

Chitosan-based modalities with multifunctional attributes for adsorptive mitigation of hazardous metal contaminants from wastewater



Shan E.Zehra Syeda*, Muhammad Shahzeb Khan, Anna Maria Skwierawska

Department of Chemistry and Technology of Functional Materials, Faculty of Chemistry, Gdańsk University of Technology, 11/12 Narutowicza Street, 80-233 Gdańsk, Poland

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ABSTRACT

The increase in population and industrialization has intensified water scarcity and stress, and contaminated water bodies. Therefore, the development of advanced water and wastewater treatment technologies has gained global attention from researchers. Adsorption, using natural materials (nano, polymer, and bio) is one of the most cost-effective, less challenging, and well-known technologies for wastewater treatment and improving water quality. Among them, chitosan (CS) has demonstrated a set of unique features, such as biodegradability, eco-friendliness, availability, low cost, and biocompatibility. Hence, this review provides an overview of some recent advancements in the removal of heavy metals, including As (III) and (V), Cd (II), Cu (II), Cr (VI), and Pb (II) by CS-based adsorbents, and their potential effects on human health. It also covers the synthesis of CS-based adsorbents for the elimination of mentioned contaminants in recently reported studies. In addition, this study recommends encountering potential drawbacks by enhancing the adsorption capacity by incorporating functional groups, nanoparticles, and other materials. These modifications may help increase selectivity for specific metal contaminants and synthesize adsorbents that can perform better over a wide range of pH. Insights gained from this study will guide researchers in the future toward optimal water treatment and pollutant elimination strategies.

1. Introduction

The world is now more concerned with the simultaneous problems of water scarcity and contamination than ever before. These are complex issues that require a variety of approaches to solve. The urgent challenges of both quantity and quality have become more linked as growing populations and expanding industrial activity increase the burden on water resources [1]. Pollutants including heavy metals, industrial effluents, and agricultural runoff contaminate water, making a large amount of available water sources unfit for human consumption and exacerbating the scarcity issue. A critical turning point has been reached in the navigation of the complicated terrain of water management: improved water treatment technology. These technologies have become essential in lessening the effects of contamination on water resources as a result of the realization that focused and effective cleanup solutions are required. Now, let us examine this groundbreaking trip from the general problems of water scarcity and contamination to the field of cutting-edge water treatment technologies, clarifying the rationale for our work and its contributions. Researchers from across the globe have been trying to resolve water-related issues

and remove the contamination from the water. Water contamination has caused many human health issues, and about 0.7 million people die from water-related diseases around the globe [2]. The most common water contaminants include dyes, heavy metals, and phenols [3]. Heavy metal's presence in water has gained more attention due to their higher toxic levels and carcinogenic effects on the health of human beings at even lower concentrations [4]. They lead to acute and chronic effects such as different kinds of cancers, improper development of organs, nerve damage, and even death [5]. After the industrial revolution, the world has seen drastic growth in industrial and economic sectors that has also contributed to the heavy metals accumulation on the surface and groundwater which has sought global attention [6–9]. As a consequence, the researchers have shifted their focus to the quantification of heavy metals and their overall effects on human life [8,10–13]. The heavy metals have different toxic levels due to their chemical properties and characteristics, and they pose different health implications discussed later in this review.

Within the broad field of water treatment techniques, various technologies are essential in tackling the intricate problems related to water quality. Among them are processes such as membrane filtration,

* Corresponding author.

E-mail address: abc@123.com (S.E.Z. Syeda).

chemical precipitation, electrochemical reactions, and others that are noteworthy due to their unique mechanisms and uses.

Membrane filtration uses semi-permeable membranes to filter impurities and particles from water according to their molecular weight and size. Chemical precipitation is the process of adding chemicals to create precipitates that are insoluble and readily separated from water. Electrical current is used in electrochemical processes to create reactions that help remove or change pollutants. Although there is a wide range of water treatment technologies available, this article deliberately focuses its discussion on one aspect: adsorption. One well-known and adaptable technology that is particularly notable for its effectiveness in reducing water pollution is adsorption. It has gained recognition for its low cost, easy operation [14] and modifications, high effectiveness, sludge-free operation, easy recovery, and regeneration capacity [15]. For the removal of heavy metal ions (HMIs), activated carbon has been widely used; however, it has limitations due to its high cost, and it also causes secondary pollution [16]. Several other adsorbents have been used to eliminate HMIs, including nanomaterial adsorbents, bio adsorbents, industrial by-products, and their composite.

The adsorbents prepared using CS exhibit commendable efficiency in removing dyes, heavy metals, pesticides, and pharmaceutical pollutants from water. They have distinctive features, helping with selective adsorption, and are very versatile for environmental applications [17–23]. Many efforts have been in progress on using CS and its derivatives for dye removal and HMI removal from water and wastewater [24–31]. However, there is still a gap to be filled, and we believe this critical review helps researchers to work more efficiently in this field of study. This review includes the synthesis of CS-based adsorbents, their mechanism and characteristics for removing heavy metals from the environment, their interaction with human health, and the reasons for deteriorating the human body with several diseases. This article also discussed the major heavy metal ions and their chemical interaction with CS-based adsorbents. In this era of development, research plays a significant part in the progress of academic society and institutions. Moreover, this review will open doors of knowledge for the researcher and provide the gap in this field of research, and it will create pathways to achieve sustainable development goals (SDGs) and bring opportunities for better living on the planet Earth.

CS is derived from the partial deacetylation of chitin (Fig. 1) and is the second ample natural polymer in shrimp shells, crab shells, and

some fungi [32]. CS is obtained by removing acetyl groups from chitin to the extent of about 50%. The resulting structure is heterogeneous and consists of both 1–4 linked 2-acetamido-2-deoxy- β -D-glucopyranoses and 2-amino-2-deoxy- β -D-glucopyranoses as well as 2-amino-2-deoxy- β -D-glucopyranose (as shown in Fig. 2a and b).

Given structure, CS is similar to cellulose; as hydroxyl in cellulose is replaced by amino or acetamido groups in CS at carbon-2 [33]. CS and its derivatives have shown extraordinary results in the fields of pharmacy [34], medicine [35], chemistry [36], and environment [37] because they have specific characteristics that include low toxicity, high adsorption capability, biocompatibility, and biodegradability. Environmental engineers have reported successful results in removing heavy metals and treating water. CS derivatives have been found to remove pigments [38], fluorides [39], and phenols [40]. CS has not only shown remarkable results for the removal of HMIs but also has shown antibacterial properties [41]. The preparation of CS and its derivatives-based adsorbents, adsorption mechanism, and application studies have been discussed briefly in detail in this review.

2. Chitosan-based adsorbents

CS was first obtained by Rouget in 1859 when boiling chitin in the concentrated potassium hydroxide (KOH) [42,43], and later, Hoppe-Seyler named it in 1894. CS has been considered one of the most useful cationic adsorbents for removing aromatic compounds, highly toxic organic dyes, heavy metals, anions, pharmaceutical residues, and oil spills [44–48]. It holds several advantages, such as hydrophilicity, high reactivity, biodegradability, biocompatibility, and nontoxicity [49]. It is a multifunctional biopolymer and has unique properties that make it useful for treating water, especially in adsorption operations. It is environmentally friendly because it is naturally biocompatible and biodegradable. Because positively charged amino groups on CS and negatively charged ions have a favorable interaction, CS's cationic composition allows for the effective adsorption of anionic pollutants, like heavy metals. Its adsorption capacity is enhanced by its high surface area and porous structure, which offer a multitude of active sites for pollutant binding. Amino and hydroxyl functional groups, for example, contribute to a variety of interactions with different pollutants. The capacity to produce films makes it possible to create coatings that function as efficient adsorption layers. Because it can be easily

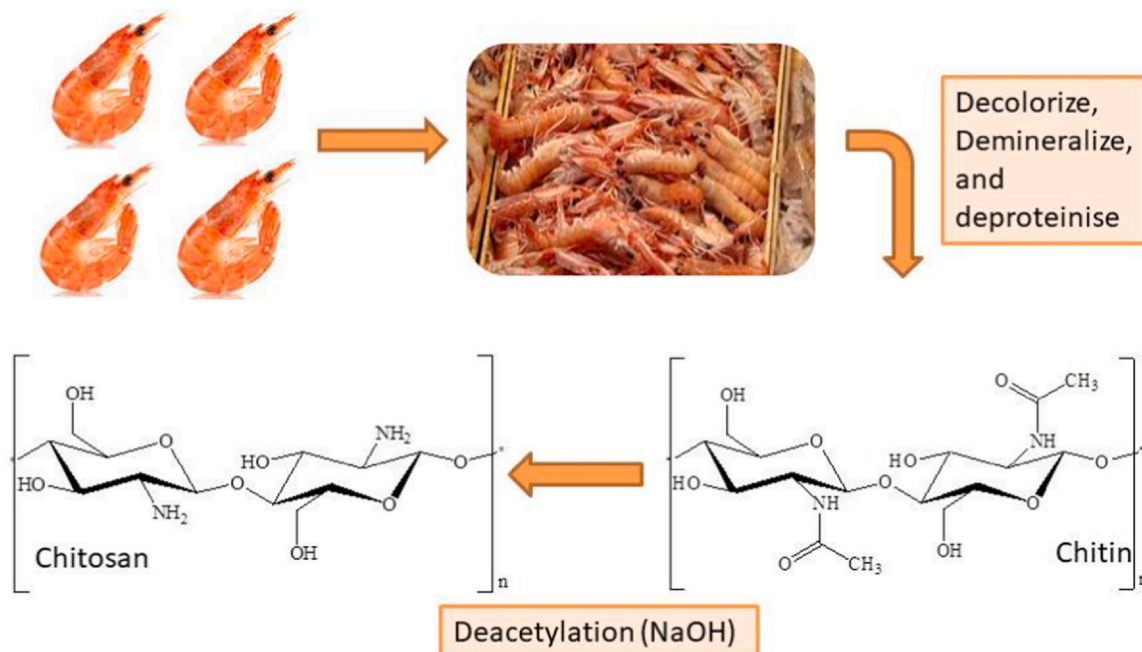


Fig. 1. Representation of CS recovery from shrimps.

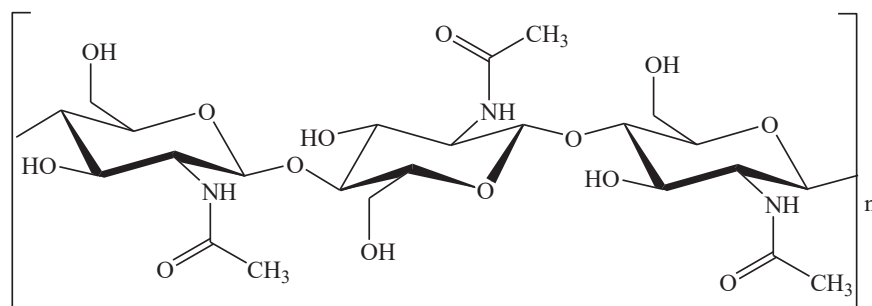


Fig. 2. a. Chemical structure of Chitin, Fig. 2b. Chemical structure of chitosan.,.

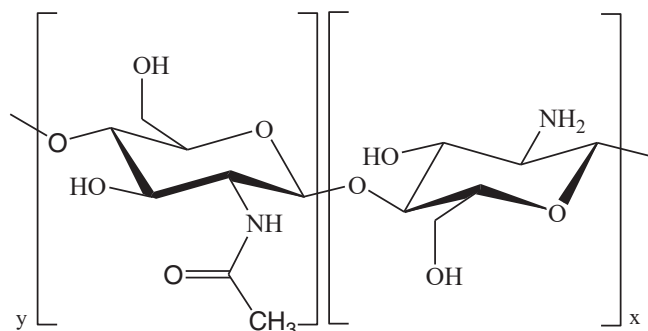


Fig. 2. (continued)

altered, customized improvements can be made, and because it is inexpensive and frequently derived from crustacean shells, water treatment procedures become more financially feasible. To summarize, it is a valuable and sustainable adsorbent for water treatment applications due to its unique mix of biocompatibility, cationic nature, high surface area, and adaptability. Moreover, Table 1 presents several conventional and non-conventional adsorbents and their features for removing contaminants from the water.

Table 1

Various conventional and non-conventional adsorbents with their features.

Adsorbents	Features	Type of adsorbent	Ref
Activated alumina	<ul style="list-style-type: none"> - Efficient for the removal of organic pollutants and bacteria - Commercially available 	Conventional	[56]
Agricultural waste	<ul style="list-style-type: none"> - Efficient - Rapid 	Conventional	[57]
Biomass obtained via microorganism	<ul style="list-style-type: none"> - More selective & effective from the ionic adsorbent 	Non-Conventional	[58]
Chitin/CS (Chitosan based derivatives)	<ul style="list-style-type: none"> - Biodegradable - Cheap - Abundant - Renewable - Exemplary diffusion properties - High Swelling properties 	Non-Conventional	[59]
Coconut waste (shell)	<ul style="list-style-type: none"> - Works in the granular form - Wastewater treatment 	Conventional	[60]
Cross-linked polymers	<ul style="list-style-type: none"> - Surface area is more - Mechanical strength is high - Has chelating properties 	Conventional	[61]
Hydrogel	<ul style="list-style-type: none"> - Efficient for metal recovery (not all types) 	Non-Conventional	[62]
Polysaccharide	<ul style="list-style-type: none"> - Low-cost and highly selective 	Non-Conventional	[63]
Resins	<ul style="list-style-type: none"> - Wastewater treatment 	Conventional	[64]
Silica gel	<ul style="list-style-type: none"> - Efficient for removing organics 	Conventional	[65]
Solid waste from the forest industry	<ul style="list-style-type: none"> - Possible degeneration - Cheap - Effective 	Non-Conventional	[66]
Wood waste	<ul style="list-style-type: none"> - Efficient for large-scale pollutants - Good surface phenomenon 	Conventional	[67]
Zeolites	<ul style="list-style-type: none"> - Good adsorbent for organic solvents and dyes - High Ion exchange capacity 	Conventional	[68]

Furthermore, CS has a linear polyamine structure with free amine groups accessible for modifications and crosslinking [50]. Several chemical and physical modification techniques have been applied to improve its adsorption selectivity and characteristics for removing heavy metals, including amination, sulfonation, and carboxymethylation [51–55].

3. Chitosan for HMI removal

They have been proven efficient for absorbing toxic heavy metal ions from water and wastewater due to various chelation sites and hydroxyl and amino functional groups that attract heavy metals using ion exchange methods or coordination bonds [69,70]. Many researchers have analyzed and evaluated the adsorption capacities of CS and their derivatives to remove HMIs as their application studies [71–73]. Fig. 3 shows the mechanism of CS-based adsorbent for the removal of heavy metals from the water.

This study includes various studies on removing metals (As, Cd, Cr, Cu, and Pb) from the wastewater through an adsorption mechanism using CS-based adsorbents. The complex relationship between CS-based adsorbents and different heavy metal ions requires a careful analysis of their interactions. Arsenic compounds, such as arsenic (III) and arsenic (V), use their hydroxyl and amino groups to form complexes and create hydrogen bonds, respectively. Lead ions (II) mostly stick to the amino

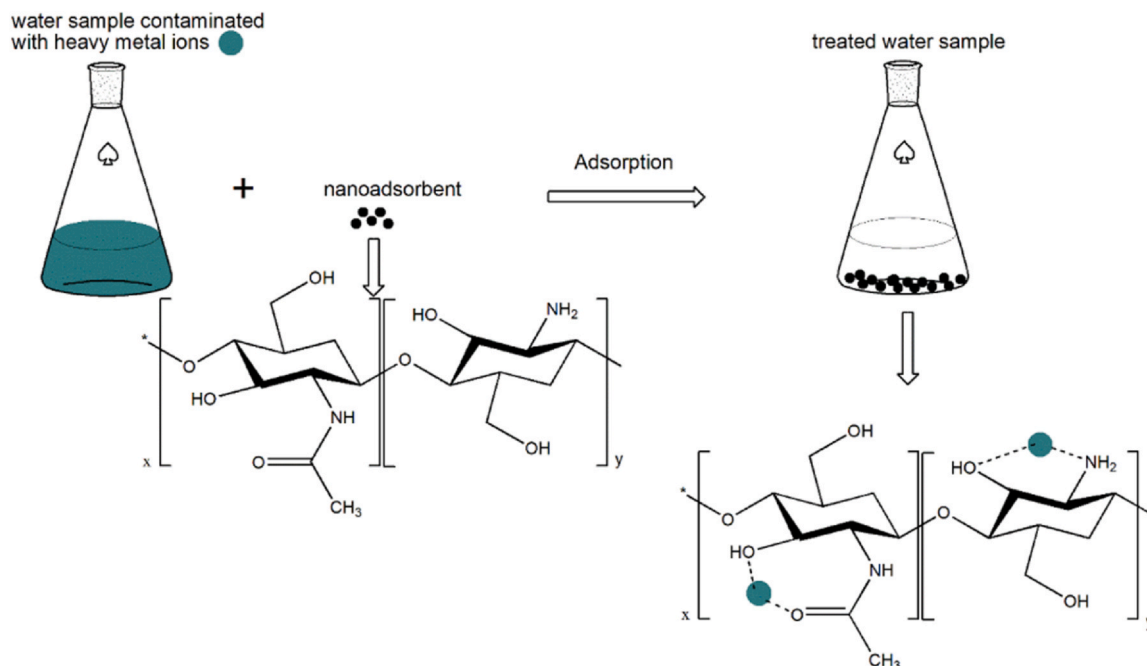


Fig. 3. Schematic diagram for the removal of heavy metals by CS-based adsorbents.

groups of CS through coordination bonds, highlighting the need to assess the density and accessibility of these amino groups. Chromium (VI) binding to CS may include redox reactions, emphasizing the need to understand electron transfer mechanisms. Cobalt ions (II) show preferential adsorption aided by the amino groups of CS, requiring a comprehensive study of its ability to form chelation complexes and coordinate bonds. Likewise, copper ions (II) bind with the amino groups of CS, which requires examination of the surface charge and the kinetics of complex formation. Comprehending these complex interactions is crucial for improving CS-based adsorbents in order to improve their effectiveness in reducing heavy metal pollution in the waste water

treatment applications. Fig. 4 shows the adsorption mechanism of heavy metals on CS-based adsorbents.

Understanding the details of the heavy metal adsorption on CS-based adsorbents requires a thorough examination of kinetics, isotherms, and thermodynamics. Kinetic studies provide vital information on the time-dependent behavior of adsorption processes, giving important details about the speed and mechanisms that control the absorption of metal ions. Methods include being influenced by time batch adsorption tests and the use of kinetic models help to understand adsorption kinetics and determine the time needed to reach equilibrium. This information is important for designing and optimizing systems.

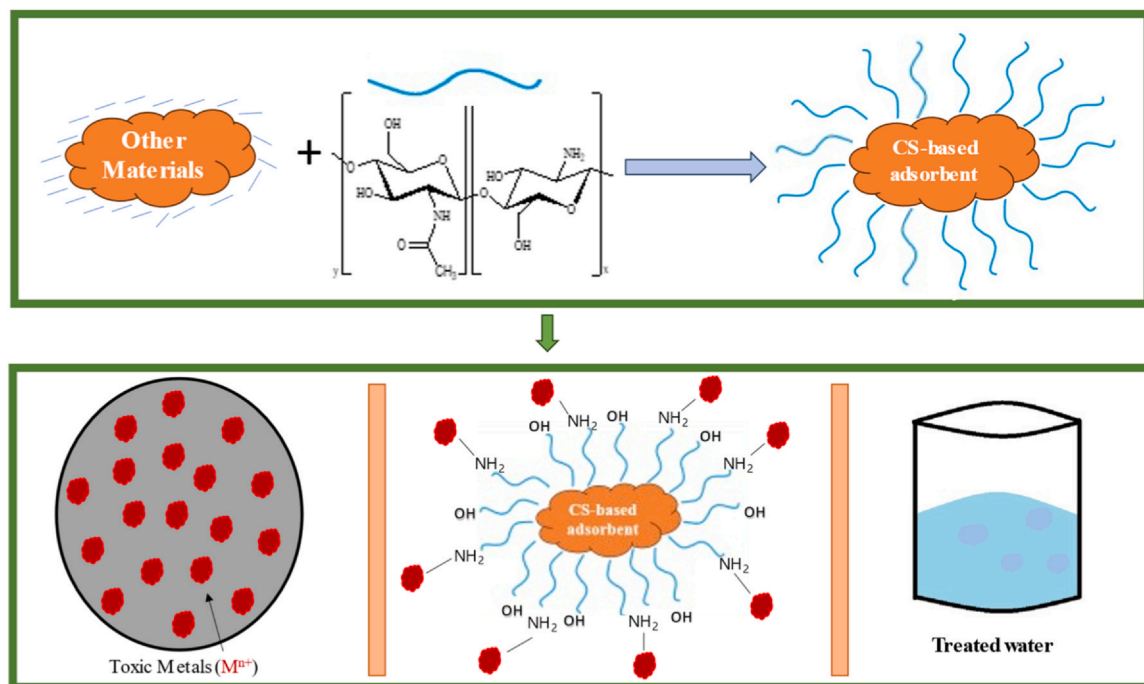


Fig. 4. Adsorption mechanism.

Isotherm analyses define the balance between the concentration of metal ions and their adsorption onto CS. This provides important information on the maximal capacity for adsorption, the characteristics of the surface, and the affinity of the adsorbent for different metal ions. Using well-known isotherm models, such as Langmuir, Freundlich, and Dubinin-Radushkevich, allows for the determination of important isotherm parameters from experimental data, which improves the ability to predict adsorption behavior in different settings.

In addition, thermodynamic studies offer a basic understanding of the spontaneity, possibility, and energy involved in metal adsorption onto CS. By conducting experiments at various temperatures and utilizing thermodynamic models like the Van't Hoff equation, important thermodynamic values like as standard enthalpy (ΔH°), standard entropy (ΔS°), and Gibbs free energy (ΔG°) can be determined. These factors provide information about the stability of metal-chitosan complexes and the impact of temperature on adsorption behavior, helping to optimize operational settings for practical use. To summarize, a thorough analysis of the speed of reactions, temperature effects, and energy changes is essential for improving the efficiency of removing heavy metals from water using CS-based adsorbents. This analysis provides important guidance for designing water treatment systems and implementing effective environmental cleanup strategies.

3.1. Removal of Arsenic

Arsenic (As) is a metalloid in the air, rocks, organisms, soil, and water. It has been a source of environmental pollution using natural processes and a combination of anthropogenic activities, including biological actions, weathering reactions, and vehicular and other emissions [74]. Fig. 5 elucidates the natural and anthropogenic sources of As contamination. Moreover, it is among the elements that are multivalent and cannot be easily removed, though, it can convert into several different forms or combine with other elements [75]. However, the most dominant and toxic forms of arsenic include arsenite and arsenate [76].

Due to its toxicity, the World Health Organization (WHO) in 1993 reduced the exposure limit of arsenic from 50 to 10 μg^{-1} [78]. Until today, many researchers have used advanced adsorbents to remove As from wastewater [70], however, many drawbacks need to be addressed.

Recently, CS has gained drastic attention for its exceptional characteristics for arsenic removal application from the waters [79]. Utilizing gel, microsphere, and cross-linker of CS are a few advanced techniques that help to enhance mechanical strength, stability, and its

reusability; embedding molybdenum or iron, etc., into CS microsphere is an efficient technique to increase the adsorption property of CS [80–82]. Furthermore, iron (Fe) is always considered an arsenic lover as it possesses excellent adsorption properties towards As. Interestingly, the Fe-CS composite has gained attention for adsorption from water; Fe-CS granules (ICSB) and Fe-CS flakes (ICSF) have also been studied and reported [83].

Among several studies in the last decade that were carried out to analyze the adsorption capacity and efficiency of As (III); graphene oxide (GO), GO-modified CS derivative is recognized as a cost-effective (cheap) and efficient adsorbent [84–86], and graphene oxide-chitosan (GO-CS) has various application studies other than As. In a study, both toxic forms of As were removed from contaminated water with clays or zeolite CS-based adsorbents. In addition to other research, Wang and coauthors experimented with the CS coating biopolymer on iron oxide nanoparticles, showing a significant increase in As adsorption (V) [87]. Table 2 summarizes the q_{max} for arsenic on several CS-based adsorbents.

CS-based adsorbents have a remarkable ability to adsorb arsenic thanks to their positive charge, which allows them to interact with negatively charged arsenic species. In addition, these materials have a high level of compatibility with biological systems and are also environmentally friendly, which helps to minimize any potential risks to both human health and the environment. Nevertheless, the relatively sluggish adsorption kinetics of these substances may necessitate longer contact durations, while the pH dependence may present difficulties in upholding ideal conditions. In addition, the restricted surface area of CS matrices may limit their adsorption capacity in comparison to other materials.

3.2. Removal of Cadmium

Cadmium (Cd) is among the extremely toxic elements due to its teratogenic and carcinogenic effects on human life [95]. It is disposed of majorly into the environment through human-made activities due to mining operations, industrial effluent, waste incineration, and coal and oil combustion. Fig. 6 shows the different sources of cadmium contamination. According to WHO, the maximum permissible limit of Cd in potable water is 3–5 ppb [96]. Among several other adsorbents utilized to remove cadmium, hydrogels, and CS-based composites have acquired great attention [97].

Babakhani and coauthors reported an efficient, low-cost, and effective technique for removing Cd (II) from wastewater using a benign

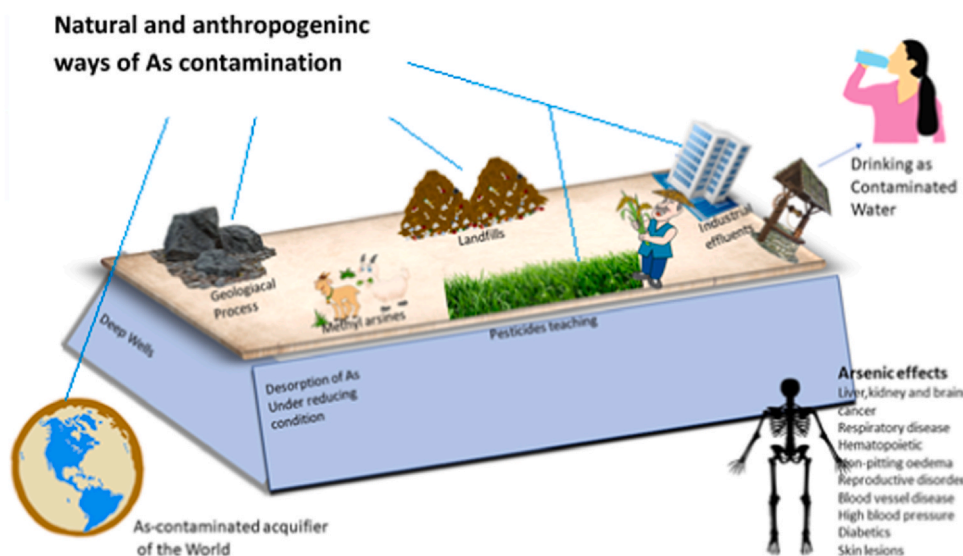


Fig. 5. Schematic diagram of As contamination and health effects [77].

Table 2
Chitosan-based adsorbents for the removal of Arsenic (As).

Adsorbent	Arsenic (III/V)	Maximum Adsorption Capacity (mg g^{-1})	Isotherms model	Kinetics model	Surface area	Contact time (min)	pH	Ref
Iron (III)-Chitosan	(III)	19.7	Langmuir	-	-	-	6	[88]
Fe CS Microspheres	(V)	120.7	Langmuir	2nd Order	1.3 mm (dia)	1440	4 – 9	[89]
α -FeO(OH)/GO/CS	(III)	289.4	Freundlich & Sips	2nd Order	-	3000	3 – 10	[85]
Magnetic CS-coated GO	(III)	45.0	Langmuir	2nd Order	$152 \text{ m}^2 \text{ g}^{-1}$	-	7.3	[84]
Chitosan coated Iron magnetite nanoparticles	(V)	10.8	Langmuir	2nd Order	-	120	7	[90]
MCS/GO with ethylenediamine tetraacetic acid (EDTA)	(III)	43.0	Langmuir	2nd Order	$81.36 \text{ m}^2 \text{ g}^{-1}$	660	8.0	[91]
Chitosan coated Iron magnetite	(III)	10.5	Langmuir	2nd Order	10 nm (dia)	90	9	[92]
Magnetite nanoparticles impregnated chitosan beads	(V)	35.7	Langmuir	2nd Order	$50.20 \text{ m}^2 \text{ g}^{-1}$	1500	6.8	[93]
CCM	(V)	3.4	Freundlich	2nd Order	$5.1 \text{ m}^2 \text{ g}^{-1}$	-	3 – 9	[94]
Iron-Chitosan composite	(III)	16.2	Langmuir	-	$96.8 \text{ m}^2 \text{ g}^{-1}$	-	7.0	[83]
Iron-CS composite	(V)	22.5	Langmuir	-	$96.8 \text{ m}^2 \text{ g}^{-1}$	-	7.0	[83]

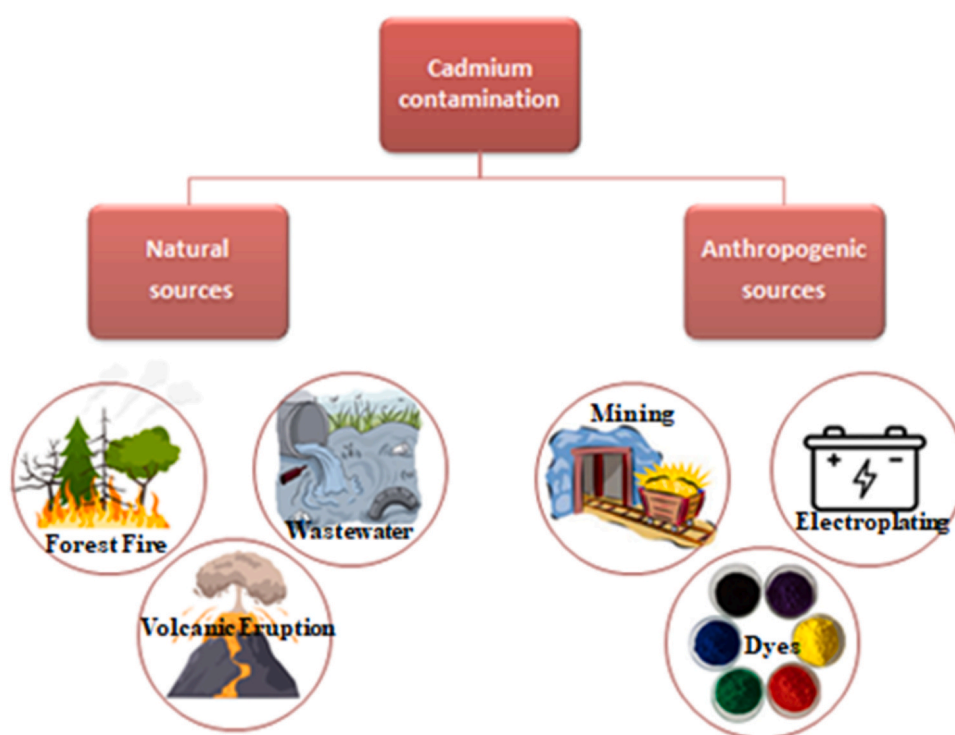


Fig. 6. Different sources of Cd contamination.

adsorbent. Sodium tripolyphosphate CS beads (STPP-CLCS) were fabricated to access cross-linked CS adsorption capacity and behavior. In the experiment, the lower cross-linked beads revealed a higher concentration of adsorption when the concentration of Cd was low; consequently, the lower CS beads had higher adsorption even at a higher concentration [98]. In a recent study, a hollow nanofibrous membrane (HNM) was synthesized from CS, polyvinyl alcohol (PVA), and polyvinylpyrrolidone (PVP) through electrospinning. It was analyzed on lead, nickel, cadmium, and copper, and maximum adsorption capacities were 87.8 , 97.5 , 88.1 , and 106.7 mg g^{-1} [99]. In another study, biocomposites based on clay minerals and CS have gained interest in removing cadmium, and Vilela reported the maximum adsorption capacity was 234.8 mg g^{-1} onto the CS-based hydrogel [100]. In a study, Chen et al., 2012 prepared an effective new composite of CS with thiourea, modified it to a magnetic ion, and imprinted it on CS/TiO₂ (MICST). Later, results found that the MICST's efficiency in removing Cd (II) decreased barely after the fifth cycle.

In another attempt, Chen and coauthors prepared CS-vermiculite (CS-VMT) in reaction with epichlorohydrin and used it for the removal of Cd (II) from water. The results showed that on the external surface, CS was cross-linked but could not intercalate in the vermiculite [104]. Also, Wang and coauthors (2020) also synthesized a low-cost and novel cobalt ferrite@SiO₂-CS/EDTA composite with higher adsorption capacity of cadmium and recyclability using sol-gel and solvothermal process [102]. Table 3 summarizes q_{max} for Cd on CS-based adsorbent.

CS-based adsorbents have been found to exhibit remarkable selectivity for cadmium, thanks to the strong metal-ligand interactions they form. This property effectively reduces interference from other ions, making them highly effective in Cd removal. Its remarkable versatility enables the creation of customized adsorbents that exhibit a heightened affinity for cadmium ions. Additionally, its biodegradability helps minimize any potential negative effects on the environment. Nevertheless, the adsorption behavior that is dependent on pH and the limited surface area may necessitate optimization in order to achieve

Table 3
Several CS-based adsorbents for the removal of Cadmium (Cd).

Adsorbent	Maximum Adsorption Capacity (mg g^{-1})	Isotherms model	Kinetics model	Surface area	Contact time	pH	References
Chitosan/PVP/PVA-HNM	88.1	Langmuir	2nd Order	$17.16 \text{ m}^2 \text{ g}^{-1}$	-	7	[99]
Chitosan and pectin beads	177.6	Langmuir	2nd Order	$23.66 \text{ m}^2 \text{ g}^{-1}$	380	7	[101]
STPP-CLCS	99.8	Langmuir	-	-	-	4 – 8.5	[98]
CoFe_2O_4 @ SiO_2 -CS/EDTA	127.8	Langmuir	-	$17.57 \text{ m}^2 \text{ g}^{-1}$	180	2 – 7	[102]
Chitosan/PVA/PEL	11.1	Langmuir	2nd Order	$0.95 \text{ m}^2 \text{ g}^{-1}$	-	6	[103]
Chitosan-VMT composite	58.5	Langmuir	2nd Order	$7.91 \text{ m}^2 \text{ g}^{-1}$	1400	4	[104]
Chitosan@NZVI	142.8	Freundlich	2nd Order	$78.3 \text{ m}^2 \text{ g}^{-1}$	180	4 – 9	[105]
Vermiculite (Vm) blended with CS	169.0	Langmuir	2nd Order	-	300	5.0 – 5.5	[106]
$\text{Ca}_5(\text{PO}_4)_3/\text{CS}$	81.1	Langmuir	2nd Order	-	1440	9	[107]
MICST	256.4	Langmuir	2nd Order	-	360	6 – 7	[108]

efficient removal. Furthermore, the process of regenerating after cadmium adsorption may pose challenges, affecting the potential for reusability and potentially leading to higher operational costs.

3.3. Removal of Chromium

Chromium (Cr) is naturally present in two oxidation states, such as chromium (III) and (VI), whereas, Cr (III) is relatively less threatening to animals and plants as compared to Cr (VI). It is widely used in various industries, including textile dyeing, steel and automobile manufacturing, leather tanning, and electroplating, and it causes a potential threat [109,110]. Fig. 7 presents the sources of chromium contamination. According to the International Agency for Research in Cancer (IRCA), Cr (VI) is carcinogenic to human beings and considered in group 1, while Cr (III) is not classified as carcinogenic [111,112].

Another study describes the synthesis of CS/polyethyleneimine fixed hydrophobic sodium alginate composite (MCPS) for sorptions of dyes and heavy metals. The maximum adsorption capacities were 351.0 for Cu, 87.5 for Cr (VI), 66.4 for methyl orange, and 286.5 mg g^{-1} for methylene blue [113]. Table 4 summarizes the maximum adsorption capacities for Cr on CS-based adsorbent.

In a study, Omer and coauthors (2021) examined the adsorption characteristics of aminated CS (AmCS)-modified MOF to remove

chromium (VI). Moreover, the result depicted that the induction of amine groups made CS neat and strengthened the cationic nature, which is more helpful in removing anionic Cr (VI) [117]. In another study, the attapulgite clay and magnetic Fe_3O_4 modified with AmCS (ATP@ Fe_3O_4 -AmCS composite) was developed by Eltaweil and co-authors in 2021 to remove anionic Cr (VI). The examination depicts rapid and efficient adsorption, and q_{max} was achieved at 294.1 mg g^{-1} [127]. Dinh (2020) reported an effective and rapid adsorption process for Cr (VI) ions onto MnO_2/CS nanocomposite. At pH 2.0 and in an hour, the adsorption efficiency reached 92% [118]. In one of the studies, fabricated CS-Fe (III) was proven efficient in removing Cr (VI) more rapidly. Furthermore, the q_{max} for removing Cr (VI) on the prepared complex was 173.1 mg g^{-1} within 10 min [125].

Chromium, specifically hexavalent chromium [Cr(VI)], is strongly attracted to CS-based adsorbents because of their exceptional ability to form robust complexes with metal ions. Due to their versatility, these substances can be easily modified to improve their ability to selectively adsorb chromium species. In addition, the matrices are biocompatible and environmentally friendly, reducing potential health and ecological hazards. Nevertheless, the effectiveness of CS-based adsorbents may be influenced by the pH of the solution, which requires precise adjustment of the solution conditions to achieve optimal chromium removal. In addition, the small size of its particles may limit their ability to adsorb

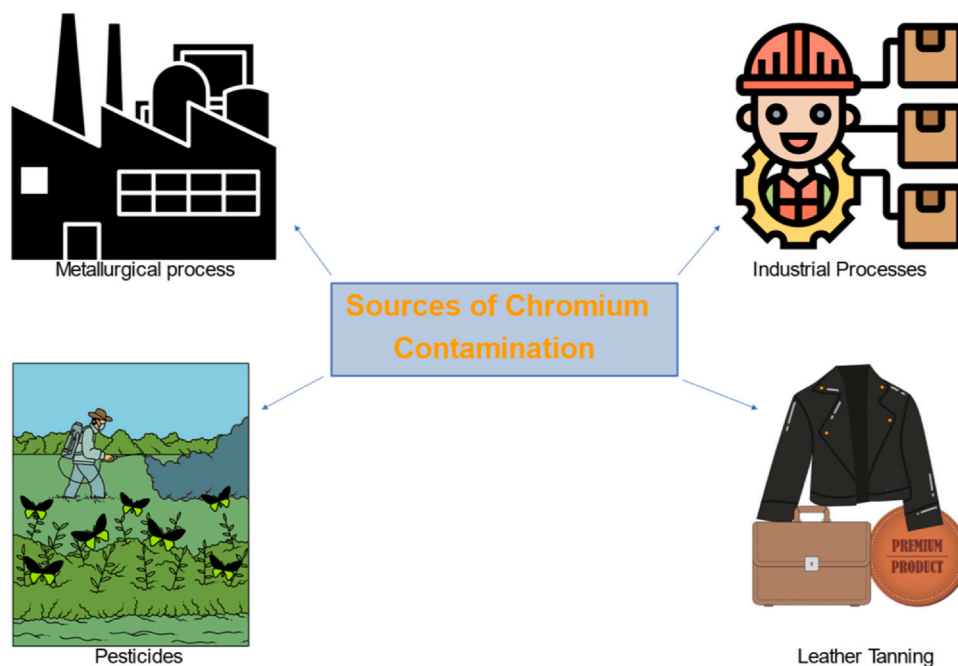


Fig. 7. Sources of Cr contamination.

Table 4
Various Chitosan-based adsorbents for the removal of Chromium (Cr).

Adsorbent	Maximum Adsorption Capacity (mg g ⁻¹)	Isotherm model	Kinetics model	Surface area	Contact time	pH	Ref
CS-based hydrogel	234.8	Langmuir	2nd Order	-	1440	4.5	[114]
Magnetic CS/polyethyleneimine sodium alginate	87.5	Langmuir	2nd Order	0.0506 m ² g ⁻¹	-	3	[113]
Chitosan/g-C ₃ N ₄ /TiO ₂ nanofibers	68.9	Langmuir	2nd Order	-	1440	1–7	[115]
Citratw-cross linked Zn-MOF/chitosan composite	225.0	Langmuir	2nd Order	16.28 m ² g ⁻¹	-	5.0	[116]
zeolite imidazolate framework–67-MOF@Am-chitosan	119.1	Langmuir & Freundlich	2nd Order	220.76 m ² g ⁻¹	60	2–9	[117]
CS-MnO ₂ nanocomposite	61.6	Sips	Intra diffusion	17.80 m ² g ⁻¹	120	2	[118]
Aerogel from nano-bentonite/Nano-cellulose/chitosan	98.9	Halsey	2nd Order	-	1440	2–8	[119]
Fe ₃ O ₄ /SiO ₂ /chitosan-TETA composite	254.6	Langmuir	2nd Order	131.4 m ² g ⁻¹	-	2–8	[120]
CA- C ₆ H ₁₀ O ₂ /chitosan nanofiber	126.0	Freundlich	2nd Order	249.1 m ² g ⁻¹	360	2–7	[121]
Fe ₃ O ₄ @SiO ₂ -chitosan	96.2	Johnson-Mehl-Avrami-Kolmogorov	2nd Order	-	-	-	[122]
Mchitosan/GO	270	Langmuir	2nd Order	74.35 m ² g ⁻¹	600	2	[123]
Chitosan/Montmorillonite- Fe ₃ O ₄ microsphere	58.8	Langmuir	2nd Order	-	180	2	[124]
Chitosan-Iron (III) complex	173.1	-	-	-	-	-	[125]
Polyethyleneimine-magnetic CS microspheres	134.9	Langmuir	2nd Order	-	300	1–8	[126]

substances, which could mean that larger amounts of the adsorbent are needed for effective treatment. In addition, the regeneration of CS matrices following chromium adsorption may present difficulties, impacting their reusability and leading to higher operational expenses.

3.4. Removal of Copper

According to the World Health Organization (WHO), Copper (Cu) is among the essential nutrients in the water for all human beings if the concentration is below 0.05 ppm [128], but if the concentration is higher, it may lead to water pollution, especially heavy metals contamination. If the concentration of Cu (II) ions gets higher in the human body, it affects the nervous system, damages the liver, and can cause cancer by triggering several mutations [129,130]. Due to anthropogenic activities, the concentration of Cu (II) is increasing in water bodies and a few reasons include electrical combustion, dyes, mining,

printing, and electroplating; hence, researchers have given great attention to the treatment of industrial effluent [102,131]. Fig. 8 shows the copper contamination and its bioaccumulation in the food chain.

In an experimental study, He et al. fabricated amidoxime-functionalized CS (AM/AO/AEBI-CS) for the removal of Cu (II). After the complete investigation, the Cu (II) adsorption capacity on the synthesized material was 190.7 mg g⁻¹ [132]. In a recent study, magnetic CS hydrogel beads (MCHB) were prepared with different ratios to remove Cu (II) by blending magnetite (Fe₃O₄) and CS in the solution of sodium alginate. The highest removal efficiency for Cu (II) was 56.51 % by MCHB-0.5 and determined by several parameters (pH, contact time, and various ratios of adsorbent) [133]. Zhang et al. examined the formation of a CS membrane that was stacking and based on an electro-spinning technique and greatly enhanced the efficiency of Cu (II) adsorption on CS via multi-layer. The electro-spinning technique boosted the surface area, and the q_{max} was 276.2 mg g⁻¹ [134].

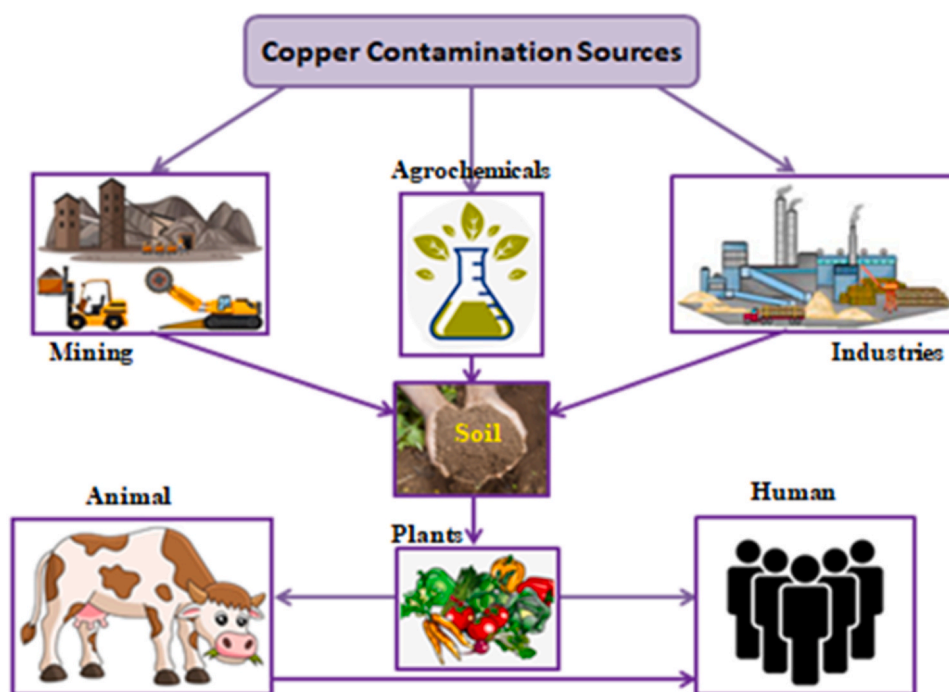


Fig. 8. Flow diagram of copper contamination.

Table 5
Various Chitosan-based adsorbents for the removal of Copper (Cu).

Adsorbent	Maximum Adsorption Capacity (mg g^{-1})	Isotherm model	Kinetics model	Surface area	Contact time	pH	Ref
Chitosan/PVP/PVA-HNM	106.7	Freundlich	2nd Order	17.16	-	-	[99]
Magnetic CS/polyethyleneimine sodium alginate	351.0	Langmuir	2nd Order	0.0506	-	6	[113]
AM/AO/AEBI-CS	190.7	Sips	2nd Order	247.4 $\text{m}^2 \text{g}^{-1}$	360	2–6	[132]
DTPA-chitosan/PEO nanofibers	177.0	Langmuir	2nd Order	-	90	5	[135]
CNTs-CHO-Chitosan	115.8	Langmuir	2nd Order	-	90	2–11	[136]
Chitosan-g-MA composite	312.4	Langmuir	2nd Order	-	180	6	[137]
Chitosan/PVA/PEL membrane	86.1	Langmuir	2nd Order	0.95 $\text{m}^2 \text{g}^{-1}$	720	6	[103]
MSC/GO gel beads	55.0	Langmuir	2nd Order	-	-	1–7	[138]
Magnetic bentonite/Carboxymethyl Chitosan/SA hydrogel beads	56.8	Langmuir	2nd Order	-	240	2.0–6.3	[134]
MSC/GO	217.0	Langmuir	2nd Order	132.9 $\text{m}^2 \text{g}^{-1}$	75	7	[131]
TEPA/Chitosan/ CoFe_2O_4	168.1	Langmuir	2nd Order	-	50	5	[139]
MChitosan/GO with EDTA	207	Langmuir	2nd Order	81.36 $\text{m}^2 \text{g}^{-1}$	300	5.5	[91]
Chitosan-MMT hydrogel	132.7	Freundlich	2nd Order	-	-	5	[140]
Chitosan/TEOS/APTES nanofiber	640.5	Langmuir	1st Order	-	60	2–7	[141]
Zeolite X/Chitosan hybrid microspheres	152.0	Langmuir	2nd Order	406 $\text{m}^2 \text{g}^{-1}$	-	5.5	[142]
Silica/Chitosan composite	870.0	Freundlich	-	119.29 $\text{m}^2 \text{g}^{-1}$	30	1–6	[143]
Chitosan-g-PAA/APT	303.0	Langmuir	2nd Order	1.83 $\text{m}^2 \text{g}^{-1}$	180	5.85	[144]

Wang & Li prepared three-dimensional porous CS aerogels for copper ions. The CS aerogel showed low adhesion, super hydrophilicity, and selectivity. The maximum adsorption capacity was 116.7 mg g^{-1} [145]. In another experimental study, He et al. synthesized the beads of EDTA on a polyvinyl alcohol (PVA)-CS surface. In addition, newly prepared beads exhibited much better adsorption than the previously prepared beads and q_{max} was reported 127.8 mg g^{-1} of Cu (II) [146]. Wang et al., CS-g-poly modified attapulgite (CS-g-PAA/APT) for removing Cu (II) from contaminated water. This combined formation enhanced the specific porous surface and surface area; in 15 min, 90 % efficiency was reported [144]. Table 4 summarizes the q_{max} for Cu on CS-based adsorbent.

CS-based adsorbents have a remarkable ability to selectively bind copper ions, thanks to the strong interactions between the metal and the ligand. This property helps to minimize any unwanted interference from other ions present in the solution. Their compatibility with living organisms and their positive impact on the environment help mitigate the health and environmental hazards linked to copper removal procedures. In addition, the versatile nature of CS enables easy modifications to improve its capacity and selectivity for copper adsorption. CS-based adsorbents have been found to show adsorption behavior that is dependent on pH. This means that it is important to carefully adjust the solution conditions to achieve optimal copper removal. The surface area of CS particles is limited, which can restrict their adsorption capacity. As a result, higher doses of adsorbent may be necessary for effective treatment. In addition, the regeneration of CS matrices following copper adsorption could present difficulties, affecting their reusability and leading to higher operational expenses.

3.5. Removal of Lead

Lead (Pb(II)) is a persistent heavy metal that can deteriorate ecosystem and human health when it is introduced to more than 10 ppb in potable water as authorized by WHO [147,148], whereas the United States Environmental Protection Agency (US-EPA) allows 15 ppb concentration in drinking water [149,150]. Lead contamination sources are mentioned in Fig. 9.

Many studies have been reported on the development of adsorbents, such as CS, for the adsorption of Pb. In a recent study, CS and PVA were combined to remove Zn, Pb, and Fe. The maximum adsorption capacities were 4.0 for Pb, 135.1 for Fe, and 222.2 mg g^{-1} for Zn [151]. Gao and coauthors prepared alginate/melamine/chitosan (SA/ME/CS) aerogel for Lead (II) adsorption in this context. The results showed high

adsorption between pH 5–6 with a maximum adsorption capacity of 1331.6 mg g^{-1} towards Pb (II) [78]. Amin et al., synthesized magnetic nanoparticles via a thermal decomposition process and coated them with silica (mesoporous) layers using cetyltrimethylammonium bromide (CTAB) as a surfactant agent. The prepared adsorbent exhibited a maximum capacity of 150.3 mg g^{-1} for Pb^{2+} and 126.3 mg g^{-1} for Cd^{2+} [152]. Table 6 summarizes q_{max} for Pb on CS-based adsorbent.

In another research, Dinh and coworkers (2018) fabricated CS-loaded manganese dioxide (MnO_2/CS) nanoparticles where the pores surface area of MnO_2/CS was larger than the lead ions, proposing the possibility of Pb (II) ions to enter in the surface of the beads [156]. In one attempt, Guo et al. examined the utilization of CS-PDA aerogel for Pb (II) adsorption from the wastewater. The q_{max} was reported to be 441.2 mg g^{-1} , and the chemisorption process occurred [157]. Li et al. examined the adsorption of Pb (II) onto yeast biomass modified with ethylenediamine and coated with magnetic-CS micro-particles (EYMCS). The q_{max} was reported to be 134.9 mg g^{-1} at 40°C [158]. Furthermore, Liang et al. experimented with beads that were solid and synthesized MOF and CS via the solvothermal method, and as a cross-linker, sodium tripolyphosphate (Na-TPP) was utilized. The q_{max} of 406.5 mg g^{-1} was found at normal room temperature [159].

CS-based adsorbents have proven to be highly effective in the removal of lead contaminants. This effectiveness can be attributed to the strong interactions that occur between lead ions and the functional groups present on the surfaces of CS. Their compatibility with living organisms and their positive impact on the environment help alleviate health and environmental issues related to lead removal methods. In addition, its versatility allows for easy modifications to improve its ability to absorb lead and selectivity. CS-based adsorbents have been found to show pH-dependent adsorption behavior. Therefore, it is important to carefully control the solution conditions in order to achieve optimal lead removal. The surface area of CS particles is limited, which can limit their adsorption capacity. This means that higher doses of adsorbent may be needed for effective treatment. In addition, the regeneration of CS matrices following lead adsorption presents a potential challenge, as it may affect reusability and lead to higher operational costs.

4. Regeneration of CS-based adsorbents

The regeneration of CS-based adsorbents is an important aspect in assessing their practical feasibility and sustainability for removing heavy metals from wastewater and there are several factors to examine.



Fig. 9. Several sources of Pb contamination.

To begin with, the conversation focuses on the ability to use these adsorbents multiple times and their cost-efficiency, and CS is a cheap source [160]. It underscores their potential for repeated use and the financial considerations of the regeneration process. Additionally, it is important to optimize the circumstances for regeneration, including elements such as the kind and concentration of the regenerating agent, temperature, and contact time [161]. Elution with an eluent is the most used method in the literature to regenerate chitosan-based adsorbents. The proportion used of eluents was in the sequence of salts, alkalis, chelators, and acids. The HCl, EDTA, NaOH, and NaCl solutions are frequently employed to remove substances [162]. This is necessary to develop effective protocols and improve desorption efficiency. Moreover, focus is given to the stability and durability of the adsorbent, examining any changes in structure or alterations in functional groups that may occur over repeated regeneration cycles to appropriately assess long-term performance. Studying how desorption works provides information about how metals and CS interact, which helps improve methods for regeneration. Environmental factors, such as the possible creation of additional pollutants and the impact on the environment

caused by regenerating agents, are important for assessing the overall environmental impact of the adsorption-desorption cycle. Finally, including actual uses, like continuous-flow systems or large-scale water treatment procedures, requires dealing with scaling issues and suggesting methods to match regeneration elements with real-life situations. Fig. 10 shows the regeneration of CS-based adsorbents for the metals.

5. Effect of heavy metals on human health

Heavy metals are available naturally in the environment, and a few are vital for living on Earth, but when they bioaccumulate in the food chain, they become hazardous [163] and seriously harm human health. Arsenic is an extremely toxic metalloid. Long-term exposure to As has been linked to a number of health problems, such as skin lesions, bladder, lung, and skin cancers, as well as cardiovascular disorders [164]. Long-term consumption of water tainted with As has been connected to the emergence of several malignancies, making it a serious public health risk. Furthermore, exposure to arsenic has been linked to

Table 6

Various CS-based adsorbents for the removal of Lead (Pb),.

Adsorbent	Maximum Adsorption Capacity (mg g ⁻¹)	Isotherm model	Kinetics model	Surface area	Contact time	pH	Ref
Alginate/Melamine/Chitosan aerogel	1331.6	Langmuir	2nd Order	-	850	5.5	[78]
Chitosan/PVP/PVA-HNM	87.81	Langmuir	2nd Order	17.16 m ² g ⁻¹	-	-	[99]
Chitosan-pectin beads	266.5	Langmuir	2nd Order	23.66 m ² g ⁻¹	160	1 – 9	[101]
Chitosan/Polyvinyl alcohol	4.02	Langmuir	2nd Order	1.96 m ² g ⁻¹	720	3.64	[151]
Cross-linked carboxylated Chitosan/ carboxylated nano-cellulose hydrogel beads	334.9	Langmuir	2nd Order	-	30	4 – 4.5	[153]
Magnetic-Chitosan-Peracetic acid nano-composite	204.9	Langmuir	2nd Order	-	120	2 – 5	[154]
Chitosan-Polyvinyl alcohol nano-fibers	266.12	Langmuir	2nd Order	-	240	2 – 11	[155]
Magnese oxide/Chitosan nano-particles	126.1	Langmuir	2nd Order	15.75 m ² g ⁻¹	240	2 – 15	[156]
Polydopamine-modified Chitosan aerogels	441.2	Langmuir	2nd Order	77.3 m ² g ⁻¹	900	2 – 8	[157]
Hydroxyapatite/Chitosan composite	132.1	Langmuir	2nd Order	-	240	6	[107]

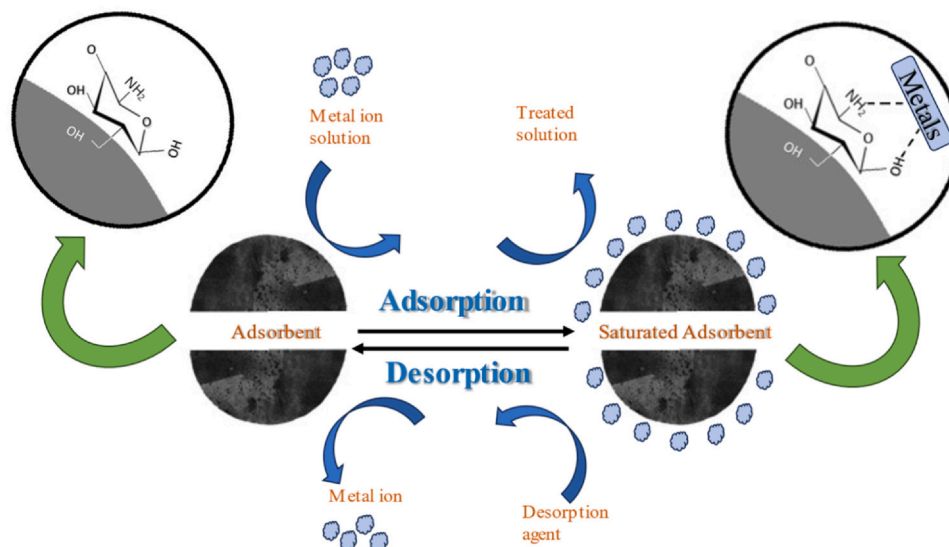


Fig. 10. Regeneration of CS-based adsorbents for metals.

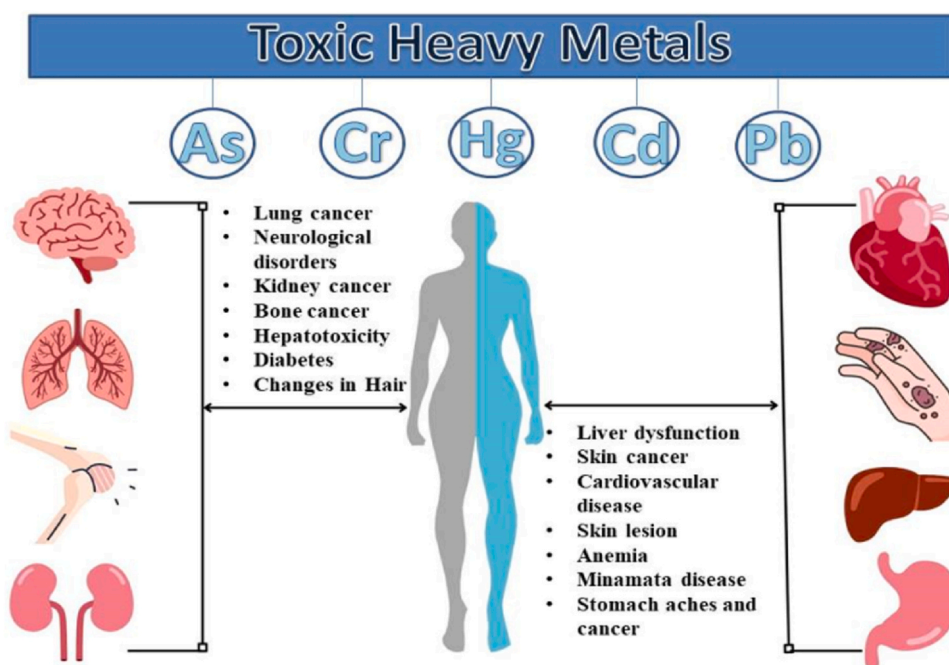


Fig. 11. Adverse effects on human health by toxic heavy metals.

neurological diseases and other effects on the nervous system, including the ability to reproduce. To lessen these harmful effects on health, the World Health Organization (WHO) and other regulatory agencies have set strict limits for arsenic in drinking water.

Cadmium is naturally present and released into the atmosphere by manmade activities (mainly released into the air via tainted food, drink, and tobacco smoke), and it has different effects on humans and animals. Chronic exposure to cadmium has been linked to kidney damage, which can result in painful and incapacitating illnesses like Itai-Itai disease, a form of osteomalacia. In addition, cadmium has been linked to cardiovascular problems, pulmonary problems, and a higher risk of some cancers, especially prostate and lung cancer. Cadmium can also have a detrimental effect on bone health, increasing the incidence of fractures and reducing bone density. Also, a study reported that cadmium hinders in plant metabolic processes and growth [165].

The metal chromium can be found in a number of oxidation states, the most dangerous of which is hexavalent chromium [Cr(VI)]. Long-

term exposure to high concentrations of hexavalent chromium, which are frequently present in industrial effluent, has been connected to lung cancer and other respiratory problems. Skin disorders, renal damage, and irritation of the nose and gastrointestinal tract can also be brought on by hexavalent chromium ingestion or inhalation [166]. Because of its link to lung cancer, hexavalent chromium has been categorized as a Group 1 human carcinogen by the International Agency for Research on Cancer (IARC). Even though copper is a trace element vital to human health, too much of it can have negative effects. Severe copper poisoning in drinking water can lead to nausea and vomiting as well as other gastrointestinal problems. Copper poisoning is especially dangerous for those with Wilson's disease, a hereditary illness that affects copper metabolism. Chronic exposure to high copper concentrations may also aggravate the kidneys and liver. Copper is routinely monitored in drinking water to ensure that levels stay within acceptable limits for human consumption, despite any potential health hazards. Fig. 11 shows the human health effects of contaminated water with toxic heavy metals.

Table 7
Different toxic heavy metals and their human health impacts.

Heavy Metal	Diseases	Research Published
Arsenic	Skin lesion lung cancer diabetes skin cancer Cardiovascular dysfunction Liver damage Changes in hair	[174–176]
Lead	CNS injury GI colic Liver damage Lungs dysfunction Reduced pulmonary function Hematological changes (Anemia)	[177–180]
Mercury	CNS injuries Renal dysfunction GI ulceration Hepatotoxicity Minamata disease	[181–184]
Cadmium	Kidney dysfunction GI disorders Cancer Lungs injuries Degenerative bone disease Itai-itai disease	[185–188]
Chromium	Kidney dysfunction Dermal diseases GI disorders Cancers (lung, bone, thyroid, kidneys, testicular, bladder, and larynx)	[189,190]

Mercury is present in the biosphere and is a highly hazardous heavy metal. It converts to methyl-mercury when it comes in contact with aquatic sediments, which is highly toxic [167]. Manganese is the most abundant toxic heavy metal found naturally in several oxidation states. It is required in many physiological activities, and its excessive consumption results in high levels of toxicity [168,169]. It has adverse human health effects and causes lung and nasal cancer, kidney disorders, cardiovascular diseases, and allergies via inhalation of nickel in the air [170–172], whereas cobalt usually has no negative impacts on human life but may cause death when massive discharges into the environment [173]. It is a very poisonous heavy metal and may possess negative effects on the body's organs. Exposure to lead throughout childhood has the greatest health hazards as it can disrupt cognitive development and result in behavioral issues. Adults who are exposed to Pb have a higher chance of developing hypertension, cardiovascular illnesses, and decreased renal function. It can also build up in bones, which presents long-term health hazards. Strict laws limiting lead exposure have been implemented due to the negative consequences of lead, especially in paint, drinking water, and other consumer goods.

Moreover, copper and zinc are considered vital nutrients for human life and plants, and their toxicity makes them lethal. The deficiency of copper alters vital metabolic processes [191]. Zinc affects ecosystems when emitted into the environment [192].

6. Conclusion and recommendations

Adsorbents based on CS demonstrate remarkable characteristics in the removal of environmental pollutants, demonstrating significant adsorption capacities and efficiencies against a variety of pollutants. This review focuses on the incorporation of different materials with CS, including forms like beads, hydrogels, membranes, etc., that greatly reduce the separation difficulties that come with CS. According to analysis, CS can be modified with promising materials to increase its adsorption capacity. These materials include clays, carbon materials,

metal-organic frameworks, layered double hydroxides, etc., which help to overcome the low adsorption complexity that CS naturally possesses. Moreover, adding the right functional groups to CS improves its electrostatic interaction with contaminants, making it a very powerful method for increasing CS selectivity.

This thorough analysis investigates the adsorption phenomena of CS toward extremely harmful heavy metals, such as As(III) & (V), Cd(II), Cu(II), Cr(VI), and Pb(II), and clarifies the implications for human health. Notwithstanding these positive qualities, disadvantages of CS-based adsorbents are noted; they include problems with reusability, pH dependence, restricted surface area, cost and scalability, and low adsorption capacity. The authors acknowledge that pollutant selectivity is a crucial component in the assessment of CS-based adsorbents and stress its vital importance in the investigation of actual wastewater.

However, this review includes future recommendations to address the drawbacks:

- Enhanced Adsorption Capacity:** Researchers can investigate CS-based adsorbents with various modifications to improve their adsorption capacity. This may incorporate functional groups, nanoparticles, or materials to increase efficiency.
- pH Tolerant Adsorbents:** Synthesis of adsorbents that can efficiently perform over a diverse pH range would improve their practical applicability.
- Selectivity:** Synthesis of CS-based adsorbent with surface modification or specific functional group could help improve selectivity for targeted metal contaminants.
- Thermodynamic Constraints:** The thermodynamic capability of heavy metal adsorption onto CS is governed by parameters such as temperature and pressure. It is essential to comprehend the thermodynamic parameters, such as enthalpy, entropy, and Gibbs free energy changes, in order to forecast the feasibility and spontaneity of the adsorption process under various circumstances.
- Influence of Ionic Strength:** Its adsorption capacity for metals is sensitive to differences in ionic strength. Concentrated solutions can reduce the electrostatic attraction resulting in the overall lower adsorption.
- Diffusion Limitations:** When heavy metal ions diffuse slowly into CS matrices, equilibrium may not be reached in a reasonable amount of time. This constraint is linked to the necessity for mass transfer across the aqueous outer layer and the internal pores of the adsorbent, demanding longer contact durations.

By addressing these challenges and implementing recommendations, CS-based adsorbents can potentially improve in terms of selectivity, cost-effectiveness, and environmentally friendly metal removal solutions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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