Crosslinking

Crosslinking is often used to increase the mechanical strength of chitosan as it will result in better stability at lower pH (Vakili et al. 2019b). As mentioned before, chitosan has higher dissolution at lower pH and this could cause difficulties in its application as an adsorbent. This limitation can be overcome by binding the chitosan with crosslinking agent through irreversible covalent bond which provide stability and acid resistance (Saheed et al. 2021). As the crosslinked chitosan structure stabilizes, the coiling of chitosan chains can be minimized, thus increasing the surface area for the heavy metal adsorption and may lead to higher adsorption capacity (Webster et al. 2007). This process can be performed via using various common crosslinking agents such as dialdehydes and epoxy compounds. However, some conventional crosslinkers such as glutaraldehyde, formaldehyde and epichlorohydrin has been classified as toxic and excessive crosslinking of glutaraldehyde with chitosan may cause steric hindrance which will reduce the adsorption of heavy metal onto the adsorbent (Ehrmann 2021). Another issue that may be encountered by using this modification method is crosslinking process may take place at the adsorption sites (amine and hydroxyl), and leaving little to no space for the heavy metal adsorption to occur (Osifo et al. 2008). As a result, a high degree of crosslinking can reduce the number of accessible amino groups, lowering the adsorption capacity of the chitosan adsorbent (Zhang et al. 2020a). Nonetheless, more recent studies have managed to overcome these challenges by employing multiple kinds of crosslinking agents.

An alternative that is currently used to mitigate the blocked adsorption site problem is by using a crosslinking agent with multiple adsorption sites for the heavy metals.

Table 1 Differences between crosslinking and grafting chemical modification

Chemical modification	Method	Modifying agents	Benefits	Drawback
Crosslinking	Uniting two polymer chains together by chemical bond	Dialdehydes (glutaraldehyde, formaldehyde, etc.), epoxy compounds (epichlorohydrin, diepoxyoctane, etc.), ionic crosslinkers (tripolyphosphates, sulfuric acid)	Increase the mechanical strength of chitosan, better stability at lower pH	Lower adsorption capacity
Grafting functional groups	The addition of functional groups onto the chitosan by covalent binding of a molecule onto the chitosan backbone	Copolymer and acyl, alkyl, hydroxyalkyl, carboxyalkyl, quaternization, thiol, phosphoryl groups	Increase the adsorption sites for heavy metal adsorption	Excessive grafting may cause steric hindrance

For instance, arginine could be a suitable crosslinking agent which provide both chemical stability and new adsorption sites for heavy metal ions as it contains numerous amino and carboxyl groups. In a recent study, arginine was used as a crosslinker to chemically modify chitosan with carboxymethyl cellulose (Manzoor et al. 2019). Arginine as the crosslinker formed crosslinked chitosan through covalent bonds with both chitosan and carboxymethyl cellulose. Meanwhile in another study, pectin, a complex anionic polysaccharide, was employed as a crosslinker for chitosan modification (Shao et al. 2021). Pectin is known to be non-toxic, flexible and rich in carboxyl and hydroxyl groups, which may increase the adsorbent affinity for the metal ions. After optimization, the pectin modified chitosan adsorbent shows high acid stability and high adsorption capacity towards Cu (II), Cd (II), Hg (II) and Pb (II) ions.

Some of the most common crosslinkers, such as glutaraldehyde, epichlorohydrin, and formaldehyde, though may enhance the mechanical strength and stability, are known to be hazardous. The presence of free traces of these hazardous crosslinking agents may increase the risk of toxic product formation during the biodegradation process due to the reaction between the substrate and the crosslinking agent (Fideles et al. 2018). Glutaraldehyde for example is renowned for its cytotoxicity, with prolong exposure may pose mutagenic risk as suggested by some studies which can lead to disruption in aquatic system (Speit et al. 2008; Thumtecho et al. 2021). Epichlorohydrin also poses serious risk to the environment due to its carcinogenicity, mutagenicity and neurotoxicity, while being persistent in the environment (Romano et al. 2007). Meanwhile formaldehyde is often linked to carcinogenicity, respiratory irritant and has neurological and reproductive effects (Sun et al. 2025).

As a result, some research advocates the use of ionic crosslinking agents to mitigate this disadvantage while avoiding secondary pollution. This can be achieved by using crosslinking agents such as tripolyphosphate and citric acid which are non-toxic. In a study by Zhang et al. (2019a, b, c) (Zhang et al. 2020b), citric acid was used to crosslink chitosan to improve its properties for Cr (VI) adsorption. The chitosan citrate microspheres (CSC) were developed by crosslinking chitosan with citric acid through microwave-assisted heating and oil bath methods. The protonated chitosan forms intermolecular or intramolecular ionic bond with the citrate, which consists of multivalent counterions, leading to the formation of CSC. It also shows higher adsorption capacity at 172 mg/g compared to raw chitosan. Another work has also described the use of citrate-crosslinked chitosan as an adsorbent to extract Cr (VI) ions with adsorption capacity of up to 106.15 mg/g following optimisation (Bagheri et al. 2015).

Aside from citric acid, another green crosslinker gaining popularity is sodium tripolyphosphate, which is both economical and non-hazardous (Kosuri 2016). In a study by Babakhani and Sartaj (2021), sodium tripolyphosphate was used as the crosslinking agent for chitosan as an adsorbent for Ni (II) and Cd (II) ions. At lower pH, amine group from chitosan will be protonated to -NH^{3+} which will react with PO_4^{3-} of tripolyphosphate through ionic interaction and form crosslinked chitosan. The study observed an increase in its acid stability after being crosslinked and became insoluble at lower pH. However, it was found that the adsorption capacity of chitosan for both Ni (II) and Cd (II) was reduced by 40% upon crosslinking with tripolyphosphate. This is because the amine group from chitosan which is the dominant adsorption site has become less available for the heavy metals due to the crosslinking process. Therefore, further studies on the usage of tripolyphosphate might be required to allow better adsorption capacity. Some recent studies have reported the fabrication of chitosan crosslinked with sodium tripolyphosphate by using ionic gelation method developed by Calvo (1997). For example, Hussain et al. (2020) applied this method, in which chitosan is dissolved in an acidic aqueous solution and then added dropwise to a tripolyphosphate solution while stirring. The interaction of cationic chitosan and anionic TPP results in ionic gelation, which precipitates and forms nanoparticles (Tarhini et al. 2021; Hussain et al. 2020). The synthesized chitosan-tripolyphosphate nanoparticle recorded an average size of 24.9 nm and its highest adsorption capacity for As (V) was 77 mg/mg (Hamidi et al. 2021).

These crosslinkers are favoured for their low toxicity and environmental friendliness. However, the long-term stability of these green crosslinkers is also a critical factor in determining their suitability for industrial-scale applications of chitosan-based adsorbents. Sodium tripolyphosphate a complex structure and substantial molar mass, contributing to its overall stability. However, its stability is not absolute and can be compromised by adverse environmental factors, particularly high temperatures, ionic strength and acidic pH leading to breakdown and loss of performance (Farrokhpay et al. 2012; Di Santo et al. 2021). Meanwhile, citric acid as crosslinking agent has high stability in dry and controlled environments but prone to hydrolyse depending on process temperature and duration, medium pH, and doses of reagents used (Ma et al. 2021; Miller et al. 2024). Ester bonds of citric acid may break down over time, hence making them unsustainable in a long run. Genipin, a natural crosslinker which is derived from gardenia fruit has also been regarded as green crosslinking agent due to its low toxicity and biocompatibility (Inthamat et al. 2022). Aside from that, it has excellent stability as it forms stable covalent crosslink with amine group of chitosan, exhibiting strong mechanical strength and resistant to degradation, making it an exceptional alternative to toxic and unsustainable crosslinking agents (Inthamat et al. 2022; Khezerlou et al. 2025). It can be concluded that the crosslinking process may result in increased adsorption effectiveness when compared to raw chitosan, particularly in acidic media. However, choosing the right crosslinking agent is critical to avoiding secondary contamination and minimising the number of adsorption sites available for metal ions. The adsorption capacities for the crosslinked chitosan obtained from these studies are summarized in Table 2.

Grafting

Grafting involves the addition of functional groups onto the chitosan by covalent binding of a molecule onto the chitosan backbone (Kyzas and Bikiaris 2015). Chitosan derivatives with stronger and higher density chelating groups tend to possess higher heavy metal removal (Seidi et al. 2021). The characteristic of the grafted chitosan can be heavily influenced by the molecular structure, length and number of the side chains (Saheed et al. 2021). Although chitosan itself contains amino and hydroxyl functional groups that could interact with heavy metal ions, for some studies it is still considered as inadequate. Hence more functional groups are added to the chitosan structure aimed to increase the adsorption sites for heavy metal adsorption. Grafting modification can be performed through various methods which include acylation, alkylation, hydroxyalkylation, carboxyalkylation, quaternization, thiolation, phosphorylation, sulfation, and graft copolymerization (Yu et al. 2018).

Graft copolymerization method has been widely used by many studies to improve the properties of chitosan as an adsorbent. It is a method used to combine two or more different polymers into a single unit as the backbone polymer with higher molecular weight, such as chitosan (Nayak et al. 2018; Sanchez-Salvador et al. 2021). The most common method to produce a graft copolymer is by activating the backbone polymer and initiating copolymerization of the second polymer (Chapiro 2004). This results in formation of grafted branches covalently attached to the backbone polymer. The formation of free radicals which leads to the copolymerization reaction can be initiated through irradiation or chemical initiators. However, as compared to common chemical reactions, radiation-initiated copolymerization has additional benefits because the products are free of harmful additives from chemical initiators and toxic crosslinkers (Kumar et al. 2020). As a result, secondary contamination from the chitosan modified adsorbent might be avoided. Grafting process can be carried out with facilitation from gamma irradiation as the initiator. Gamma irradiation is often applied as it has large initiating energy, minimal usage of initiator or crosslinking agents, can operate at room temperature and produce fast reaction. It is also more preferred compared to other radiation as it initiates higher free radical production which helps to improve the grafting process. Vijayasri and Tiwari (2021) uses gamma radiation to initiate the graft copolymerization of 2-Hydroxyethyl methacrylate (HEMA) and 4- Sodium Styrene Sulphonate (SSS) onto chitosan structure. Chitosan solution was immersed in HEMA and SSS before irradiated with gamma ray. Gamma radiation induce the formation of radicals at the C5-OH functional group of chitosan which becomes the grafting site for SSS and HEMA. The radicals will initiate the graft polymerization by attacking the double bonds in SSS and HEMA, forming bond with the structures. Meanwhile, Hu et al. (2020) modified chitosan structure through graft copolymerization by grafting it with polyacrylic acid (PAA) to improve the acid stability of the adsorbent. The observation showed that PAA grafted chitosan still maintained its characteristic despite being tested in very low pH which indicate its high acid stability upon grafting.

As opposed to graft copolymerization method, some functional groups were incorporated into chitosan structure directly without initiators. This can be performed through reactions such as acylation, alkylation, hydroxyalkylation etc. The amino and hydroxyl functional groups in chitosan allows them to directly react with various compounds and hence producing a modified chitosan with added functional groups from the grafted compounds. Mone et al. (2020) grafted 5-hydroxymethylfurfural (HMF) onto chitosan to improve the adsorption capacity of chitosan. The amine group of chitosan act as a nucleophile and react with the carbonyl of HMF that leads to imine formation which was then reduced to amine as $NaBH_4$, a reducing agent was added to the solution. The grafted chitosan's adsorption capacity is observed to increase with grafting percentage. The maximal adsorption capacity of the HMF-grafted chitosan with 310% grafting was higher for both Cu (II) (133 mg/g) and Cd (II) (125 mg/g) than the one with 130% grafting (Cu (II), 107 mg/g; Cd (II), 105 mg/g). In a study by Zhuang et al. (2021), chitosan was grafted with ethylenediaminetetraacetic acid (EDTA) for the development of adsorbent. EDTA is known for its ability to chelate metal ions as it has four carboxyl groups and two amine groups which can act as the binding sites for the metal ions. Through these research, it is possible to see an increase in adsorption effectiveness as additional functional groups are grafted to raw chitosan, hence contributing to its potential as an efficient heavy metals adsorbent. The adsorption capacities of the chitosan derivatives modified through grafting method are summarized in Table 3.

Combination of crosslinking and grafting

Since both approaches have demonstrated their own advantages, many recent studies have resorted to combining both techniques in the fabrication of an effective chitosan adsorbent to overcome the instability of chitosan in acidic media

Table 2 The adsorption capacities of crosslinked chitosan derivatives for heavy metal ions

Adsorbent	Crosslinking agent	Adsorbate	pH	Contact time (min)	Initial metal conc. (mg/L)	Adsorbent dosage (mg)	Adsorption capacity (mg/g)	References
Cross-linked chitosan diepoxyoctane beads (CS-DEO)	Diepoxyoctane (DEO)	Cr (VI)	2	2160	500	20	325.2	Vakili et al. (2018)
Arginine cross-linked chitosan-carboxymethyl cellulose beads (CS-ag-CM)	Arginine	Pb (II)	6.5	40	325	–	182.5	Manzoor et al. (2019)
		Cd (II)			300		168.5	
1,2-Bis- (2-formylphenoxy) ethane crosslinked chitosan (CS-L1)	1,2-Bis- (2-formylphenoxy)ethane	Cu (II)	6	360	100	50	84	Timur and Paşa (2018)
		Cd (II)					83.8	
		Fe (II)					80.6	
		Co (II)					78.4	
		Ni (II)					78.0	
1,2-Bis- (2′-acetylphenoxy) ethane crosslinked chitosan (CS-L2)	1,2-Bis- (2′-acetylphenoxy)ethane	Cu (II)	6	360	100	50	71.8	
		Cd (II)					57.2	
		Fe (II)					56.0	
		Co (II)					39.0	
		Ni (II)					20.2	
1,2-Bis (4′-formyl-3′-hydroxyphenoxy) crosslinked chitosan (CS-L3)	1,2-Bis (4′-formyl-3′-hydroxyphenoxy)	Cu (II)	6	360	100	50	59.6	
		Cd (II)					49.4	
		Fe (II)					59.2	
		Co (II)					29.8	
		Ni (II)					9.2	
1,2-Bis (4′-acetyl-3′-hydroxyphenoxy) crosslinked chitosan (CS-L4)	1,2-Bis (4′-acetyl-3′-hydroxyphenoxy)	Cu (II)	6	360	100	50	64.0	
		Cd (II)					60.8	
		Fe (II)					59.8	
		Co (II)					33.6	
		Ni (II)					12.2	
1,10-phenanthroline-2,9-dicarbaldehyde crosslinked chitosan (Ch-PDC)	1,10-phenanthroline-2,9-dicarbaldehyde	Pd (II)	5	120	25	10	262.6	(Mincke et al. (2019)
		Pt (IV)	3				119.5	
[2,2′-bipyridine]-5,5′-dicarbaldehyde crosslinked chitosan (Ch-BPDC)	[2,2′-bipyridine]-5,5′-dicarbaldehyde	Pd (II)	5	120	25	10	154.7	
		Pt (IV)	1				98.3	
sulfate-crosslinked chitosan (SCC)	Sulfuric Acid	Cr (VI)	6	45	50	400	156.85	Kahu et al. (2014)
sulphate cross-linked chitosan (SCC)	Sulfuric Acid	Zn (II)	5	165	50	1000	21.276	Jeyaseelan et al. (2021)
Sodium tripolyphosphate crosslinked chitosan	Sodium tripolyphosphate	Ni (II)	6.5	1440	50	27.5	52.24	Babakhani and Sartaj (2021)
		Cd (II)				22.5	68.57	
Chitosan-pectin gel beads	Pectin	Cu (II)	7	100	400	50	169.4	Shao et al. (2021)
		Cd (II)			350		177.6	
		Hg (II)			500		208.5	
		Pb (II)			150		266.5	
Cross-linked chitosan tripolyphosphate (CS-TPP) nanoparticles	Sodium tripolyphosphate	As (V)	6	90	0.5	100	21.3	Hamidi et al. (2021)

Table 2 (continued)

Adsorbent	Crosslinking agent	Adsorbate	pH	Contact time (min)	Initial metal conc. (mg/L)	Adsorbent dosage (mg)	Adsorption capacity (mg/g)	References
Chitosan citrate microspheres (CSC)	Citric Acid	Cr (VI)	5	30	100	10	172	Zhang et al. (2020b)
Chitosan-citric acid nanoparticles	Citric Acid	Cr (VI)	3	60	70	50	22.4	Bagheri et al. (2015)

Table 3 The adsorption capacities of grafted chitosan derivatives for heavy metal ions

Adsorbent	Grafting agent	Adsorbate	pH	Contact time	Initial metal conc. (mg/L)	Adsorbent dosage (mg)	Adsorption capacity (mg/g)	References
5-HMF grafted chitosan (CS-HMF)	5-hydroxymethyl furfural	Cu (II) Cd (II)	5	75	100	20	133 125	Mone et al. (2020)
EDTA grafted chitosan	EDTA	Co (II) Sr (II)	7 3	1440	40	10	61 8.8	Zhuang et al. (2021)
Poly (N-vinyl imidazole) grafted chitosan	Poly (N-vinyl imidazole)	Hg (II)	6	90	300	200	112.35	Labidi et al. (2019)
Methyl acrylate and tetraethylenepentamine grafted chitosan (MCS-MA-TEPA)	Methyl acrylate, Tetraethylene-pentamine	Cd (II)	5	150	250	30	251.22	Zhang et al. (2019a)
Polyacrylic acid grafted chitosan (MCS–PAA)	Polyacrylic acid	Pb (II)	6	70	100	10	204.89	Hu et al. (2020)
2-Hydroxyethyl methacrylate (HEMA) and 4- Sodium Styrene Sulphonate (SSS) grafted chitosan	2-hydroxyethyl methacrylate, 4-Sodium styrene sulphonate	As (V)	3–4	35	60	100	16.8	Vijayasri and Tiwari (2021)
Lignosulfonate grafted chitosan	Lignosulfonate	Cu (II) Co (II)	6	60	100	30	283 386	Mu et al. (2020)
Benzothiazole functionalized chitosan	Benzothiazole	Cu (II)	6	120	200	100	1439.7	Gamal et al. (2021)

while also improving adsorption sites. In a study by Hussain et al. (2020), the chitosan was cross-linked first with tripolyphosphate before being grafted with salicylaldehyde to increase the adsorption site. The crosslinker, tripolyphosphate, electrostatically attracts the protonated amino group of chitosan to its negatively charged phosphate group. Through Schiff base condensation, the crosslinked chitosan then interacted with salicylaldehyde. Chitosan's amine functional group interacts with aldehyde in salicylaldehyde, resulting in imine formation as shown in Fig. 2.

In a study by Ge and Du (2020), chitosan was modified by cross-linking chitosan with melamine by using glutaraldehyde as the crosslinker to enhance the adsorption of Pb (II) and Hg (II). Melamine was selected as it contains abundant amine groups which can increase the chelating site for adsorption of metal ions. However, melamine cannot be grafted directly onto chitosan. Hence, this study employed glutaraldehyde as the medium to crosslink chitosan and melamine. Three chemically modified chitosan developed by Mincke et al. (2019), which are 1,10-phenanthroline-2,9-dicarbaldehyde cross-linked chitosan (Ch-PDC), [2,2′-bipyridine]-5,5′-dicarbaldehyde cross-linked chitosan (Ch-BPDC) and glutaraldehyde cross-linked chitosan grafted with 8-hydroxyquinoline-2-carbaldehyde (Ch-GA-HQC) were applied as adsorbents for Pd (II) and Pt (IV) removal (Mincke et al. 2019). For Pd (II) removal, Ch-GA-HQC has the highest adsorption capacity at 340.3 mg/g, followed by ChPDC (262.6 mg/g) and

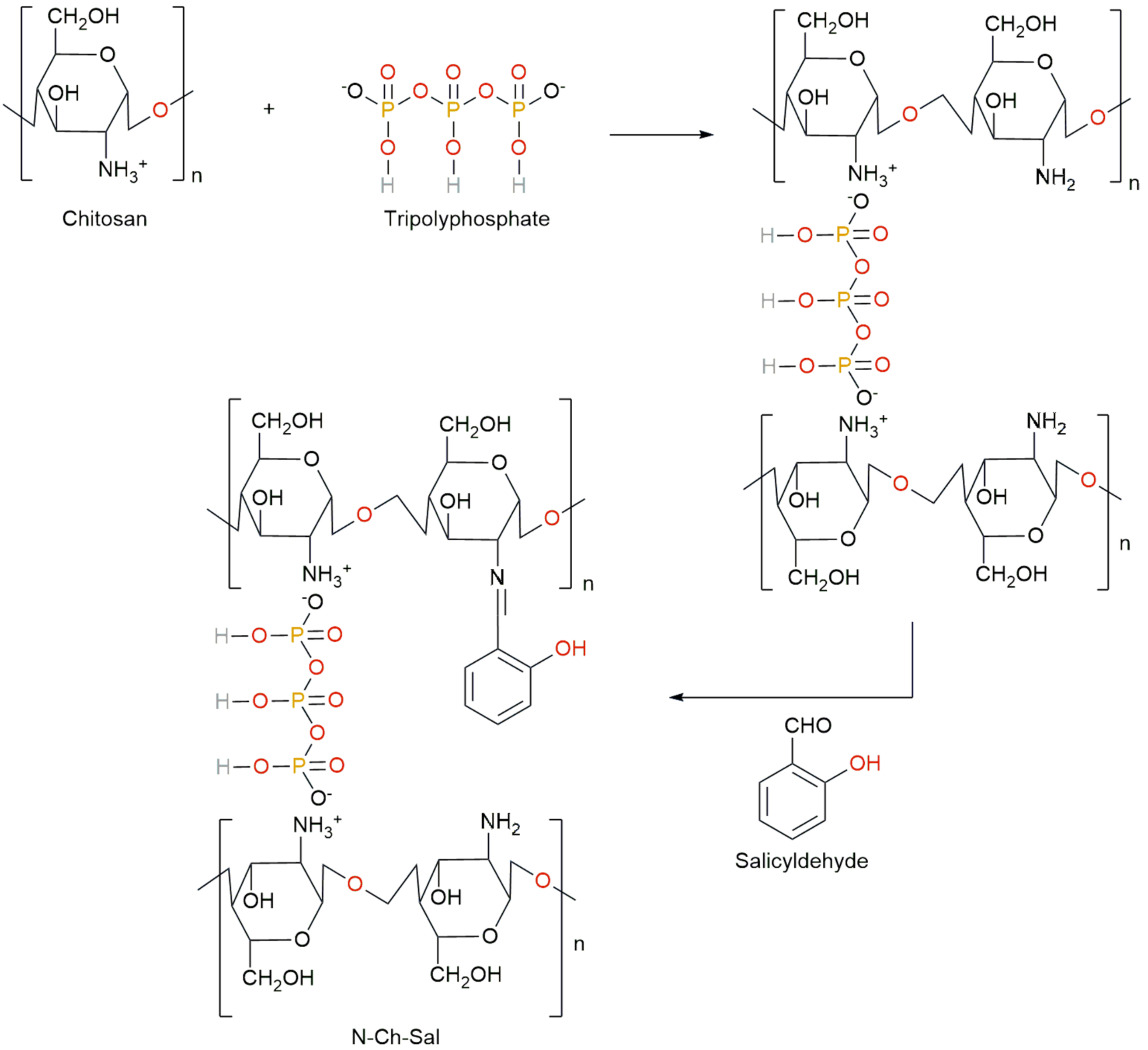


Fig. 2 Route of synthesis for tripolyphosphate crosslinked and salicylaldehyde grafted chitosan (Hussain et al. 2020)

Ch-BPDC (154.7 mg/g). As for Pt (IV) adsorption, Ch-GA-HQC also recorded the highest adsorption capacity (203.9 mg/g), succeeded by ChPDC (119.5 mg/g) and Ch-BPDC (98.3 mg/g). This can be attributed to the method of modification for the chitosan derivatives. Ch-PDC and Ch-BPDC was synthesized by solely crosslinking while Ch-GA-HQC was synthesized through both crosslinking and grafting methods. The simultaneous crosslinking and grafting method in synthesizing the adsorbent helps to achieve higher stability, strength and adsorption capacity (Sheth et al. 2021). The adsorption capacities of the chitosan derivatives modified through simultaneous grafting and crosslinking method are summarized in Table 4.

Selectivity through hard soft acid base theory

In developing an effective adsorbent towards heavy metals, the selectivity of the adsorbent towards the target heavy metal is important to ensure high adsorption efficiency in the presence of other non-target heavy metals. Despite having hydroxyl and nitrogen based functional groups as adsorption sites for heavy metal ions, the performance of chitosan as a heavy metal adsorbent can further be improved by increasing its selectivity towards the target heavy metal ion to develop a superior adsorbent. One way to design a selective heavy metal adsorbent is by employing the hard-soft, acid–base (HSAB) principle as the guide

Table 4 The adsorption capacities of simultaneous crosslinked grafted chitosan derivatives for heavy metal ions

Adsorbent	Modifying agent	Adsorbate	pH	Contact time (min)	Initial metal conc. (mg/L)	Adsorbent dosage (mg)	Adsorption capacity (mg/g)	References
Tripolyphosphate crosslinked and salicyldehyde grafted chitosan	Graft: salicyldehyde Crosslink: tripolyphosphate	Pb (II) Cu (II) Cd (II)	7	120	100	5	123.67 84.6 63.71	Hussain et al. (2020)
Glutaraldehyde cross-linked chitosan grafted with 8-hydroxyquinoline-2-carbaldehyde (Ch-GA-HQC)	Graft: 8-hydroxyquinoline-2-carbaldehyde Crosslink: glutaraldehyde	Pd (II) Pt (IV)	3	120	25	10	340.3 203.9	Mincke et al. (2019)
Crosslinked chitosan grafted with methyl methacrylate (M -CTS)	Graft: Methyl methacrylate Crosslink: glutaraldehyde	Cu (II)	4	100	100	50	192.31	Sutirman et al. (2020)
EDTA functionalized magnetic chitosan composite adsorbent (Fe$_3$O$_4$-CS/EDTA)	Graft: EDTA Crosslink: glutaraldehyde	Pb (II) Cu (II)	6	60	100	–	220 225	Chen et al. (2019)
functionalized chitosan-based adsorbent (CS-PAR)	Graft: 4- (2-pyridylazo) resorcinol Crosslink: formaldehyde	Cu (II)	5	300	600	10	170.23	Wang et al. (2022a)
Ninhydrin-functionalized chitosan (CS-Ninhydrin)	Graft: Ninhydrin Crosslink: Glutaraldehyde	Pb (II)	4	120	550	10	196	Chen et al. (2021)
Melamine-grafted chitosan (GMCS)	Graft: Melamine Crosslink: Glutaraldehye	Pb (II) Hg (II)	5 6	240	2072 2005.9	20	618.2 490.7	Ge and Du (2020)

in selecting the suitable surface functional moieties to achieve the required selectivity for the adsorption of target metal ion (Lam et al. 2006).

HSAB theory has been widely used in adsorption studies to describe the heavy metal adsorption onto the adsorbent as an acid–base reaction. Adsorbents can be expressed as a base as it provides pair of electrons to donate to heavy metals, which are considered as acids due to their vacant d-orbitals (Zhang et al. 2022). Adsorbents with functional groups such as –OH, –NH$_2$, CH$_3$COO$^-$ and CO$_3$$^{2-}$ are classified as hard bases while those with groups such as -RSH, RS$^-$, CO and CN$^-$ are grouped as soft bases. Heavy metals are also grouped according to their hardness/softness as shown in Table 5. In HSAB theory, it is mentioned that hard acids tend to bind with hard bases while soft acids tend to bind to soft base and form relatively stable complexes (Pearson 1963). Numerous adsorption studies with chitosan as the heavy metal adsorbent has utilized this concept to improve the adsorbent's selectivity.

Hard base-hard acid

In order to further enhance the selectivity of chitosan towards hard acids such as Be^{2+}, Cr^{3+}, Mg^{2+} and Fe^{3+}, the chitosan need to be modified with compounds containing moieties with hard bases such as R-NH$_2$ and CO$_3$$^{2-}$. For example, Ayub et al. (2020) developed magnetic chitons biosorbent beads (MCBB) as an adsorbent for As (III) removal. The As (III), which is a hard acid, is binded to –OH and –NH$_2$ functional groups of the adsorbent, which are hard bases. In a study by (Abd El-Magied et al. 2018), the developed glutaraldehyde crosslinked carboxymethyl chitosan adsorbent contains carboxylate which is a hard base, and is predicted to form strong interaction with beryllium ions which are hard acid. Polyacrylic acid grafted chitosan (PAA/CTS/BAA) contains carboxyl, hydroxyl and amine groups which can potentially become the adsorption sites for heavy metals (Zhang et al. 2019b). However, the selectivity of heavy metals adsorption onto these bases differed based on

Table 5 Groups of soft and hard acid and base

Acid			Base		
Hard acid	Borderline acid	Soft acid	Hard base	Borderline base	Soft base
Fe (III), As (III), Cr (III), Ce (IV), Ga (III), Be (I)	Ni (II), Co (II), Fe (II), Pb (II), Cu (II), Bi (II), Sn (II)	Cd (II), Hg (II), Ag (I), Mn (II), Pt (II), Hg (I), Au (I)	OH^-, NO_3^-, CH_3COO^-, ROH, RO^-, NH_3, RNH_2, H_2O, SO_4^{2-}	NO_2^-, pyridine, SO_3^{2-}, N_2, $C_6H_5NH_2$, C_5H_5N	R_2S, RSH, RS, SCN^-, CN^-, RNC, C_2H_4

HSAB theory. Cr (III), which is considered as a hard acid has the tendency to bind with hard bases in PAA/CTS/BAA which are carboxyl groups.

Soft base-soft acid

The available adsorption sites on chitosan consists of hard bases, namely -NH_2 and -OH. Therefore, reducing the free amino group of chitosan and adding an S-containing ligand are required to create a superior adsorbent that can selectively adsorb soft acids such as Hg (II), Cd (II) and Ag (I) ion. 2-thiophenecarboxaldehyde functionalized chitosan have high adsorption efficiency (~90%) towards Hg (II) ion in the presence of other metal ions due to the strong interaction between S in thiophene moiety which acted as the soft base and Hg (II) as soft acid resulting in stable complexation (Maity et al. 2021). The presence of soft base (C=N) in rhodamine modified chitosan (RMC) causes the adsorbent to have high binding affinity towards soft acid, Hg (II) ion than other studied metal ions (Cu (II), Cd (II) and Pb (II)) which are hard acids (Qiu et al. 2021). This is in agreement with the resulting XPS analysis that shows higher amount of adsorbed Hg (II) ion compared to other metal ions. Chauhan and Kumar (2022) recorded highest removal for Hg (II) as compared to Zn (II) and Cd (II) metal ions as the adsorbent contains functional groups of –C=N and =N which are soft bases.

In a study by Becker et al. (2000), six chemically modified chitosan with different chelating groups were studied for their adsorption for Ni (II), Zn (II) and Cd (II). After testing the adsorption capacities of each chitosan derivatives for cadmium, nickel and zinc ions, it was observed that derivatives with carbonyl and amine showed only slight improvement in adsorption efficiency compared to ungrafted chitosan. Meanwhile derivative 6 which contains S group along with amine and carbonyl/carboxyl demonstrate significantly higher adsorption capacity for Cd (II) than other derivatives. Derivative 6 was found to be highly selective towards cadmium (II) ion compared to zinc (II) and nickel (II) as aligned with HSAB theory. Cadmium ion which is a soft acid has higher tendency to form strong bond with soft base, sulfur, in derivative 6 as compared to other groups, hence showing highest adsorption. From this study, it can be observed that the selection of derivatives with suitable chelating group for the target heavy metal plays an important role in developing an effective heavy metal adsorbent. HSAB theory should be employed in selecting the suitable chelating groups in chitosan derivatives to adsorb the targeted heavy metal.

Numerous investigations have demonstrated that the HSAB hypothesis is a fundamental idea in predicting the stability and chemical reactivity of complexes. Nonetheless, the HSAB theory has been shown to have limitations in a number of circumstances. Abu El-Soad et al. (2022) synthesized chitosan modified with carboxyl groups (CTS-CAA) and evaluated its adsorption performance toward Cu^{2+} and Zn^{2+} ions (Abu El-Soad et al. 2022). Although Cu^{2+} is considered a borderline soft acid and Zn^{2+} a borderline hard acid, both showed strong affinity for the modified chitosan, indicating that the adsorption was not strictly governed by HSAB theory. In a study with hydroxyapatite (HA) as adsorbent, Cu (II) and Zn (II) were assessed both in single and binary systems (Ramesh et al. 2012). Although HSAB would predict similar behavior (both are borderline-hard acids, with almost identical ionic radii: $Cu^{2+} \sim 71$ pm, $Zn^{2+} \sim 74$ pm), the HA exhibited much higher adsorption capacity for Cu (125 mg/g) than for Zn (30.3 mg/g). This size-sensitive selectivity, tied to preferential sorption and ionic radius nuances, demonstrates that geometric and structural factors outperformed the acid–base principle in determining adsorption performance. Biochar derived from biomass due to its high porosity, large surface area, and diverse surface functional groups, has been widely explored for adsorption of heavy metals like Cu (II), Cr (VI), Cd (II), and Pb (II). The studies show that adsorption efficiencies are highly dependent on parameters such as pH, pyrolysis temperature, and contact time, and can reach up to 99.86% removal at pH 4 for certain metals (Wang et al. 2022b; Georgieva et al. 2025). The dominating factors are physicochemical properties and surface chemistry, such as pore accessibility and reactive sites, rather than the simplistic HSAB-based ligand–metal matching. The results suggested that factors such as surface morphology, functional group density, and coordination environment played a more significant role than acid–base hardness alone.

Optimization of variables during heavy metal removal

The adsorption efficiency of an adsorbent can be influenced by various factors which include the amount of adsorbent used, the concentration of metal ion, contact time, pH and temperature (Kanamarlapudi et al. 2018). Therefore, these factors need to be optimized for the modified chitosan to achieve the maximum adsorption efficiency.

pH effect

pH is a quantitative measure of acidity and alkalinity based on the concentration of hydrogen ion of a solution. The pH of the solution has a significant impact on the adsorption of the metal ions onto the modified adsorbent. This is because it affects the structural characteristic and surface charge of the modified chitosan (Mu et al. 2020). At lower pH, the surface charge of the adsorbent is positive due to the protonation of amine group, hence higher tendency to attract metal-containing polyatomic anions. The effect of pH towards the adsorption of heavy metal ions by the chemically modified chitosan are evaluated through the adsorption efficiency obtained after tested with different pH. The values of the other adsorption factors which are temperature, adsorbent dose, initial metal concentration and contact time were kept constant. Most studies that develop chemically modified chitosan as heavy metal adsorbent use pH ranges from pH 1 to pH 7. At pH higher than pH 7, the heavy metal ions have the tendency to form precipitates of metal hydroxide which in undesirable for adsorption reaction (Manzoor et al. 2019).

The optimum pH mainly depends on the type of modification of the chitosan derivatives and the metal ions adsorbed. The crosslinked chitosan achieved the maximum adsorption at lower pH as they have high stability in acidic environment. The optimum pH for adsorption of Cr (VI) ions onto chitosan crosslinked with diepoxyoctane (DEO) is at lower pH. Vakili et al. (2018) tested the modified chitosan with different initial pH of metal solution which ranges from pH 2 to pH 10 and the highest adsorption capacity was found at pH 2. In solutions, Cr (IV) may exist in various forms such as chromate, hydrogen chromate and dichromate which are negatively charged. At lower pH, the protonation of amine groups of the modified chitosan leads to the formation of positively-charged amine group (NH_3^+), which may form electrostatic attraction with the anion form of the Cr (IV) ions. This explains the high adsorption of Cr (IV) ions on the modified adsorbent at low pH. This study also mentioned that the maximum adsorption of DEO crosslinked chitosan was achieved at 94.8 mg/g while the raw chitosan was at 23.38 mg/g at pH 4. This shows that the crosslinked chitosan not only help to improve the adsorption efficiency but also enhance the acid stability of the adsorbent.

Mainly, the optimum adsorption for chitosan is obtained in slightly acidic environment (pH 4–6). The lower adsorption of heavy metal ions for chitosan at lower pH could be due to its instability at lower pH and the protonation of the adsorption sites which may lead to repulsion effect with the metal cations. Mincke et al. (2019) study the pH effect on adsorption of Pt (IV) and Pd (II) onto the cross-linked chitosan between pH 1 to pH 5 since the study focuses on the removal of the heavy metal ions from acidic wastewater. For adsorption of Pd (II), the adsorption capacity of 1,10-phenanthroline-2,9-dicarbaldehyde and [2,2′-bipyridine]-5,5′-dicarbaldehyde crosslinked chitosan derivatives increased as pH increase to pH 5. Meanwhile for adsorption for Pt (IV) ions, the adsorption efficiency increases as pH increases to pH 4 and achieved maximum adsorption capacity. However, the efficiency decreases with pH higher than 4. Glutaraldehyde crosslinked and melamine grafted chitosan was developed as an adsorbent for Pb (II) and Hg (II) ions and the pH effect was studied between range of pH 1–6 (Ge and Du 2020). It was found that the adsorption of the metal ions increased as the pH increases to reach a maximum value at pH 6 for Hg (II) ion and at pH 5 for Pb (II) ion.

Adsorbent dose

The amount of adsorbent used for the adsorption process plays a significant role in the adsorption efficiency. In this variable test, the other independent variables especially the initial metal concentration was fixed and tested with different amount of adsorbent. It can be deduced that higher adsorbent dose used will lead to higher adsorption efficiency. At lower adsorbent dose, the adsorption efficiency is low due to inadequate presence of adsorption sites. By increasing the adsorbent dose, higher amount of adsorption sites will be available for the heavy metal ions and hence, leads to higher percentage removal or adsorption efficiency. However, in some studies, it is discovered that the adsorption capacity decreases with the increasing amount of adsorbent used. At lower adsorbent dose, the adsorption capacity is high due to higher amount of metal ions present compared to the adsorption sites. Higher amount of metal ion is adsorbed per unit mass of the adsorbent. As the adsorbent dose increases, the amount of adsorbent will be too excessive for the fixed amount of metal ion to the point that there is no metal ion left that could be adsorbed (Zhang et al. 2019a). Hence, less amount of metal ions are adsorbed per unit mass of the adsorbent, thus lower the adsorption capacity.

The adsorbent dose effect on the adsorption of Hg (II) ion by N-vinyl imidazole grafted chitosan was tested with doses in the range of 0 g/L -6 g/L. It was observed that the percentage removal of Hg (II) ion increased as the adsorbent dose increased to 6 g/L (Labidi et al. 2019). The dose for polyacrylic acid grafted chitosan was varied between 0.5 and 2.0 mg/mL and tested with Pb (II) ions to compare the adsorption efficiency towards the metal ion. The percentage removal of Pb (II) ions increased with the increasing adsorbent concentration up to 2 mg/mL. However, it is found that the adsorption capacity significantly decreases as the adsorbent dose increases. Since at adsorbent concentration 1.0 mg/mL both the adsorption capacity (96.21 mg/g) and percentage removal of Pb (II) ion (96.21%) is relatively higher than other doses, it was selected as the optimum adsorbent dose (Hu et al. 2020).

Metal concentration

Initial concentration of the heavy metal can also affect the adsorption efficiency. The increase of initial metal concentration can cause increment in the adsorption capacity. Higher initial number of adsorbates will reduce the mass transfer resistance of metal ions between aqueous and solid phase, resulting in higher likelihood of the metal ions colliding with the adsorption sites of the adsorbent and hence enhancing the adsorption capacity (Gamal et al. 2021). The adsorption capacity will stop increasing once the adsorption has reached an equilibrium and the adsorption sites of the adsorbent are fully occupied. However, the percentage removal of the metal ions decreases as the initial concentration of metal ions increases. Higher amount of metal concentration with constant amount of adsorbent creates competition for the limited adsorption sites and thus resulting in decreasing removal percentage (Dubey et al. 2016).

The adsorption capacity of crosslinked and ninhydrin grafted chitosan towards Pb (II) ions was investigated in different initial metal concentration from 10 to 700 mg/L (Chen et al. 2021). The adsorption capacity increases with increasing metal concentration until it reached a plateau at 500 mg/L. The effect of initial concentration of Cu (II) from 100 to 600 mg/L towards the percentage removal and adsorption capacity of crosslinked chitosan grafted with polymethyl methacrylate were investigated (Sutirman et al. 2020). The percentage removal of Cu (II) decreases while the adsorption capacity peaks as the initial concentration increases. The percentage removal decreases from 78.9% at 100 mg/L Cu (II) to 57.4% at 600 mg/L metal concentration. However, the adsorption capacity increases significantly from < 30 mg/g at 100 mg/L concentration to 140 mg/g at 600 mg/L Cu (II) concentration.

Time

Contact time is essential to the adsorption process as it enables the dispersion and adhesion of adsorbates molecules (Kurniawati et al. 2021). The contact time between the metal ions and adsorbent also have the tendency to affect the adsorption capacity. At the initial stage, the adsorption capacity increases rapidly as the adsorbates directly interact with the free adsorption site upon contact. However, when the vacant adsorption sites have become limited, along with the repulsion between the adsorbed and unadsorbed metal ions, the rate of adsorption becomes slower (Zhang et al. 2019a). The adsorption capacity will gradually increase upon addition of metal concentration until a plateau is observed. The plateau occurred when dynamic equilibrium is achieved between the adsorbed metal ions and the metal ions being desorbed (Sutirman et al. 2020). The time taken by the adsorption process to reach the equilibrium state will be stated as the equilibrium time.

Chitosan grafted with hydroxymethyl furfural shows increasing adsorption of Cu (II) and Cd (II) ion from 5 to 75 min before reaching a plateau, while unmodified chitosan reaches equilibrium at 180 min for Cu (II) removal and 120 min for Cd (II) (Mone et al. 2020). EDTA grafted chitosan adsorption of Cu (II) and Pb (II)) occurred at a fast rate initially and gradually increased with time until reaching maximum value and equilibrium at 60 min (Chen et al. 2019). In a study by Cheraghipour and Pakshir (2020), a statistical approach, RSM was used to optimize the adsorption

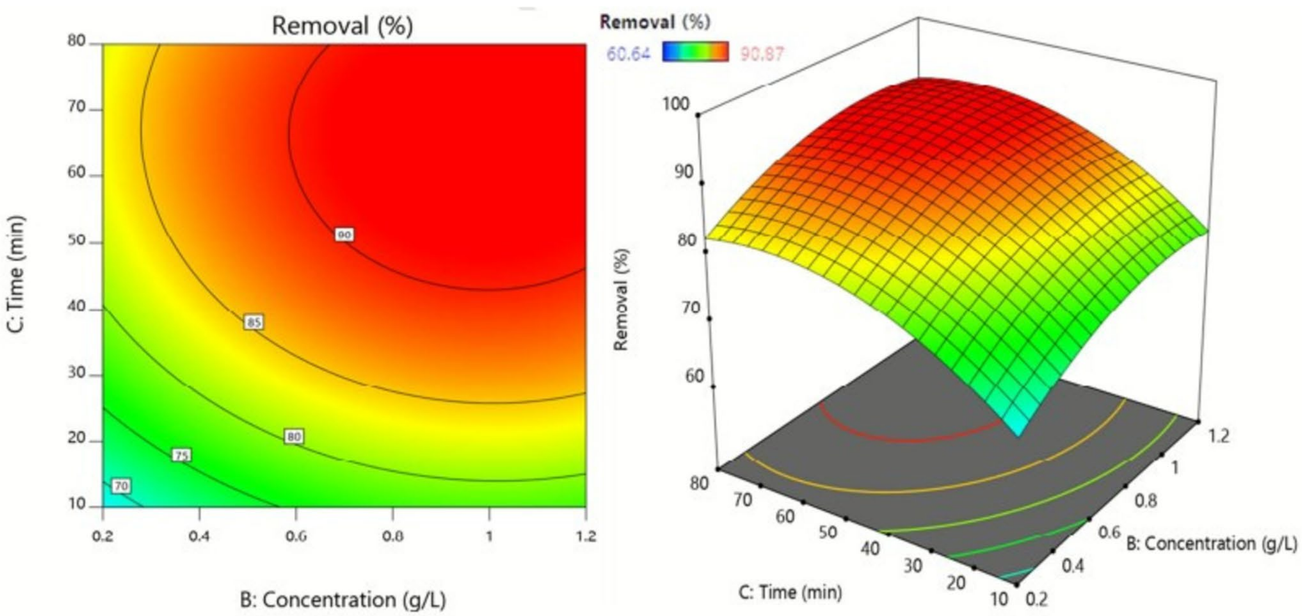


Fig. 3 3D and contour plots of the interaction between adsorbent concentration and time on the Pb (II) removal by chitosan conjugated magnetite nanoparticle (CH-MNP) (Cheraghipour and Pakshir 2020)

parameters for adsorption of Pb (II) onto chitosan conjugated magnetite nanoparticle (CH-MNP) and the optimal contact time is at 59.9 min with maximum adsorption percentage at 92.15%. RSM also studied the interaction between parameters, and in this study, it is found that the interaction between contact time and adsorbent dose give significant effect towards the adsorption efficiency as shown in Fig. 3.

Temperature

To determine whether the adsorption is endothermic or exothermic, it is crucial to test it at various temperatures. In general, adsorption is considered to be an exothermic reaction. However, there are some cases in which the adsorption capacity may increase at higher temperature. Hence, we can deduce that finding an optimum temperature may significantly improve the adsorptive forces between the adsorbent and heavy metals. The increasing adsorption capacity with increased temperature is attributed to endothermic reaction in which the reaction between adsorbent and adsorbent is more favourable at high temperature (Al-Ghouti and Al-Absi 2020). High temperature can provide adequate energy for the metal ions to interact with the adsorbent's active sites, thus enhancing the adsorption (Manzoor et al. 2019). The Cu (II) and Cd (II) ions uptake by 5-hydroxymethyl furfural grafted chitosan was studied at different temperatures from 25 and 65 °C (Mone et al. 2020). The adsorption capacity for both Cu (II) and Cd (II) ions adsorption achieved a maximum value at the highest tested temperature, 65 °C. This shows that the reaction that took place is an endothermic reaction. The adsorption capacity decreases as the temperature exceeded these temperatures. This is because as the temperature further increase, the thermal vibration might exceed the interaction between the adsorbent and metal ions, causing the metal ions to be released and hence leads to decreasing adsorption (Manzoor et al. 2019). Meanwhile the decreasing of adsorption capacity with rising temperature can be related to the adsorption process being an exothermic reaction. In exothermic reaction, reverse reaction or desorption may occur with increase in temperature (Horsfall and Spiff 2005). Hence, under exothermic nature, adsorption is favoured at lower temperature. In a study by Zhang et al. (2019a, b, c), on the methyl acrylate and tetraethylenepentamine grafted chitosan adsorption towards Cd (II) ion, a declining trend was observed for the adsorption capacity when the temperature is increased. The maximum Cd (II) adsorption was obtained at 25 °C. This proves that the adsorption process is an exothermic reaction.

Adsorption mechanism

Studying the mechanism behind the adsorption process helps in further understanding and optimizing the metal adsorption, which is important in designing an efficient adsorption process. The adsorption of metal ions onto the adsorption site of the adsorbent may occur in various mechanisms. The common types of interaction between heavy metal ions and the adsorbent are complexation, electrostatic attraction, ion-exchange and physical adsorption (Sahoo and Prelot 2020).

These mechanisms are often deduced based on FTIR, XPS and enthalpy change. The enthalpy change (ΔH) plays a pivotal role in distinguishing between physical and chemical adsorption mechanisms, particularly in the context of heavy metal ion removal using chitosan-based adsorbents. Physical adsorption, which involves weak van der Waals forces or electrostatic interactions, typically exhibits low enthalpy changes, usually in the range of 5–40 kJ/mol (Alsharif and Alsharif 2025). In contrast, chemical adsorption (chemisorption) involves the formation of stronger, often covalent or coordinate bonds between metal ions and the functional groups on chitosan, such as amino (–NH_2) and hydroxyl (–OH), and is characterized by higher enthalpy changes, often exceeding 40 kJ/mol and reaching up to 100 kJ/mol or more (Alsharif and Alsharif 2025). For example, a study investigated the adsorption of Cu (II) on a chitosan-/PVA-coated magnetic nanoparticles showed that the adsorption process was endothermic with ΔH = 127.37 kJ/mol, indicating that the adsorption is governed by chemisorption (Altinisik and Yurdakoc 2016). Thermodynamic studies often complement kinetic and spectroscopic analyses (e.g., FTIR and XPS) to confirm the nature of adsorption, with ΔH values serving as a quantitative indicator of the interaction strength between chitosan and heavy metal ions. Thus, enthalpy change not only reveals the type of adsorption but also the selection of chitosan modifications for targeted metal removal.

Meanwhile, XPS and FTIR techniques help identify how chitosan interacts with metal ions. FTIR detects changes in vibrational frequencies of functional groups, indicating their involvement in metal binding, while XPS reveals shifts in binding energies and elemental composition, confirming whether interactions are physical, ionic, or covalent. Electrostatic attraction, which occurs due to the interaction between the negatively charged groups on chitosan and positively charged metal species (or negatively charged metal ions under certain conditions), typically results in minimal spectral changes. In FTIR, such interactions may cause slight shifts in the –NH or –OH stretching vibrations, but no new pronounced peaks or significant alterations indicative of strong covalent bond formation are usually observed (de Godoi et al. 2013; Kindi et al. 2021). XPS analysis similarly reveals little to no significant change in the binding energies of core-level electrons (N 1 s, O 1 s), as the interaction is primarily charge-based rather than involving direct electron transfer or covalent bond formation (Dambies et al. 2001; de Godoi et al. 2013). Minor shifts in surface potential might occur due to changes in charge distribution.

Ion exchange, often involving the replacement of native cations (such as H^+ or Na^+) associated with the chitosan matrix by heavy metal ions (e.g., Pb^{2+}, Cd^{2+}, Cu^{2+}), can be inferred from more noticeable spectroscopic changes. In FTIR, this may manifest as shifts or intensity changes in the –OH and –NH_2 vibrational bands, reflecting changes in local chemical environments and hydration shells (Nicomel et al. 2021). In XPS, ion exchange is typically evidenced by the disappearance or reduction in signal intensity of the original cation and the concurrent appearance or increase of the heavy metal signal (Eltaweil et al. 2021). However, binding energy shifts for the N 1s and O 1s core levels are usually minimal compared to coordination, indicating that the interaction is primarily ionic rather than covalent (Dambies et al. 2001).

Coordination or complexation, which involves the formation of coordinate covalent bonds between heavy metal ions and electron-donating groups on chitosan (such as amine or hydroxyl groups), results in the most pronounced spectral changes, typically show stronger and more specific spectral changes than physical or electrostatic interactions. FTIR spectra often show clear shifts in –NH_2 and –OH bands (Bombuwala Dewage et al. 2018) and in some cases, new bands associated with metal–nitrogen or metal–oxygen vibrations may appear, particularly in the fingerprint region below 600 cm^{-1} (e.g., broad bands near 550, 480, and 250 cm^{-1} for metal ion-ligand vibrations) (Jiang et al. 1997). Coordination can also reduce or eliminate the intensity of free –NH_2 peaks, indicating their involvement in bond formation. XPS provides further confirmation through noticeable shifts in the binding energies of N 1s and O 1s core levels, which reflect significant changes in the electronic environment upon metal coordination (Dambies et al. 2001; Sutirman et al. 2020). For example, electron-donating ligands will lower the binding energy of core level electrons. The heavy metal peaks themselves may also shift slightly, indicating changes in oxidation state or ligand field effects (Dambies et al. 2001). Table 6 shows the summary of the adsorption mechanisms of chitosan-based adsorbents for heavy metal removal, interpreted through FTIR and XPS diagnostic peaks. Adsorption mechanisms are complicated in general because the potential mechanisms depend on various factors such as the chemical components of the adsorbents, the type of pollutants, and the environment of the solution (solution pH and the presence of coexisting ions). Hence, a combination of different types of interaction may occur simultaneously (Dong et al. 2022).

Chelation/complexation

Chitosan-based adsorbents are highly effective for heavy metal removal due to their significant ability to chelate and complex metal ions. This characteristic is primarily attributed to the presence of abundant amino and hydroxyl functional groups on the chitosan backbone, which act as active sites for coordination (Sharifi et al. 2021; Zhang et al. 2021). These functional groups possess lone-pair electrons that can readily form coordination bonds with transition metal ions.

Table 6 Proposed mechanisms of heavy metals adsorption onto chitosan based adsorbents based on FTIR and XPS analysis

Adsorbent	Metal Ions	FTIR diagnostic Peaks	XPS observation	Proposed mechanism	References
Chitosan-modified biochar (CMBC)	Pb^{2+}	N–H bending vibration shifted from 1638 to 1681 cm^{-1}; Transmittance drops in N–H stretching, bending, scissoring, and wagging, and C–N stretching bands (at 3534, 1612, 1396, and 1045 cm^{-1})	XPS spectra for CMBC before and after lead adsorption showed nearly identical peak positions for C, N, O, but with different intensities, suggesting successful coating and involvement of chitosan	Complexation with amino groups	Bombuwala Dewage et al. (2018)
Dendritic polyamine–pyridine-grafted chitosan beads	Cu^{2+}	Stretching vibrations of pyridine (1548 cm^{-1}) and C–N (1463 cm^{-1}) significantly weakened or disappeared; New peaks at 1608 and 1384 cm^{-1} attributed to C=N and NO_3^-	Two peaks involving neutral nitrogen (N1) and pyridine nitrogen (N2) showed obvious shifts to 398.79 and 399.62 eV, confirming the coordination effect	Chelating interaction involving pyridine and aliphatic amines; Simultaneous adsorption of NO_3^- for charge balance	Wang et al. (2020)
Chitosan/Hyaluronan multilayers	Co^{2+}, Ca^{2+}, Fe^{3+}, Cu^{2+}	Slight shift to higher wavenumber of band at 1602 cm^{-1} (up to 1605 cm^{-1} for Co^{2+} or Ca^{2+}, and 1608 cm^{-1} for Fe^{3+} and Cu^{2+}); Broadband at 3300 cm^{-1} (O–H and N–H stretching) remained similar or increased in intensity	–	Coordinating bonds with hydroxyl or carbonyl oxygen or nitrogen in amino groups; Electrostatic binding by carboxylic groups	Kindi et al. (2021)
O-carboxymethyl chitosan	Cu^{2+}	C=C vibrations of metal complexes shifted to a higher wavenumber (1732 cm^{-1}) compared to O-CSPX (1730 cm^{-1}); One additional signal observed at 1397 cm^{-1} attributed to carbonyl groups of CH_3COO^-	–	Coordination of Cu ions with the p-π conjugate group; Involvement of carbonyl groups	Liu et al. (2018)
Chitosan	Ni^{2+}	shift in some characteristic peaks, at 3330 cm^{-1}, 1422 cm^{-1}, and 1382 cm^{-1}, which imply the involvement of amide, alcohol, ether, and alkane functional groups of chitosan	the binding energy of N 1 s (amine groups) increased from 399.3 eV to 399.8 eV and 399.6 eV after Ni (II) adsorption; binding energy of the major C 1 s peak corresponding to C–OH increased from 286.3 eV to 286.5 eV; Ni observed in the XPS spectra	Coordination with O- and N-containing groups	Nicomel et al. (2021)

Table 6 (continued)

Adsorbent	Metal Ions	FTIR diagnostic Peaks	XPS observation	Proposed mechanism	References
Recyclable magnetic biochar modified by chitosan–EDTA	Pb	Overlapping peaks of the –OH and –NH group vibrations shifted from 3416 to 3230 cm^{-1} after Pb adsorption; C=O (–NH–C=O and –COOH) stretching vibration peak shifted from 1653 cm^{-1} and 1407 cm^{-1} to 1624 cm^{-1} and 1375 cm^{-1}, and intensity decreased	new peaks of Pb 4p$_3$, Pb 4d$_3$, Pb 4d$_5$, Pb 4f$_{7/2}$, and Pb 4f$_{5/2}$ appeared at 652.08 eV, 401.08 eV, 415.08 eV, 437.08 eV, 138.93 eV, and 143.78 eV, respectively	Complexation of amine and carboxyl functional groups with Pb	Zheng et al. (2020)

Electrons are exchanged between the adsorption site and heavy metal ions to form strong and stable chemical bonds with high interaction energy (Sahoo and Prelot 2020). In a study by Zhang et al. (2019a, b, c), the mechanism of Cd (II) adsorption onto methyl acrylate and tetraethylenepentamine grafted chitosan was studied through XPS analysis. It was observed that the binding energy of N and O increased after Cd (II) adsorption which indicate the interaction between the atoms and Cd (II). It was suggested that the lone pair of electrons from these atoms were donated to form a bond with Cd (II) which shows that the adsorption occurred through chelation of Cd (II) with N and O. In a study by Yang et al. (2021), the mechanism for the adsorption of both Pb (II), Cd (II) and Cu (II) ions onto crosslinked and sulfhydryl grafted chitosan was suggested to occur through chemical complexation. The FTIR and XPS analysis proved that O from carboxyl and S from sulfhydryl group of the adsorbent were involved in the adsorption process and formed chemical bonds.

Another example is the adsorption process of Pb (II), Cd (II), and Cu (II) ions onto ethylenediaminetetraacetic acid crosslinked chitosan (CS-EDTA) which was investigated by Verma et al. (2022). The adsorption of the heavy metals was attributed to complexation with EDTA, which was confirmed by the elemental mapping, EDS and FT-IR techniques. The presence of EDTA enhanced the metal-binding efficiency by introducing additional carboxyl and amine groups, which facilitated multidentate chelation. One notable example is a study by Zhang et al. (2024) on mercapto-functionalized chitosan-kaolin composites (TGL-CS), which introduced thiol (–SH) groups via a mercapto-alkenyl click reaction (Zhang et al. 2024). This modification significantly improved the adsorption capacity for Pb (II), with FTIR and XPS analyses confirming that sulfur, amino, and hydroxyl groups all participated in coordination with lead ions. The thiol groups, in particular, offered strong affinity due to their ability to donate lone pair electrons, forming stable coordinate bonds. Liu et al. (2025) examined EDTA-chitosan/alginate porous beads (EC-AB) for simultaneous removal of Pb (II) and methylene blue (Liu et al. 2025). The composite leveraged the chelating ability of EDTA and the functional diversity of chitosan and alginate. FTIR and XPS revealed significant shifts in the N 1 s and O 1 s binding energies after adsorption, indicating that amino and carboxyl groups formed coordination complexes with Pb (II). Similarly, in a study by Sutirman et al. (2018) chitosan beads grafted with poly (methacrylamide) (Chitosan-g-PMAm) were employed to adsorb Cu (II) and Cd (II) ions (Sutirman et al. 2018). The grafted polymer introduced more carbonyl and amine functionalities, which XPS analysis confirmed as being responsible for chemical interactions with the metal ions. The adsorption followed pseudo-second-order kinetics, implying that chemisorption dominated the process through coordination mechanisms rather than physical adsorption or ion exchange. Moreover, research on porous carboxymethyl chitosan (PCMC) beads for Co (II) adsorption revealed that the carboxyl and hydroxyl groups played critical roles in the chelation process (Luo et al. 2022). Post-adsorption FTIR spectra showed noticeable shifts in the carboxyl and amine regions, and XPS analysis further confirmed the formation of coordinate bonds involving lone pair electrons from nitrogen and oxygen atoms with Co (II). Collectively, these studies underscore the importance of amino, hydroxyl, and carboxyl functional groups in the coordination-based removal of heavy metals, and demonstrate how chemical modifications to chitosan can significantly enhance its adsorption performance by increasing the availability and strength of metal-binding sites.

Ion exchange

Ion exchange involves the exchange or replacement of charged ions in the adsorbent in stoichiometric amount with other ions in the surrounding solution (Sahoo and Prelot 2020). Adsorbent which contains negatively charged groups such as COO^- and SO_3^- are referred as anion exchanger while those with positively charged groups such as NHR_2^+, NR_3^+ and PR_3^+. In heavy metal adsorption, metal cations may undergo ion exchange with cations present in adsorbent while heavy metals in anionic form may exchanges with anions from the adsorbent during adsorption process. This mechanism was observed in a study by Zheng et al. (2018), in which it is assumed as the dominant mechanism of Cr (VI) adsorption onto poly ([2- (methacryloxy)ethyl] trimethylammonium chloride) modified magnetic chitosan particles (DMCP). The adsorption capacity decreased significantly in the presence of Cl^- ions which indicates that Cl^- inhibit the adsorption of Cr (VI) onto the adsorbent. Cl^- ion in the solution is assumed to compete with Cr (VI) to interact with ammonium in the adsorbent. Hence, it was concluded that the ion exchange is the dominant mechanism. In the XPS analysis carried out by Wang et al. (2019a, b), it was discovered that sodium (Na) content in the hydrogel disappeared after the heavy metal adsorption whereas Pb (II) content shows up after adsorption process with chitosan-2D montmorillonite (2DMMT). This signifies the role of ion exchange in the adsorption mechanism, in which the adsorption occurred due to exchange between Na^+ in 2DMMT and Pb^{2+} in the solution. Elanchezhiyan et al. (2021) reported the ion exchange was occur simultaneously with complexation mechanism. Based on the XPS analysis, the Pb (II) and Cd (II) ions possibly interact with hydroxyl groups on the chitosan adsorbent via ion exchange and undergo complexation with amino groups (–NH and $–NH_2$).

Electrostatic attraction

Electrostatic attraction occurs when positively charged atoms are attracted to the negatively charged atoms or vice versa. Since most of adsorption studies was performed under acidic condition, the potential adsorption sites (hydroxyl, amine etc.) tend to be protonated. Hence, they are likely to undergo interaction with anions as opposed to metal cations. This explains why most of studies that reported electrostatic attraction as the adsorption mechanism involves the adsorption of heavy metals in their anionic form. For example, Cr (VI) existed in $HCrO_4^-$ form at lower pH and tends to form electrostatic interaction with the positively charged surface of chitosan-lignosulfonate which consists of protonated amine and hydroxyl groups (Gu et al. 2019). In a study by Dinh et al. (2020), the electrostatic attraction between the Cr (VI) anions and protonated adsorption sites of MnO_2/CS was proven through analytical spectroscopy. In the FTIR spectra, it is discovered that there is no peak shifting or new peaks observed before and after adsorption, which indicates that no covalent bond is formed. However, the intensity of the peaks is found to be decreased due to the electrostatic attraction.

Vakili et al. (2018) tested the modified chitosan with different initial pH of metal solution which ranges from pH 2 to pH 10 and the highest adsorption capacity was found at pH 2. In solutions, Cr (IV) may exist in various forms such as chromate, hydrogen chromate and dichromate which are negatively charged. At lower pH, the protonation of amine groups of the modified chitosan leads to the formation of positively-charged amine group (NH_3^+), which may form electrostatic attraction with the anion form of the Cr (IV) ions. This explains the high adsorption of Cr (IV) ions on the modified adsorbent at low pH. Meanwhile, Zhuang et al. (2021) proposed the adsorption of Co (II) and Sr (II) may occur through both complexation and electrostatic interaction. Electrostatic interaction possibly played a role in the adsorption process at neutral condition (pH 7). The negatively charged EDTA grafted chitosan may attract the positively charged heavy metal ions through electrostatic attraction. Ablouh et al. (2019) carried out FTIR, SEM and EDX analysis to investigate the mechanism of Pb (II) and Cr (VI) adsorption onto crosslinked and sodium alginate modified chitosan. The adsorption mechanism for Cr (VI) involves electrostatic attraction. This is because at lower pH, the chromium ion exists in its anionic form of $HCrO_4^-$, which may form electrostatic interaction with the protonated surface of the modified chitosan. Sutirman et al. (2020) reported the adsorption mechanism of Cu (II) ion onto crosslinked chitosan grafted with methyl methacrylate which was governed by complexation reaction with N and O of the adsorbent.

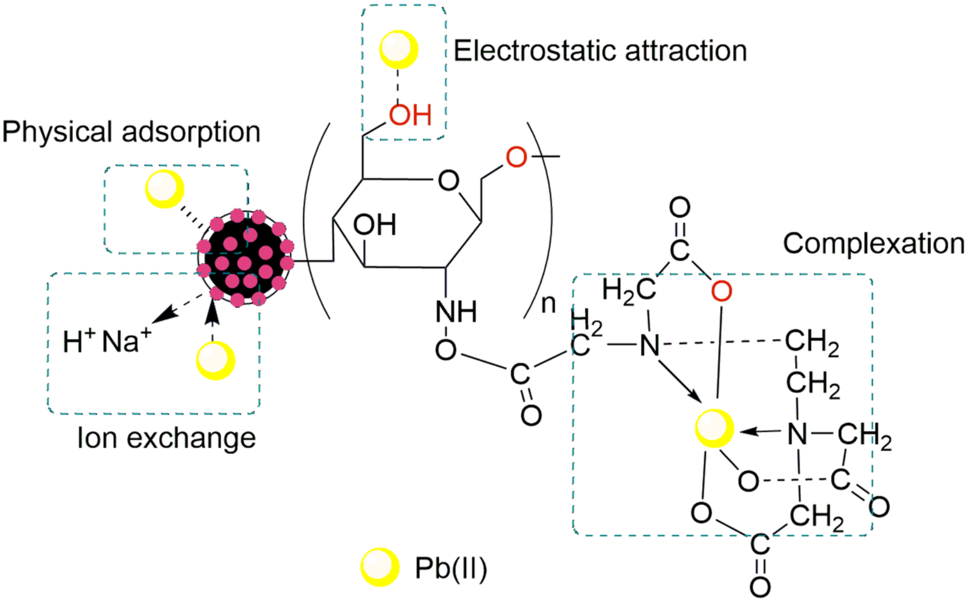


Fig. 4 Probable mechanisms of Pb (II) adsorption onto magnetic biochar functionalized with chitosan and ethylenediaminetetraacetic acid (E-CMBC) (Zheng et al. 2020)

However, the mechanism is also influenced by pH. At higher pH, electrostatic attraction mechanism may take place as the increased negative charge on the carboxyl group of the adsorbent could attract the metal cations.

Physical Adsorption

Through physical adsorption, the metal ions are adsorbed to the adsorbent surface via weak forces such as hydrogen bonding, Van der Waals or π-π interaction. It does not involve electron transfer, has low interaction energy (15–30 kJ/mol) and is reversible (Sahoo and Prelot 2020).

Chen et al. (2020) reported the occurrence of physical adsorption along with chemical adsorption during the adsorption of Cu (II) ions onto chitosan-carboxymethyl starch through XPS analysis. Cu (II) is adsorbed to CTS-CMS through Van der Waals force in the form of $Cu_4 (SO_4) (OH)_6 (H_2O)$. According to Zheng et al. (2020), the adsorption of Pb (II) ion by magnetic biochar functionalized with chitosan and ethylenediaminetetraacetic acid (E-CMBC) took place mainly through metal complexation. However, they also proposed other mechanisms that may have involved in the adsorption process which include physical adsorption as shown in Fig. 4. Omidinasab et al. (2018) reported the involvement of physical adsorption in the adsorption process of V (V) and Pd (II) ions onto Fe_3O_4-CSN. This was proven through the value of mean free energy of sorption (E) in which physical adsorption shows E value of < 8 kJ/mol. The E value for V (V) and Pd (II) are 5.42 and 3.49 kJ/mol respectively, which implies that physical adsorption governs the adsorption process for both metal ions. The Gibbs free energy (G^0) value is also found to be within the range values for physical adsorption (0–20 kJ/mol).

Fixed-bed breakthrough adsorption studies

Currently, experts prefer the batch absorption technique in their research as it is simple and cheap. However, batch sorption technique is only suitable for small amount of wastewater with low content of pollutants. Hence, it is rarely applicable in the water treatment industry. To ensure the practicality of the developed chitosan adsorbent, researchers should include continuous fixed bed adsorption technique in their studies to accommodate the industrial need. This technique is simple, inexpensive and feasible for removal of higher amount of wastewater with high pollutant content. It involves the continuous flow of polluted water across an adsorbent bed at a consistent rate (Patel 2019). The parameters influencing adsorbent efficiency in a fixed-bed column system may differ from those in a batch adsorption system. Process parameters such as heavy metal solution flow rate, column bed height, and initial metal concentration all have a substantial impact on the column's performance in this system (Patel 2019). Breakthrough curves, which depict the column performance in a form of normalized effluent concentration versus time or bed volume profile from multiple chitosan adsorbents are reviewed in this paper. The vital parameters that can be extracted from the breakthrough curves include the breakthrough time (tb), exhaustion time (te) and the area above the curve, in which the adsorption capacity of the column can be obtained (qe) (González-López et al. 2020).

In order to further evaluate and analyze the fixed-bed column effectiveness, the kinetics results were often fitted in some dynamic models such as Thomas, Adam-Bohart and Yoon-Nelson models. Amongst these models, Thomas model is most commonly applied in the column adsorption studies. It assumed that the driving force rate follows the second order kinetics without considering axial dispersion in the column (Patel 2019; González-López et al. 2020). It is based on the assumption that internal and external diffusion is not rate-limiting. Adam-Bohart model states the rate of adsorption is proportional with the concentration of adsorbent and the residual adsorption capacity, which used to describe the initial part of the breakthrough curve (Nwabanne et al. 2022). Yoon-Nelson model proposes that rate of adsorption is directly proportional to the adsorption of adsorbates and the adsorbent breakthrough (Yoon and Nelson 1984).

In a study by Dinu et al. (2022) the efficiency of aminopolycarboxylic acid-functionalized chitosan-clinoptilolite (CS-PL) and EDTA modified CS-PL (CSEDTA-CPL) in adsorbing various heavy metals (Zn,Pb,Cd,Ni and Co) in column system were studied through the breakthrough curves. The CS-PL showed a much steeper breakthrough curve for all metal ions compared to CSEDTA-CPL, which indicates the unmodified CS-SPL has lower adsorption capacity and undergoes rapid active site saturation. As of EDTA modified CS-PL, the breakthrough curves for all of the metal ions show different gradient, which stipulates the different affinity of the adsorbent towards the metal ions. CSEDTA-CPL shows the lowest affinity towards Cd (II), as indicated through the steep breakthrough profile, while Ni^{2+} curve shows it has the highest affinity. Overall, CS-CPL reaches exhaustion time at a faster rate, 100 min while CSEDTA-CPL reached only 80% saturation even after 300 min, which emphasized that the EDTA modified chitosan adsorbent shows much higher adsorption capacity than CS-CPL. After fitted the experimental results to both Thomas and Yoon-Nelson models, the theoretical maximum adsorption capacity of CSEDT-CPL was obtained at 145.55 mg/g and reach 50% breakthrough at 121.5 min, which are higher than CS-CPL (68.72 mg/g; 30.64 min).

Effect inlet metal concentration

The initial metal concentration mostly influences adsorption through alterations in the mass transfer driving force or the concentration gradient (Banerjee et al. 2019). At high initial concentration, the transfer driving force increases due to the concentration gradient, and increase mass transfer zone length which leads to increased adsorption capacity (qb) (Tsai et al. 2016; Verduzco-Navarro et al. 2020). However, some studies found that the percentage removal and adsorption capacity at exhaustion point (qe) decreased, which may be caused by the inadequate active sites to accommodate the high concentration of metals at fast rate (Lavanya et al. 2020; Radnia et al. 2013). The column may not efficiently adsorb the high amount of metal ions as the contact time between the adsorbate and the adsorbent is inadequate for it to reach equilibrium before the solution leaves the column (Sánchez-Machado et al. 2016; Verduzco-Navarro et al. 2020). At high initial concentration, the adsorption tends to reach the breakthrough and exhaustion time at faster rate, resulting in steeper breakthrough curve. This indicates that the high metal concentration leads to faster column saturation.

Verduzco-Navarro et al. (2020) reported the effect of the initial metal concentration fed to the column of both alginate chitosan sulfate (Alg-ChS) and unmodified alginate chitosan (Alg-Ch) by feeding different Cu (II) concentrations, 50 and 100 mg/L to each column with other parameters fixed at constant values (pH, 5; flow rate, 100 ml/h; bed height, 13 cm) (Verduzco-Navarro et al. 2020). The breakthrough curve with a function of normalized effluent concentration to the number of interstitial bed volume (NIVB) shows that the higher concentration, 100 mg/L, have steeper curve for both adsorbents, which indicates lower treated volume at breakthrough and exhaustion point. The adsorption capacity at breakthrough point (qb) shows increment at higher concentration, but the adsorption capacity at exhaustion point (qe) decreases. The experimental data fitted well with Thomas model curve with 95% significance level. Based on Thomas model, the adsorption capacity for Alg-Ch shows reduction at higher concentration, but the adsorption capacity for Alg-ChS increases. Meanwhile in study by González-López et al. (2020), the breakthrough curve of different initial Cr (VI) concentration of 100,200 and 300 mg/L shows that the highest concentration (300 mg/L) have the shortest breakthrough and exhaustion time but also recorded the highest adsorption capacity at 9.69 mg/g, according to Thomas model (González-López et al. 2020).

Effect of metal solution flow rate

In a column study, the influent flow rate plays a significant role in affecting the adsorption behaviour. Generally, high flow rate resulted in faster breakthrough time and lower adsorption capacities (Zhang et al. 2019c). At high flow rate, high amount of metal ions was passed through the column at a high rate, which does not enough time for the metal ions to interact with the adsorbent active site (Verduzco-Navarro et al. 2020; Arenas-Flores et al. 2021). The removal efficiency of the column is also affected as the metal ions do not reside in the column long enough to reach equilibrium (González-López et al. 2020). The metal ions will simply leave the column without utilize the adsorbent's full potential. Meanwhile a lower flow rate will allow the heavy metals to have longer residence time in the column and fully interact with the adsorbent active site, resulting

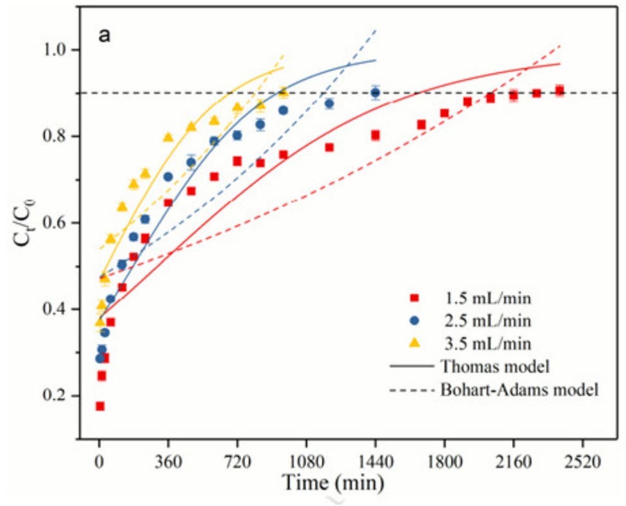


Fig. 5 Actual and predicted breakthrough curves for Cr (VI) by triethylenetetramine-chitosan/alginate composite at different influent flow rate (Zhang et al. 2019c)

in higher adsorption capacity (Sánchez-Machado et al. 2016). In the column adsorption of Pb (II) ions onto chitosan-g-maleic anhydride-g-methacrylic acid, the breakthrough curves of flow rates 1,2 and 3 mL/min indicates that the breakthrough time was recorded in the following order: 3 mL/min > 1 mL/min > 2 mL/min (Lavanya et al.). The highest percentage removal (54%) was observed at the lowest flow rate, 1 mL/min.

González-López et al. (2020) had conducted continuous adsorption study with three different flow rates, 3, 4 and 5 mL/min (bed height: 27 cm; initial concentration: 200 mg/L) (González-López et al. 2020). In this study, different results were obtained as the lowest flow rate does not show maximum adsorption capacity, as observed in other studies. Although the lowest flow rate, 3 ml/min display higher breakthrough time, the highest adsorption capacity was observed at flow rate 4 ml/min, which can be considered as the optimum flow rate. At this optimum rate, the residence time provided is adequate for the adsorption between Cr (VI) and chitosan composite to reach equilibrium and the high amount of metal ions entering the column leads to improved adsorption capacity. In an adsorption study of Cr (VI) onto triethylenetetramine-chitosan/alginate composite, the breakthrough curves of various flow rates were plotted as shown in Fig. 5 and it was observed that the highest flow rate, 3.5 mL/min, recorded the lowest breakthrough time (960 min), followed by 2.5 mL/min (1440 min) and 1.5 mL/min (2400 min) (Zhang et al. 2019c). After analysed with dynamic models, Thomas and Bohart-Adams, the column adsorption fits Thomas model better and the calculated adsorption capacities decreased in value when the flow rate increases.

Effect bed height column

The bed height of the column plays a vital role in the overall adsorption kinetic as it can be associated with the amount of adsorbent used in the column study. Higher bed height equals to higher amount of adsorbent in the column bed and higher contact time (Tsai et al. 2016). Generally, low bed height will attain a steeper breakthrough curve, reaching the breakthrough and exhaustion time at a faster rate (Igberase and Osifo 2019). Meanwhile larger column provides more active sites to interact with the metal ions before leaving the column (Radnia et al. 2013; Sánchez-Machado et al. 2016). In the adsorption of Cu (II) onto adsorbent grafted cross-linked chitosan beads (XCSA), the breakthrough curves of different bed heights of 0.21, 0.28 and 0.35 m were plotted and fitted to shrinking core mass transfer model (Igberase and Osifo 2019). According to the model, the diffusion rate corresponds to the adsorption rate in the particle, with diffusion serving as the rate-limiting phase. The breakthrough time (tb) was observed to increase from 2.4 to 12 h as the bed height increases.

In a study by Arenas-Flores et al. (2021), the column adsorption of Pb (II), Cd (II) and Cr (VI) was conducted with different bed heights of 6, 13 and 25 cm (Arenas-Flores et al. 2021). For adsorption of Pb (II), all three studied bed heights recorded the same breakthrough time, which is at 2 min. However, the percentage removals increased with the bed heights, with the highest removal at 85% recorded at bed height 25 cm. Meanwhile cadmium breakthrough curve shows higher bed height reached breakthrough time at a faster rate. The highest bed recorded breakthrough time at 1 min, with highest percentage removal at 70%. The continuous adsorption of Cr (IV) also demonstrate a similar result, with the highest percentage removal at 69% and lowest breakthrough time was achieved by using highest bed height, 25 cm. These results indicate that applying larger bed height results in higher column adsorption efficiency at a faster rate. The effect of bed height of two different adsorbents, Alg-Ch and Alg-ChS was compared at 13 cm and 33 cm through the breakthrough curves (pH: 5; inlet concentration: 50 mg/L; flow rate: 50 mL/h) (Verduzco-Navarro et al. 2020). Regardless of the different type of adsorbent, at high bed height, the adsorption capacity at breakthrough time (qb) was observed to be higher. Despite that, larger column requires more time to reach breakthrough point, hence, the breakthrough curve is less steep.

Regeneration studies

Regeneration of chitosan-based adsorbents is a crucial aspect of their sustainable and economical application in heavy metal removal from wastewater. It allows for the repeated use of the adsorbent, reducing costs and minimizing secondary pollution (Upadhyay et al. 2021). Chitosan's functional groups, primarily amine (–NH_2) and hydroxyl (–OH) allow strong interactions with metal ions such as Pb^{2+}, Cd^{2+}, Cu^{2+}, and Ni^{2+}. However, for practical deployment, especially in fixed-bed column systems, the ability to regenerate and reuse the adsorbent without significant loss of performance is essential. Although desorption can be challenging due to the strong affinity between adsorbates and the adsorbent surface, various studies have successfully demonstrated regeneration techniques (Vakili et al. 2019a).

A variety of chemical desorption methods using acids, chelating agents, and salt solutions have been explored to restore adsorption capacity after repeated use. Among these, acid treatments (such as HCl), EDTA-based chelation, and saline desorption with NaCl have emerged as the most commonly studied approaches, each with distinct advantages and limitations. One study by Hu et al. (2023), for instance, investigated a magnetite–chitosan composite regenerated with a simple NaCl solution over eight cycles (Hu et al. 2023). While initial removal efficiencies for Cu (II) and Cd (II) were high at 87.67% and 82.45% respectively, these values plummeted to around 33–34% by the eighth cycle.%. The removal of both Cu (II) and Cd (II) dropped below 80% after the fourth cycle. The significant drop in performance after just four cycles underscored the limitations of salt-based regeneration, particularly in maintaining long-term adsorbent effectiveness.

In contrast, EDTA, a well-known chelating agent, demonstrated a more nuanced behaviour when used to regenerate a poly-ε-caprolactone-reinforced chitosan composite designed for multi-metal ion removal (Martínez et al. 2022). Utilizing a 15 g/L EDTA solution with 0.5 N NaOH (pH 13.6), the system showed promising desorption of Zn (II), Fe (II), Al (III), and Cu (II) in the first cycle. However, a sharp decline in performance was observed over six cycles, with adsorption efficiencies dropping to 10–30% for most metals. Interestingly, Pb (II) and Cd (II) behaved differently, in which their adsorption efficiencies increased to 43.3 ± 6.8% and 62.3 ± 2.1%, after the second cycle and remained stable throughout, suggesting a unique interaction between these ions and the EDTA-treated surface, possibly due to precipitation or stable complex formation.

Among all tested strategies, acid regeneration remains the most widely used and effective method for restoring chitosan-based adsorbents. For example, porous magnetic chitosan regenerated with 0.1 M HCl retained over 80% of its original adsorption capacity for Cd (II) even after seven adsorption–desorption cycles (Yadav et al. 2023). This resilience is largely attributed to the ability of acids to protonate the amino groups in chitosan, promoting the release of bound metal ions without compromising the structural integrity of the polymer matrix. Further study by Patel et al. (2024a, b) comparing a variety of eluents including NaOH, HNO_3, H_2SO_4, KOH, and HCl found that 2 M HCl consistently provided the highest desorption efficiencies (Patel et al. 2024a).

Meanwhile in another study by Abu El-Soad et al. (2022), different eluents like HCl, H_2SO_4, HNO_3, urea, EDTA, and NH_4Cl were quizzed for the desorption of both copper and zinc metal ions from the (CTS-CAA) surface (Abu El-Soad et al. 2022). The tailored eluent choices, 0.5 M HNO_3 for copper and 0.2 M urea for zinc achieved effective regeneration from the composite surface. A more detailed data on the regeneration study of chitosan-based adsorbents for heavy metal removal can be referred in Table 7. These findings underscore that while regeneration is feasible, the choice of eluent and structural modifications such as crosslinking or composite formation play a critical role in preserving the adsorbent's integrity and performance. As the demand for low-cost, reusable materials grows, regeneration studies continue to shape the future of chitosan-based water treatment technologies.

Cost analysis

Chitosan-based adsorbents are often highlighted for their cost-effectiveness and environmental friendliness in heavy metal removal, particularly when compared to other conventional treatment methods. This is largely due to chitosan being a natural, abundant, and biodegradable biopolymer derived from chitin, the second most abundant biopolymer after cellulose (Upadhyay et al. 2021; Sheth et al. 2021). Chitosan itself is considered a low-cost adsorbent, especially when derived from abundant natural sources like crustacean shells (Upadhyay et al. 2021; Sheth et al. 2021; Gamage et al. 2023).

However, while the raw material (chitosan flakes) can be relatively inexpensive, the total production cost of modified chitosan composites can vary. A hidden aspect often not reported in the literature is the specific synthesis cost of adsorbents, making direct comparisons challenging (Gkika et al. 2019). Table 8 tabulates the production cost for developing chitosan-based adsorbents based on several studies. For instance, one study estimated the total cost for producing 1 kg of a magnetic chitosan crosslinked tripolyphosphate/TiO2 hybrid nanocomposite to be around 2413.63 INR (approximately $29 USD), with the highest contributor being reagent cost (Tamang and Karar Paul 2025).

Meanwhile Sopanrao et al. (2025) listed a retail cost breakdown for various chemicals (high-molecular-weight chitosan, acetic acid, glutaraldehyde, sodium hydroxide, phosphoric acid) and utilities (electricity cost for drying in a hot air oven, DI water purifier and orbital shaker) in the synthesis of phosphoric acid-modified biochar–chitosan nanocomposite (PGB-CS) (Sopanrao and Sreedhar 2025). The analysis revealed that

Table 7 Regeneration studies of chitosan-based adsorbents for heavy metal removal

Adsorbent type	Heavy Metal	Desorbing agent	Number of Cycles	Regeneration Efficiency	References
Ethylenediamine-tetraacetic Acid-Functionalized β-Cyclodextrin-Chitosan	Ni (II)	1 M HNO3	5 cycles	97% (initial) to 91% (after 5 cycles)	Verma et al. (2021)
grafted chitosan-dialdehyde cellulose	Ni (II), Pb (II), Cu (II)	0.1 M HCl	3 cycles	Pb (II)- maintained 86.4% of original Ni (II)-retained 84.4% Cu (II)- 91.4% retained	El-Sayed et al. (2023)
β-Cyclodextrin-Chitosan based cross-linked adsorbent	Hg (II)	1 M HNO3	3 cycles	> 90%	Usman et al. (2021)
chitosan/ β-cyclodextrin beads	Cr (VI)	0.1 M HCl/0.1 M NaOH	4 cycles	~ 80% (initial) to ~ 60% (after	Kekes et al. (2021)
chitosan/polyether sulfone/Fe$_3$O$_4$ modified with mercapto and amine groups	Pb (II), Ni (II)	0.1 M HNO3	5 cycles	Ni (II)- 39.7 mg/g (initial) to 36.2 mg/g Pb (II)- 70.2 mg/g (initial) to 65.4 mg/g	Jafarnejad et al. (2021)
porous magnetic chitosan	Cd (II)	0.1 M HCl	7 cycles	99.99% (initial) to 80.44% (after 7 cycles)	Yadav et al. (2023)
Citric Acid-chitosan	Zn (II), Fe (II), Pb (II)	2 M HCl	3 cycles	Zn (II)- 75.65% (initial) to 57.76% (after 3 cycles) Fe (II)- 75.31% (initial) to 53.78% (after 3 cycles) Pb (II)- 68.59% (initial) to 49.83% (after 3 cycles)	Patel et al. (2024a)
hydrogel composite integrating chitosan-polyvinyl alcohol and Fe$_3$O$_4$ nanoparticles	As (V)	0.1 M acetic acid	5 cycles	75% to 43% (after 5 cycles)	Weerasundara et al. (2023)
Chitosan Functionalized with Carboxyl Groups	Cu (II), Zn (II)	0.5 M HNO3 (for Cu (II)), 0.2 M urea (for Zn (II)	3 cycles	Cu (II)- 100% (initial) to 88.47% Zn (II)- 100% (initial) to 88.74%	Abu El-Soad et al. (2022)
Magnetite–Chitosan Composite	Cu (II), Cd (II)	0.1 M NaCl	8 cycles	Cu (II)- 87.67% to 33.45% (after 8 cycles) Cd (II)- 82.45% to 34.21% (after 8 cycles)	Hu et al. (2023)

producing 1 g of adsorbent costs USD 8.13/g (Rs. 682.14), with chitosan making up a significant 80.12% of the total cost. The study also shows corresponding metal removal costs of 2.73 INR/mg for Cu^{2+}, 3.56 INR/mg for Ni^{2+}, and 4.67 INR/mg for Zn^{2+}. In another study, the retail cost for the synthesis and manufacturing of chitosan-magnetic biochar composite (CHB-Fe-CS) amounts to ₹868.93 ($10.43) per 1 g, which included the cost of various chemicals and utility consumed. The chitosan itself was mentioned to (accounted for 83.78% of total cost) significantly drives the overall production costs of the adsorbent. Since simple synthesis protocols are used in the synthesis, engineering insights were not considered in this study (Sopanrao and Sreedhar 2024). Based on the breakdown of retail costs for the chemicals and utilities involved in producing phosphoric acid–modified bentonite-chitosan composite beads (PB-CS), the analysis indicates that the production cost for 1 g of adsorbent is ₹855.61 (USD 9.65), with chitosan accounting for a substantial portion of this expense (Sopanrao et al. 2024).

The ability to regenerate and reuse chitosan-based adsorbents is a critical factor for their economic viability. Regeneration significantly reduces the overall cost by minimizing the need for new adsorbent material and reducing disposal expenses (Vakili et al. 2019a; Badran et al. 2023). For example, the cost for synthesizing the crosslinked chitosan (CS/STTP) and chitosan/β-cyclodextrin beads (CS/β-CD/STTP) beads was estimated at 3.87 and 3.75 $/g adsorbent, respectively, while the cost for regenerating the adsorbents at 0.25 $/g adsorbent/cycle (Kekes et al. 2021). This included the

Table 8 The cost production for various chitosan based adsorbents

Adsorbent	Cost of adsorbent production per g	References
Magnetic chitosan crosslinked tripolyphosphate/TiO2 hybrid nanocomposite	USD 0.029 /g	Tamang and Karar Paul (2025)
Phosphoric acid-modified biochar–chitosan nanocomposite (PGB-CS)	USD 8.13/g	Sopanrao and Sreedhar (2025)
Chitosan-magnetic biochar composite (CHB-Fe-CS)	USD 10.43/g	Sopanrao and Sreedhar (2024)
Crosslinked chitosan (CS/STTP)	USD 3.87/g	Kekes et al. (2021)
Chitosan/β-cyclodextrin beads (CS/β-CD/STTP)	USD 3.75/g	
Phosphoric acid–modified bentonite-chitosan composite beads (PB-CS)	USD 9.65/g	Sopanrao et al. (2024)
ZnO grafted chitosan beads	USD 10.32/g	Nguyen et al. (2023)
Magnetic chitosan-mediated graphene oxide	USD 10.10/g	Bao et al. (2023)
Dodecyl dimethyl betaine and chitosan-modified semi-carbonized fibres	USD 11.61/g	Li et al. (2024)
Carboxymethyl-chitosan composite	USD 10.54/g	Patel et al. (2024b)

energy costs which were 0.132 $/kWh, corresponds to the world average cost for business users. Although, the cost requirement for the synthesis of the studied adsorbents is slightly higher compared to the conventional adsorbents, such as activated carbon, the overall efficiency of the proposed synthesized adsorbents combined with the possibility of regenerating them at low-cost render them as an attractive innovative solution towards the adsorption of Cr (VI).

Some research suggests that the cost incurred for extracting and utilizing chitosan for heavy metal treatment is less than that of commercial treatment facilities. Chitosan has also been found to be cheaper and more efficient than activated carbon and other conventional adsorbents in some cases (Sharifi et al. 2021). Chitosan/cellulose nanocrystals grafted with carbon dots composite hydrogel (CS/CNCD) developed by Zeng et al. (2021) shows that the cost of removing 1 g Cr (VI) for the CS/CNCD composite hydrogel was only CNY 0.62 (USD 0.085), which was nearly 58.8 times less expensive than AC (CNY 36.48/ USD 5.13) (Zeng et al. 2021).

Studies on the overall economic viability of chitosan production have shown promising results. However, it is worth noting that performance comparison and detailed cost information across different low-cost adsorbents can be difficult due to inconsistencies in experimental conditions. However, the general consensus is that chitosan and its derivatives offer an attractive, cost-effective solution for heavy metal removal from wastewater due to their inherent properties and the potential for regeneration (Vakili et al. 2019a; Upadhyay et al. 2021; Gamage et al. 2023).

Pilot scale validation

The high adsorption capacity of chitosan-based materials for a variety of heavy metals has been well-documented through numerous laboratory-scale studies, as discussed previously. However, rigorous pilot-scale validation is essential before these findings can be translated to industrial applications. The primary aim of pilot-scale studies is to simulate real-world wastewater treatment scenarios and evaluate the performance of chitosan under continuous flow conditions. This crucial step bridges the gap between laboratory efficacy and practical implementation, ensuring that chitosan adsorbents can maintain their performance in the face of fluctuating flow rates, varying contaminant concentrations, and the presence of co-occurring pollutants (Sun et al. 2024). Furthermore, the reusability and regeneration potential of these adsorbents are critical for ensuring both economic viability and environmental sustainability. Therefore, these aspects must be thoroughly assessed in continuous flow systems to confirm the long-term stability and effectiveness of the materials (Zhao and Sillanpää 2020).

A prominent example is the pilot-scale heavy metal adsorption study by Heiderscheidt et al. (2020) which utilized a continuous stirred-tank reactor coupled with a sedimentation unit to simulate a continuous-flow system (Heiderscheidt et al. 2020). In this study, three adsorbents which consists of hydrochloric acid-modified peat, Mg oxides/Mg silicates, and ground granular blast furnace slag (GGBS) were tested in both laboratory and pilot-scale experiments using real water samples. The modified peat achieved 50–70% Zn and 30–50% Ni removal in both laboratory and pilot settings. The commercially available Mg oxides/Mg silicates product removed 65–85% of Zn in both settings, although low levels of As and Ni leaching were observed. The GGBS material showed promising results in the pilot study, removing 65–80% of Zn and 60–80% of Pb, but also led to Cr and Cu leaching. Overall, the pilot-scale tests yielded lower pollutant removal efficiencies compared to initial laboratory batch studies, highlighting the complexities introduced by scale-up and continuous flow operations. These findings also highlight a crucial trade-off, while the materials are effective in metal removal, their environmental safety must be carefully evaluated due to the potential release of secondary pollutants.

Another relevant study conducted by Kim et al. (2018) used iron oxide nanoparticle-chitosan (ION-chitosan) composites as adsorbents for phosphate removal from natural water sourced from the Seoho Stream in Suwon, Republic of Korea. Both laboratory and pilot-scale experiments were conducted to assess performance. In the lab, fixed-bed column experiments (column height=10 and 20 cm, inner diameter=2.5 cm, flow rates=8.18 and 16.36 mL/min) demonstrated effective phosphate removal under dynamic flow conditions. The adsorbent also showed resilience to pH variations (pH 5–9) and could be regenerated with 5 mM NaOH. In the pilot-scale study, a treatment plant located near the Seoho Stream was used. Natural water was first passed through a chemical reactor/dissolved air flotation unit before entering an adsorption tower (height=100 cm, inner diameter=45 cm, flow rate=7.05 ± 0.18 L/min), which contained 80 L (85.74 kg) of the ION-chitosan composite. The adsorption tower achieved 52.3% removal of total phosphorus with a phosphate removal capacity of 0.059 mg P/g, which was lower than the lab-scale fixed-bed performance.

Wang et al. (2025) developed a novel chitosan-based biochar aerogel (CBA) system for the removal of high concentrations of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions from seawater desalination brine (SDB). Two types of CBA, CBA85 and CBA95 were synthesized using chitosan with different degrees of deacetylation (85% and 95%, respectively). In fixed-bed reactor experiments, CBA95 maintained over 87% Ca^{2+} and 91% Mg^{2+} removal efficiency after nine reuse cycles. The pilot-scale test, conducted in Qingdao, demonstrated removal rates of 72.3% for Ca^{2+} and 74.6% for Mg^{2+}, thereby confirming the material's industrial applicability and long-term viability.

In summary, pilot-scale studies provide critical insights into the real-world performance of chitosan-based adsorbents. Laboratory-scale studies can be useful for initial screening and optimization, but they often fail to capture the operational challenges encountered in large-scale systems. Leaching of co-contaminants, reduced efficiency, and variable regeneration performance are also among the common obstacles that must be addressed through comprehensive pilot testing. Furthermore, the incorporation of economic and environmental impact assessments are also essential to support the broader adoption of chitosan-based materials in industrial water treatment.

Challenges and future perspective

Although chitosan on its own is described as non-toxic and biocompatible adsorbent, however after modification, the property may change as new groups are added to the structure and may form new properties. Furthermore, some modified chitosan studies grafted or crosslinked with toxic compounds such as glutaraldehyde and may cause secondary pollution. Hence, studies should include the toxicity test as part of their research to ensure the modified chitosan does not bring any harm towards the environment. The traditional one-factor-at-a-time batch optimization method tend to be time-consuming and costly. Hence, the factors that may affect the heavy metal adsorption such as temperature, pH, adsorbent dose, metal ion concentration, contact time should be optimized using the statistical tools such as Response Surface Methodology and Artificial Neural Network-Genetic Algorithm to minimize the number of trials and cut the cost and time. The optimized statistical formula obtained from these optimization tools can be employed to meet the industrial scale, for easier application. Since each modified chitosan adsorbent possess different properties, hence the adsorption mechanism between chitosan adsorbents and heavy metals remains ambiguous. To deeply understand the interaction mechanism between chitosan adsorbent and the heavy metals, future studies may incorporate quantum chemical calculations and molecular dynamic simulation in the interaction analysis. In order to fabricate and design a better chitosan adsorbent in the future, it is critical to have a thorough understanding of the mechanics. Most of the chitosan adsorbent studies are carried out in a single pollutant system, which does not represent real aquatic environment. The water environment may contain various other pollutants including organic compounds which may affect the adsorbent's efficiency in removing the targeted heavy metal. Therefore, the possible competition between other pollutants and the target heavy metal ion on the adsorbent's adsorption sites in multiple pollutants system should be investigated. Most of the current chitosan based adsorbent studies mainly focuses on the application of the adsorbents in batch experiments, which may not be suitable to be applied in real life application. Hence, it is recommended for future studies to include the practical application of the developed adsorbents by testing them in real environmental solution or pilot environment with continuous flow system which is more suitable, reproducible, and practical to be applied in industrial scale.

Conclusion

In conclusion, this review highlights the progress and potential of modified chitosan as a sustainable and efficient adsorbent for the removal of heavy metals from aqueous systems. Although chitosan offers several advantages, including biocompatibility, biodegradability, and the presence of functional groups capable of binding metal ions, its practical application is hindered by limitations such as low adsorption capacity and poor acid stability. Through structural modifications particularly crosslinking and grafting, researchers have significantly enhanced chitosan's chemical stability and adsorption performance. The application of the Hard and Soft Acid–Base (HSAB) theory has further guided the design of selective functional moieties, allowing for improved specificity toward targeted metal ions. In addition to material development, the role of operational parameters such as pH, temperature, contact time, adsorbent dosage, and initial ion concentration has been extensively studied to optimize removal efficiency. The integration of these findings contributes to a deeper understanding of the adsorption mechanisms, including complexation, ion exchange, electrostatic interaction, and physical adsorption. Importantly, recent studies have begun to address the economic and practical aspects of chitosan-based adsorbents. Regeneration experiments have demonstrated that appropriately modified chitosan can retain high adsorption capacities over multiple cycles, thereby improving the cost-efficiency and sustainability of the process. Moreover, pilot-scale studies have shown promising results, confirming the feasibility of applying modified chitosan in real-world water treatment scenarios. Coupled with its low production cost, especially when derived from waste biomass, chitosan stands out as a viable alternative to conventional synthetic adsorbents. Overall, the advancements not only underscore the versatility of chitosan as a functional material for heavy metal remediation but also provide a strong foundation for future research and scale-up. Continued efforts in material design, regeneration techniques, and system optimization are essential to fully realize the potential of modified chitosan in industrial-scale water purification applications.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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