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Chitosan-Based Biostimulation: A Novel Approach for Simultaneous Remediation of Co-Existing Cadmium and Arsenic Contamination in Soil

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ABSTRACT: Cadmium (Cd) and arsenic (As) are both potentially toxic heavy metals (HMs) found ubiquitously in the environment. These HMs are prevalent in soil due to natural occurrences or anthropogenic activities. Co-contamination of Cd and As in soil is a major concern for plant and human health as well as ecosystem sustainability due to their hazardous properties. Therefore, a global imperative is developing improved technologies for managing and remediating soil co-contaminated with Cd and As. One effective solution for remediating Cd/As co-contaminated soil involves the utilization of natural biopolymers and biostimulants, such as chitosan (CS). CS offers distinct advantages, including its ready availability, biodegradability, biocompatibility, environmental friendliness, and cost-effectiveness when compared to alternative adsorbents. The adsorption mechanism of CS and CS-based adsorbents for Cd and As primarily relies on electrostatic attraction, complexation, and ion exchange. This review article provides a comprehensive overview of Cd and As co-contamination in soil, elucidating their sources, distribution patterns, exposure pathways, and the prospective remediation approaches employing CS biostimulants and CS-based adsorbents. Furthermore, it summarizes recent studies investigating the adsorption of Cd/As by CS, the factors influencing the adsorption efficiency and the challenges associated with the utilization of CS and CS-based adsorbents. In conclusion, the review underscores the need for further research to concurrently remediate Cd and As co-contaminated soil, enhance the adsorption efficiency of CS and CS-based composites, and broaden their practical applicability for remediating co-contaminated soils.

KEYWORDS: Adsorption, arsenic, cadmium, chitosan, co-contamination, soil

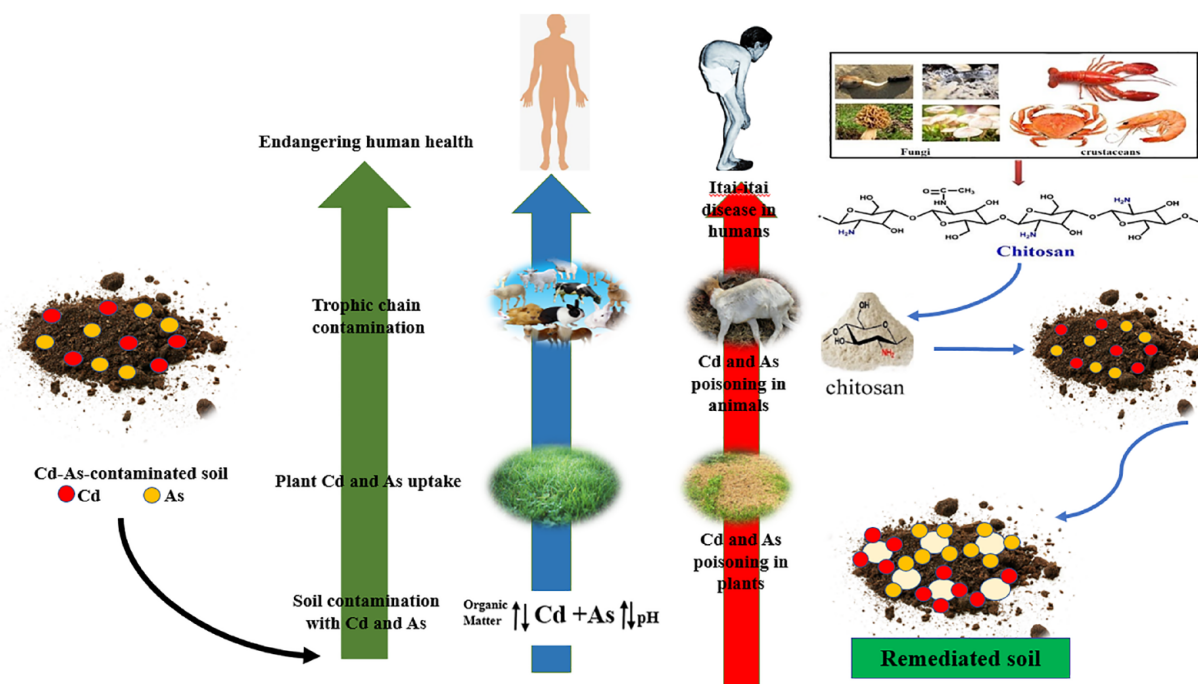
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GRAPHICAL ABSTRACT



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Highlights

- An emerging chitosan-based remediation technology for Cd and As co-contamination was proposed.
- Chitosan is a renewable, eco-friendly, low toxicity, and biodegradable biopolymer.
- The underlying mechanisms of chitosan-co-contaminant interactions were elucidated.
- Significance for environmental policy and decision-making were explored.
- Field-level validation of chitosan-based bioremediation needed.

Introduction

Cadmium (Cd) and arsenic (As) are frequently encountered in environmental matrices such as soil and water (Figure 1). Co-contamination of soils with Cd and As is a widespread concern caused by natural or anthropogenic sources (Lv et al., 2020). Cd and As naturally coexist in certain minerals and ores, such as sulfide ores. It is widely believed that both active and abandoned sulfide mining sites suffer from substantial Cd and As co-contamination, as well as downstream leaching (Gu et al., 2019; Ullah et al., 2022). Cd and As have been listed as category one carcinogens by the World Health Organization (2017). Their capacity for easy accumulation and high toxicity pose significant threats to the ecological environment, plants and human health (Adnan et al., 2022; Shaukat et al., 2022; Yu et al., 2016). The co-contamination of Cd and As in soil has also impeded food safety, especially in mining areas (Yu et al., 2016). Hence, the concurrent presence of Cd and As in the environment has emerged as a pressing environmental concern due to the substantial release of these elements (Guo et al., 2019). Notably, the co-occurrence of As and Cd has rendered them highly mobile and bioavailable in soil, surpassing the mobility and bioavailability of other HMs (Ji et al., 2022).

Addressing the urgent demand for the remediation of Cd and As contamination has spurred significant endeavors aimed at developing highly efficient and economically viable solutions. A burgeoning body of review articles focuses on using CS and its derivatives as effective adsorbents for removing dyes and/or toxic HM ions from water or wastewater (Dragan, 2014). This distinction arises from the abundant availability, facile biodegradability, non-toxic properties, cost-effectiveness, impressive efficacy, and environmentally friendly characteristics (Omer et al., 2022). Several notable contributions have illuminated the versatile applications of CS-based materials in the domain of environmental remediation. For instance, Babel and Kurniawan (2003) provided a comprehensive overview of various low-cost adsorbents, including CS and zeolites, among others, delineating their efficacy in the removal of HM ions from contaminated water sources. Jayakumar et al. (2011) conducted a meticulous review encompassing diverse preparation methodologies for modified CS, highlighting the utility of graft-copolymerized CS in mitigating diverse pollutant

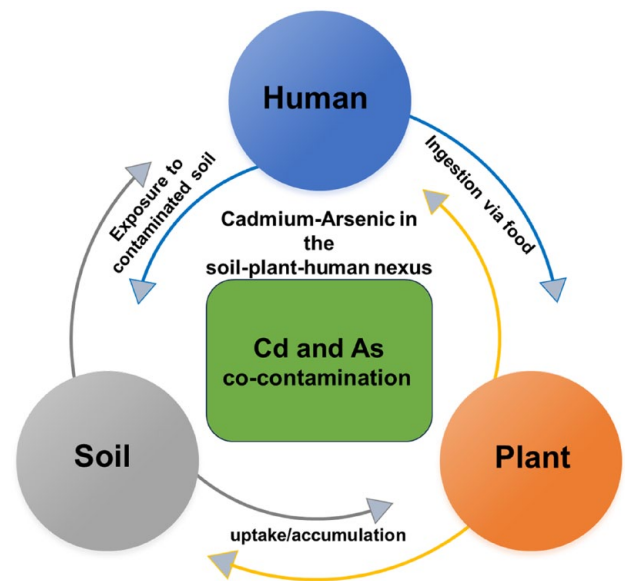


Figure 1. Impacts of cadmium-arsenic co-existence on different spheres.

species. On the other hand, Pontoni et al. (2012) directed their attention toward removing As from aqueous solutions, with a specific focus on CS and CS-derived materials. It is important to underscore the relative paucity of comprehensive reviews addressing their application in soil remediation for removing Cd and As.

Chitosan (depicted in Figure 2), an abundant biopolymer derived through alkaline N-deacetylation of chitin (exoskeletons of crustaceans like shrimp and crab shells), stands out due to its elevated adsorption capacity for HM ions, attributed to the presence of abundant reactive hydroxyl ($-OH$) and amino ($-NH_2$) groups (Ali et al., 2022; Huang, Li, et al., 2017). This binding occurs through various mechanisms, including electrostatic attraction, complexation, and chelation (Peter et al., 2021). Nevertheless, CS has some shortcomings (i.e., low acid stability, inadequate mechanical strength, and low thermal stability) that restrict its application. Thus, researchers have explored various physical and/or chemical modification techniques (Figure 3) to enhance its adsorption properties for metal ions.

Some commonly employed CSCs for HM removal include (1) Cross-linked CS: Utilizing cross-linking agents such as glutaraldehyde, epichlorohydrin, or tripolyphosphate results in the formation of a three-dimensional network structure (Crini et al., 2019). This enhances mechanical strength, stability, and the adsorption capacity of CS for HMs (Sethi et al., 2022), (2) Carboxymethyl CS: Carboxymethylation introduces carboxyl functional groups, leading to stronger complexation with HM ions and improved solubility and stability under a wider pH range (Ariani et al., 2023), (3) Thiolated CS: The introduction of thiol ($-SH$) groups onto the CS backbone strengthens thiol-metal interactions, boosting the affinity for HMs and enhancing selectivity and efficiency (Azhar et al., 2023), and (4) Quaternized CS: Quaternization involves the introduction of

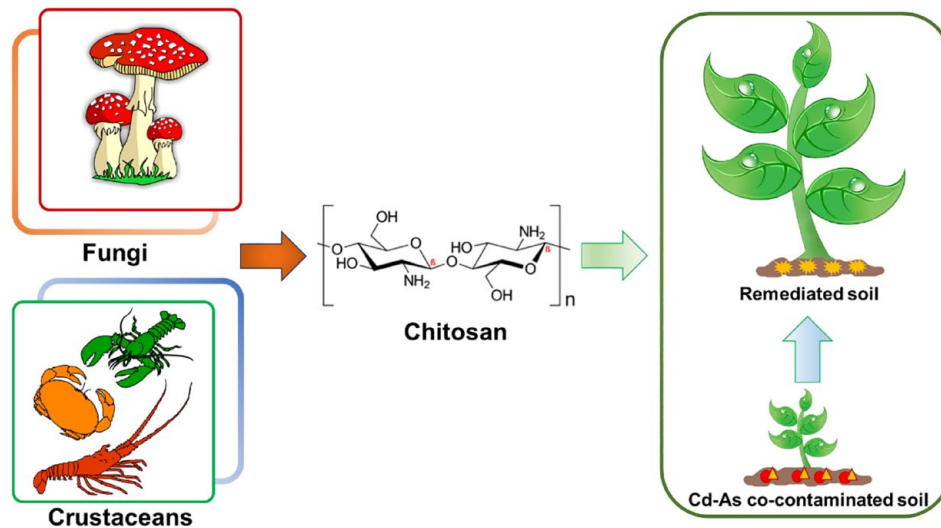


Figure 2. Remediation of Cd-As-contaminated soil by using chitosan as an adsorbent.

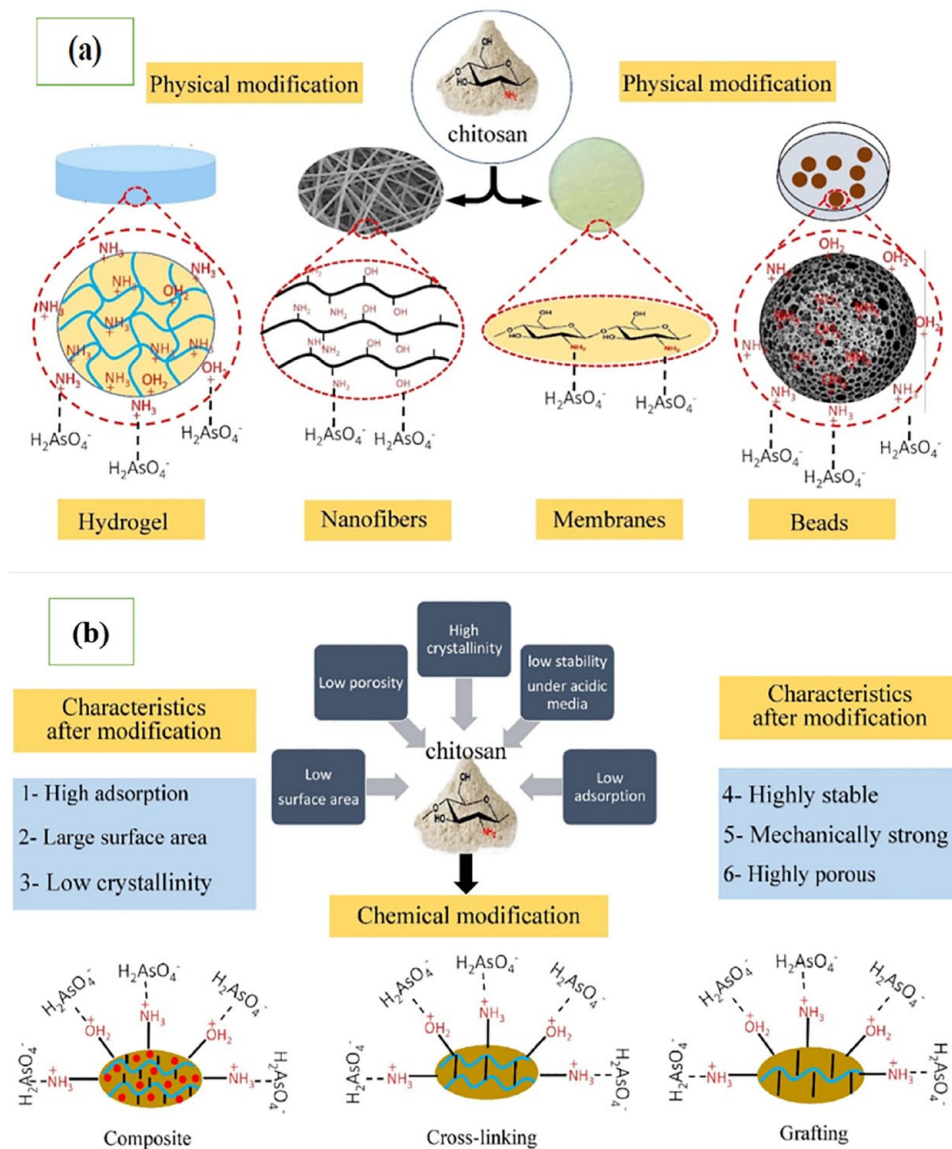


Figure 3. Schematic representations of: (a) physical and (b) chemical modification and mechanism of chitosan for As-contaminated soil and water (Ayub & Raza, 2021).

quaternary ammonium groups onto the CS structure, resulting in improved adsorption capacity through ion exchange and electrostatic attraction (K. X. Huang et al., 2023). The adsorption process involving CS-based adsorbents entails contact between the adsorbent and the contaminated medium. HM ions interact with the functional groups on the CS surface, facilitating their removal (Sajid, 2022).

Factors such as pH, temperature, contact time, adsorbent dosage, and initial metal ion concentration can significantly influence the adsorption efficiency of both CS and CSCs (Ayub & Raza, 2021). CS demonstrates selective adsorption of HMs, even in the presence of competing ions, ensuring the targeted removal of HMs (Peana et al., 2022). Its high binding affinity toward HM ions surpasses that of common ions found in wastewater. CS-based adsorbents can be regenerated and reused, contributing to their cost-effectiveness compared to other adsorbents (Zhang et al., 2014). HMs adsorbed onto CS can be eluted using appropriate desorption agents, allowing for the regeneration and multiple cycles of the CS adsorbent (Hwang et al., 2019). The robust metal-binding properties of CS enable the recovery of valuable metals from water and soil. After adsorption, metal-loaded CS can undergo further processing to extract metals, contributing to resource sustainability (Briffa et al., 2020).

Previous studies have predominantly focused on specific geographical regions to quantify Cd-As concentrations, assess pollution levels, and evaluate associated health risks. For instance, research efforts have honed in on industrial and agricultural areas in countries such as China (Huang, Li, et al., 2017), India (Adimalla et al., 2019), Iran (Sayadi et al., 2015), Africa (Yabe et al., 2010), England (Rawlins et al., 2012), Holland (Brus et al., 2009), Europe (Salminen, 2005), America (Burt et al., 2003), Pakistan (Badshah et al., 2023), and Bangladesh (S. Kumar et al., 2021). However, comprehensive reviews addressing Cd-As co-contamination remain conspicuously absent from the existing literature. Detailed data regarding the use of CS and CSCs for the remediation of soil co-contaminated with Cd and As, as well as their respective mechanisms of action, have yet to be published.

With this in mind, our study aims to assess the extent of Cd and As co-contamination in soils worldwide, including China. We aim to shed light on the promising potential of CS and CSCs as effective adsorbents for addressing this co-contamination issue. Our review underscores the need for constructive directions and adjustments in the development of CS and CSCs for future applications in the simultaneous removal of Cd and As co-contamination in soil.

Co-Existence of Arsenic-Cadmium Around the Globe

Numerous investigations worldwide have extensively explored soil HM pollution arising from human activities (see Table 1), consistently revealing alarming concentrations of Cd and As.

Wang, Zhou, et al. (2022) conducted a comprehensive assessment, estimating that nearly 10 million km² of global soil is presently contaminated, with approximately 1 million km² containing almost 80% high levels of Cd and As. This universal contamination presents a critical concern for regions like Sri Lanka, an agricultural country grappling with the highest recorded incidence of chronic renal disease worldwide, which has attributed over 50,000 fatalities to Cd and As co-contamination (Gunadasa et al., 2023). In Sri Lankan agricultural soils, these toxic elements have been detected at substantial concentrations, with As and Cd levels reaching 24 mg kg⁻¹ and 7 mg kg⁻¹, respectively (Jayatilake et al., 2013). Similar co-contamination patterns have been observed in various regions, including Pakistan (Ghani et al., 2022, Sabir et al., 2022), Bangladesh (Alam et al., 2003), India (Buragohain et al., 2010), Japan (Honma et al., 2016), and China (Yu et al., 2016). In various studies (Amphalop et al., 2020; Gunadasa et al., 2023; Jorfi et al., 2017; Khan et al., 2017; Lyu et al., 2022; Rehman et al., 2017; Tahir et al., 2022; Wang, Lu, et al., 2019), Cd and As co-contamination in soil has been extensively investigated, revealing peak concentrations ranging from 0.012 to 100 mg kg⁻¹ for As and 0.014 to 3.43 mg kg⁻¹ for Cd. These concentrations consistently exceeded the maximum allowable limits (MAL) established by the European Union (EU) (2000) and the State Environmental Protection Administration (SEPA) (1995) for soil in China and were notably higher than those of other HMs. Comprehending the mobility and availability of Cd and As co-contamination in soil is paramount for effective exposure assessment and management (Gunadasa et al., 2023) (Table 1).

Status of Cadmium-Arsenic Co-Contamination in China

Soil pollution by HMs has emerged as a critical environmental concern in China due to rapid socio-economic growth (Tang et al., 2022, Tholley et al., 2023). Despite ongoing efforts, soil HM contamination remains a significant challenge. The Ministry of Land Resources (MLR) reported that over 10% of China's farmland soil is polluted extensively with different HMs (Xiang et al., 2023), as depicted in (Table 2). Comprehensive data gathered from 138 locations indicates that approximately 16.67% of China's soil faces HM pollution, implying that one-sixth of the nation's arable land may be affected (J. Wu et al., 2022). A joint assessment by the MLR and the Ministry of Environmental Protection (MEP) in 2014 revealed that 19.4% of China's arable land exhibited contamination, with Cd ranking as the most prevalent pollutant (7.0% of soil samples exceeding MEP limits), followed by As at 3.0% (Gu et al., 2019; Wang, Wang, et al., 2022). Moreover, the co-contamination of Cd and As in arable land has led to substantial economic losses in China, with 80% of the total contamination in the country attributed to HMs, particularly Cd and As (Wang, Zhou, et al., 2022; Zhao et al., 2015).

Table 1. Worldwide Heavy Metals Contamination Level (mg kg⁻¹).

COUNTRY	CD	AS	PB	CU	NI	CR	ZN	HG	REFERENCES
India	1.76	9.99	41.80	79.05	52.44	147.05	178.50	–	Adimalla et al. (2019)
Iran	1.53	10.25	46.59	60.15	35.53	63.79	94.09	–	Sayadi et al. (2015)
Africa	5.00	14.50	150.0	100.00	100.00	250.00	500.00	–	Yabe et al. (2010)
China	0.19	8.89	30.74	25.81	27.77	67.37	85.86	0.07	Yuan et al. (2021)
Europe	0.15	6.00	15.00	12.00	14.00	22.00	48.00	0.037	Salminen, (2005)
Holland	0.14	5.60	15.60	10.20	4.94	15.70	40.30	–	Brus et al. (2009)
England	0.33	15.00	49.00	30.10	21.00	68.00	76.00	–	Rawlins et al. (2012)
America	0.16	7.55		17.30	18.30	24.00		–	Burt et al. (2003)
World	1.10	4.70	25.00	4.00	18.00	42.00	62.00	0.10	Kabata-Pendias, (2000)

Table 2. Different Sources of Heavy Metals in Chinese Soils.

SOURCES	HEAVY METALS	REFERENCES
Parent material	Cd, Pb, Zn, Cr, As, Ni, Cu	Sun et al. (2013)
Mining	As, Pb Cu, Hg, Cd, Ni	Qin et al. (2016)
Industrial	Pb, Cu, As, Cd, Ni, Hg	Han et al. (2012)
Agricultural	Cd, Cr, Zn, Cu, Pb, As, Hg	Huang, He, et al. (2017)
Precipitation	Hg, Zn, Cd, Pb, Cu, Cr	Li et al. (2015)
Transportation	As, Cd, Cr, Cu, Ni, Pb, Zn	Bai et al. (2010)

Historical mining and smelting activities have released significant amounts of HMs into the environment (L. Yan et al., 2021), resulting in widespread Cd and As co-contamination in Chinese soils (Table 3). The opposing geochemical behaviors of these metals in soil have contributed to their co-contamination (Q. Wang et al., 2023). Therefore, this review utilizes China's environmental quality standards (GB 15618–2018) as a reference, with soil pollution levels defined at 0.30 mg kg⁻¹ for Cd and 30 mg kg⁻¹ for As. Alarming figures reveal that 16.1% of China's soil exceeds these standards, with Cd, As, Cr, Hg, and Pb surpassing the limits at rates of 7.0, 2.7, 1.1, 1.6, and 1.5%, respectively (Peng et al., 2019; Xiao et al., 2017). Q. Yang et al. (2018) reported that soil Cd-As co-contamination significantly exceeds these limits, with Cd at 79.2 mg kg⁻¹ and As at 0.5 mg kg⁻¹, 5 times the allowable standards in China (GB 15618–2018). Similarly, D. Yang et al. (2021) found Cd-As co-contamination in Zhuzhou, Hunan Province, with Cd at 0.85 mg kg⁻¹ and As at 33.90 mg kg⁻¹, both exceeding environmental quality standards. Further investigations near the Dabaoshan mine in Guangdong revealed Cd-As levels exceeding standards, with Cd at 2.46 mg kg⁻¹ and As at 79 mg kg⁻¹ (H. He et al., 2020). Zhan et al. (2021) reported Cd-As co-contamination in southwest China, particularly in Yunnan, Guizhou, and Guangxi, with Cd at 1.24 mg kg⁻¹ and As at

28.5 mg kg⁻¹ in Guizhou. Ren et al. (2022) documented Cd-As co-contamination, with peak concentrations of 1.52 mg kg⁻¹ for Cd and 36.35 mg kg⁻¹ for As, both surpassing environmental quality standards. Yuan et al. (2021) reported Cd at 0.19 mg kg⁻¹ and As at 8.89 mg kg⁻¹, with Pb, Zn, Cr, Ni, and Cu also exceeding the standards. Numerous other studies (Ji et al., 2022; Ning et al., 2023; Sawut et al., 2018) have similarly identified Cd-As co-contamination in various regions of China, further underscoring the severity of this issue (Tables 2 and 3).

Chitosan and Its Derivatives

Chitosan is a highly versatile material with a broad spectrum of applications across various domains, including environmental contexts (Omer et al., 2022). Within the realm of environmental applications, CS derivatives, which represent tailored modifications of CS, play a pivotal role by endowing enhanced properties and functionalities tailored to specific environmental objectives (X. He et al., 2022). This discussion delves into key CS derivatives with a particular focus on their applications in the environmental domain. Major CS-based derivatives are: (1) Oligochitosan: This low-molecular-weight CS derivative offers improved solubility and bioactivity relative to CS itself (Boamah et al., 2015). Oligochitosan finds extensive utility as a biostimulant in both agricultural and environmental applications

Table 3. Co-Contamination of Cadmium and Arsenic in the Soil of Different Provinces of China.

PROVINCE	AS (MG KG ⁻¹)	CD (MG KG ⁻¹)	REFERENCES
Beijing	9.7	0.074	Q. Yang et al. (2018)
Xinjiang	11.2	0.120	
Tianjin	9.6	0.090	
Ningxia	11.9	0.137	
Hebei	13.6	0.094	
Qinghai	14.0	0.112	
Shanxi	9.8	0.128	
Gansu	12.6	0.116	
Shaanxi	11.1	0.094	
Tibet	19.7	0.081	
Inner Mongolia	7.5	0.053	
Yunnan	18.4	0.218	
Liaoning	8.8	0.108	
Guizhou	20.0	0.659	
Jilin	8.0	0.099	
Sichuan	10.4	0.079	
Heilongjiang	7.3	0.086	
Chongqing	6.99	0.140	
Shanghai	9.1	0.138	
Hainan	8.04	0.027	
Jiangsu	10.0	0.126	
Guangxi	20.5	0.267	
Zhejiang	9.2	0.070	
Guangdong	8.9	0.056	
Anhui	9.0	0.097	
Hunan	15.7	0.126	
Fujian	6.3	0.074	
Hubei	12.3	0.172	
Jiangxi	14.9	0.108	
Henan	11.4	0.074	
Shandong	9.3	0.084	

(Vithanage et al., 2017). (2) Carboxymethyl chitosan (CMCS): CMCS boasts superior water solubility and biocompatibility, making it well-suited for a range of environmental applications, including wastewater treatment, metal ion adsorption, and soil treatment (Ayub et al., 2020). (3) Chitosan Nanoparticles:

These nanoscale particles, derived from CS, offer a high surface area and possess the capacity to encapsulate various substances. In environmental remediation, CS nanoparticles find use in processes such as the adsorption and removal of heavy metals (HMs), dyes, and organic pollutants from water and soil (Wang, Cai, et al., 2019). (4) CS-Based Membranes: Thin films or coatings formulated from CS and other materials, CS-based membranes exhibit selective permeability, ion exchange capabilities, and robust mechanical strength (Shan et al., 2020). These membranes are pivotal components in membrane separation processes employed for water purification, including reverse osmosis and ultrafiltration (Mukhopadhyay et al., 2019). (5) CS-Based Composites: CS readily combines with various materials, including clay minerals, activated carbon, or graphene oxide, to fabricate composite materials featuring enhanced adsorption capacities for environmental pollutants (Ayub & Raza, 2021).

These exemplify only a subset of the diverse array of CS derivatives applied in environmental contexts. With its adaptability and unique attributes, CS stands as an invaluable material for addressing multifarious environmental challenges, ranging from combatting water and soil pollution to advancing sustainable agriculture and green chemistry solutions (H. Chen et al., 2018).

CS and CS-Based Composites for Cd and As Removal

An optimal adsorbent for HM ion removal must possess a set of crucial characteristics, including a large surface area, high adsorption capacity, appropriate pore dimensions and volume, mechanical stability, compatibility, accessibility, ease of regeneration, cost-effectiveness, environmental friendliness, straightforward processing procedures, and a high degree of selectivity (Jayakumar et al., 2010). It is essential to note that despite the substantial body of research dedicated to the use of CS and CS-based composites in various environmental remediation applications, there is a significant gap in the literature concerning their specific application for the removal of co-contaminants, Cd and As, from soil. No published information on using CS-based materials to address this environmental challenge is available. However, to provide context, previous studies have explored the fabrication and characterization of CS-based adsorbents for a wide range of applications.

The adsorption mechanism of CS-based adsorbents for Cd removal primarily relies on physical adsorption, complexation, electrostatic attraction, chelation, and ion exchange (Mola Ali Abasiyan et al., 2019). Several studies have reported the successful application of CS-based adsorbents for Cd removal from contaminated soil (Omer et al., 2022). For instance, CS-modified biochar has been employed to remove Cd from soil, exhibiting an impressive adsorption capacity of up to 11.85 mg g⁻¹ (X. He et al., 2022). CS-graphene oxide composites have also demonstrated high Cd removal efficiency from soil (Pal et al., 2021). Other studies have explored the use of

CS-based adsorbents such as sodium tripolyphosphate cross-linked CS beads (STPP-CLCS) and surfactant-modified CS beads (SMCB) for Cd(II) adsorption (Babakhani & Sartaj, 2020; Pal & Pal, 2019). While various advanced adsorbents have been employed to remove As from polluted soil, biopolymers like CS have attracted significant attention (Hwang et al., 2019). CS-based composites have been physically and chemically modified to enhance their As adsorption capacity and selectivity from soil and other environmental sources. Techniques such as cross-linking, gel formation, and microsphere development have improved the stability, mechanical strength, and reusability of CS (Ayub et al., 2020). Additionally, incorporating metals like iron or molybdenum into CS microspheres has proven to increase the adsorption capacity of CS-based materials (Singh et al., 2022). Notable examples include the use of iron-chitosan granules (ICSB) and iron-chitosan flakes (ICSF) for As removal from water and soil (Singh et al., 2022). Graphene oxide (GO)-modified CS has demonstrated exceptional efficiency in the adsorptive removal of As(III) (Shan et al., 2020). Studies have also explored the application of CS-based magnetic graphene oxide (CS/MGO) composites for As(III) removal (Sherlala et al., 2019). Despite these significant contributions, the lack of scientific literature addressing the potential of CS and CS-based composites in mitigating Cd and As co-contamination in soil underscores a critical research gap. This knowledge gap underlines the necessity of future research efforts aimed at unraveling the promising potential and efficacy of chitosan-derived materials in addressing this specific form of environmental pollution.

Understanding Adsorption Mechanisms of CS-Based Adsorbents

An essential aspect in the study of HM ion removal using different adsorbents is the elucidation of the adsorption mechanisms involved. However, it is noteworthy that deciphering these mechanisms, particularly when employing magnetic chitosan composites (MCS), is a complex and intricate undertaking. While researchers in this field have made considerable efforts, identifying the precise adsorption mechanisms of HM ions by MCS remains challenging. In general, the predominant mechanisms by which HM ions are adsorbed onto the surface of MCS involve a range of interactions, including electrostatic attraction, chemical bonding (e.g., complexation and chelation), ion exchange, and Van der Waals forces. The functional groups of CS and its derivatives play a pivotal role in forming coordination complexes with HM ions (Shin et al., 2023). The formation of surface complexes assists in immobilizing HM ions onto the CS surface. Moreover, CS possesses protonated amino groups that can undergo ion exchange reactions with metal ions (C. Yan et al., 2022). In this process, Cd and As ions can replace protons on the amino groups, resulting in the adsorption of the metal ions onto CS (Mukhopadhyay et al., 2019). This ion exchange

phenomenon significantly contributes to removing HM ions from the solution.

CS can also induce the precipitation of HM ions as metal hydroxides or metal sulfides (Pal et al., 2021). In alkaline conditions, Cd and As ions may react with hydroxyl ions from CS or the surrounding environment to form insoluble precipitates. These precipitates can then be separated from the solution, effectively removing the HM ions (Lee et al., 2020). In acidic and neutral pH conditions, CS and CS-based composites carry a positive charge due to the protonation of amino groups (Mola Ali Abasiyan et al., 2019). It is essential to consider that the specific mechanisms governing Cd and As adsorption may vary depending on factors such as pH, metal concentration, CS properties, and the presence of other ions in the solution (X. He et al., 2022). Furthermore, CS derivatives can exhibit distinct adsorption behaviors due to variations in their chemical structures and functional groups (Ali et al., 2022). The adsorption of Cd and As, which are oppositely charged ions, raises questions about how these elements' synergistic immobilization occurs. To date, comprehensive research addressing this specific interaction between Cd and As ions in the presence of CS-based materials is limited.

The comprehension of these underlying mechanisms is paramount for optimizing the adsorption process and developing efficient CS-based adsorbents for heavy metal remediation. Experimental evidence and theoretical models have been employed to provide insights into these mechanisms. Experimental studies often involve adsorption isotherm experiments, which assess equilibrium concentrations of adsorbates in solution at various initial concentrations. These data fit different models, such as Langmuir or Freundlich isotherms, to determine the adsorption mechanism and associated parameters. Additionally, kinetic studies help elucidate the adsorption rate and mechanism, employing various kinetic models such as pseudo-first-order or pseudo second-order kinetics. Analytical techniques such as FTIR and XRD provide structural information about CS and its interactions with adsorbates, revealing changes in functional groups and crystalline structure. Surface complexation models (SCMs) offer theoretical frameworks for explaining CS-based adsorption behavior by considering the formation of surface complexes between CS and adsorbates, accounting for interactions like electrostatic forces, hydrogen bonding, and coordination chemistry. Molecular dynamics (MD) simulations have emerged as a valuable tool to gain molecular-level insights into CS adsorption mechanisms by modeling the CS structure and simulating adsorption processes in a virtual environment. It is crucial to recognize that the specific adsorption mechanisms of CS can vary depending on the nature of the adsorbate and experimental conditions. Therefore, achieving a comprehensive understanding of CS-based adsorption mechanisms often necessitates combining experimental evidence and tailored theoretical models to suit the specific system under investigation.

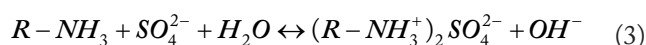
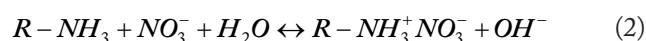
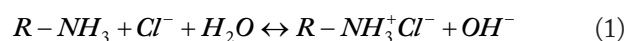
Factors Affecting Adsorption

Several factors exert influence on the efficiency of CS-based adsorbents in HM ion removal. These factors encompass various aspects of the CS adsorption process, including: pH, initial metal concentration, temperature, contact time, CS properties, competitive ions, physical characteristics, and pretreatment techniques. (Singh et al., 2022). The pH of the solution plays a crucial role in CS adsorption efficiency. CS is amphoteric in nature, meaning its charge varies with pH. At low pH values, CS is protonated, resulting in a positive charge, while at high pH values, it is deprotonated and carries a negative charge. Generally, CS-based adsorbents exhibit higher efficiency in acidic conditions due to the attraction between positively charged amino groups on CS and negatively charged adsorbates (Babakhani and Sartaj, 2020). The initial concentration of the adsorbate in the solution influences the adsorption efficiency.

Higher concentrations provide a greater driving force for adsorption, increasing adsorption capacity (Xu et al., 2013). However, the adsorption may reach a saturation point at very high concentrations, leading to decreased efficiency. Temperature impacts adsorption kinetics and thermodynamics (Xie et al., 2019). Generally, an increase in temperature accelerates the adsorption process due to enhanced molecular movement and diffusion (Muzzarelli, 2011). However, the effect of temperature on adsorption efficiency can vary depending on the specific adsorbent and adsorbate system. The duration of contact between the CS-based adsorbent and the adsorbate affects the adsorption efficiency. Longer contact times allow more interactions between the adsorbent surface and the adsorbate, leading to increased adsorption (Bhatnagar et al., 2009). However, additional contact time may not significantly enhance the adsorption efficiency once equilibrium is reached. In addition, the properties of CS, such as its molecular weight, degree of deacetylation, and surface charge, significantly affect its adsorption efficiency (An et al., 2009). Higher molecular weight CS tends to have a larger surface area and more binding sites, leading to enhanced adsorption capacity (Y. W. Chen et al., 2011). Additionally, a higher degree of deacetylation results in increased amino groups available for adsorption interactions (Yong et al., 2013, Han et al., 2021). The presence of competing ions in the solution significantly influences the efficiency of CS-based adsorbents in HM ion removal (Zhou et al., 2009). These competing ions may have a higher affinity for the adsorbent surface or may form complexes that hinder the adsorption of the target adsorbate. These competing ions can affect adsorption by vying for binding sites on the CS-based adsorbent, ultimately impacting removal efficiency.

Recent studies have shed light on the effects of co-existing ions, including Cl^- , SO_4^{2-} , NO_3^- , and PO_4^{3-} , and other metal cations, on the adsorption of HM ions onto CS-based

materials. For instance, Mishra et al. (2011) investigated the influence of NaCl and Na_2SO_4 on the adsorption of Cd(II) by Ch-g-CD at pH 8.5. Their findings revealed that the presence of NaCl and Na_2SO_4 in concentrations ranging from 0.01 to 1.0M led to a significant reduction in the removal of Cd. Specifically, the removal efficiency decreased from 36.91 to 18.34 mg g^{-1} and from 34.26 to 14.88 mg g^{-1} with increasing concentrations of NaCl and Na_2SO_4 , respectively. Similarly, Saha and Sarkar (2012) explored the impact of Cl^- , SO_4^{2-} , NO_3^- , and PO_4^{3-} ions on As(V) adsorption using CTS-g-PA. Their study indicated that the presence of Cl^- or NO_3^- ions had a relatively minimal effect on the removal efficiency of arsenate, while the presence of SO_4^{2-} or PO_4^{3-} ions led to a decrease in removal efficiency. The competitive adsorption mechanisms between co-existing anions and protonated amine groups of CS can be elucidated through the following equations:



These reactions illustrate the competition between co-existing anions and the amino groups of CS for adsorption sites. The outcomes of such competitive interactions can vary depending on factors such as the specific co-existing ions, their concentrations, and the pH of the solution.

The physical characteristics of CS-based adsorbents, such as particle size and surface area, influence the adsorption efficiency (Pal et al., 2021). Smaller particle sizes and larger surface areas provide more active sites for adsorption, leading to increased efficiency (Hwang et al., 2019). Pretreatment techniques, such as cross-linking, chemical modification, or functionalization of CS, can enhance adsorption efficiency by improving surface properties, stability, and selectivity toward specific adsorbates (Gao et al., 2021). It is important to note that the influence of these factors on the adsorption efficiency of CS-based adsorbents can vary depending on the specific adsorbent formulation, adsorbate characteristics, and experimental conditions (S.-J. Wu et al., 2013). Therefore, optimizing these parameters for each specific application is essential to achieve the desired adsorption performance.

Numerous studies have explored the optimization of key parameters to maximize CS-based adsorption efficiency for specific applications. In a study focused on copper(II) ion removal, optimal conditions included a pH of 5.5, temperature of 45°C, initial metal concentration of 50 mg L^{-1} , contact time of 60 minutes, and an adsorbent dosage of 2 g L^{-1} . For nickel removal, optimal conditions involved a pH of 6.5, temperature of 40°C, initial metal concentration of 100 mg L^{-1} , contact time

of 120 minutes, and an adsorbent dosage of 1 g L^{-1} . In the removal of Pb(II) ions, optimal conditions comprised a pH of 5.5, temperature of 45°C , initial metal concentration of 50 mg L^{-1} , contact time of 60 minutes, and an adsorbent dosage of 1 g L^{-1} . These studies underscore the importance of fine-tuning pH, temperature, initial metal concentration, contact time, and adsorbent dosage to achieve maximum adsorption efficiency using CS-based adsorbents, albeit recognizing the variability inherent in different systems and conditions.

Comparison With Other Adsorbents

Various adsorbents are commonly used for their removal, including CS-based adsorbents. A comparative analysis of CS-based adsorbents with other widely used adsorbents for Cd and As removal is as follows: Activated carbon (AC) is widely used for water purification due to its high adsorption capacity and versatility. It exhibits excellent adsorption performance for both Cd and As. However, AC is relatively expensive compared to CS-based adsorbents (Cao et al., 2019). Additionally, AC can be easily saturated and requires frequent regeneration or replacement. Iron-based adsorbents, such as iron oxide and iron hydroxide, have been extensively studied for Cd and As removal (Ali et al., 2022). These materials offer high affinity towards Cd and As ions and effectively adsorb them from water. However, iron-based adsorbents may require pH adjustment and coagulation for optimal performance, and they can produce sludge that needs proper disposal (Liu et al., 2022). Zeolites are crystalline aluminosilicates with a porous structure (Lin et al., 2021). Zeolites have good stability and a large surface area, which enhances their adsorption capacity. However, zeolites may suffer lower selectivity and affinity toward Cd and As than CS-based adsorbents (Lu et al., 2021). Chelating resins, such as ion-exchange resins functionalized with specific ligands, are commonly used for metal removal (Lee et al., 2020). These resins exhibit high selectivity for Cd and As and can be tailored to target specific metals. However, chelating resins can be expensive, and their regeneration process might require the use of harsh chemicals (Shin et al., 2023). CS-based adsorbents offer several advantages for Cd and As removal (Sajid, 2022). They have a high affinity for these metals, excellent adsorption capacity, and good selectivity. CS is also readily available, cost-effective, and environmentally friendly (Omer et al., 2022). CS-based adsorbents can be modified with functional groups to further enhance their adsorption properties (Liu et al., 2022). However, CS-based adsorbents may have limitations, such as low mechanical strength and potential pH dependence (Van Tran et al., 2018). They may also exhibit slower kinetics compared to other adsorbents (Singh et al., 2022). Nevertheless, these limitations can be addressed through various strategies, including cross-linking, blending with other materials, or employing advanced CS-based composites (Ayub & Raza, 2021). Beside

adsorbents such as activated carbon, iron-based adsorbents, zeolites, and chelating resins demonstrate good adsorption performance, CS-based adsorbents stand out for their favorable properties and suitability for treatment applications (Muxika et al., 2017).

Pros and Cons of CS and CS-Based Composites

Chitosan and CS-based composites offer several advantages and disadvantages regarding adsorption capacity, selectivity, regeneration potential, and cost-effectiveness. However, their effectiveness can vary depending on the targeted contaminants and the regeneration needs. Each of these aspects are given in (Table 4). Considerations should be made based on the specific application requirements to fully evaluate the suitability of CS and CS-based composites (Table 4).

Applications and Challenges

CS and CS-based materials, such as CS-modified zeolites, CS beads, CS powder, and CS-coated sand, have demonstrated efficacy in removing HMs from soil and water (Issahaku et al., 2023). Incorporating CS into contaminated soil can enhance binding, reduce mobility, and transform contaminants into less toxic forms, mitigating their environmental impact. Phytoremediation, an eco-friendly approach using hyperaccumulator plants, benefits from CS by promoting plant growth and facilitating Cd and As uptake (S. Kumar et al., 2021). CS-based amendments also improve soil fertility and nutrient uptake. Soil washing, a technique for removing contaminants from soil, can leverage CS as a chelating agent for Cd and As co-contaminated soils (V. Kumar et al., 2017). CS forms complexes with metal contaminants, aiding in their solubilization and removal.

Further research and field studies are needed to optimize application techniques, assess long-term efficacy, and evaluate environmental impacts. However, CS-based adsorbents face limitations and challenges. Their relatively low adsorption capacity for specific contaminants can be addressed through chemical modifications, functionalization, or nanoparticle incorporation (Aragaw et al., 2021). Enhancing surface area can also improve adsorption efficiency. CS-based adsorbents may lack selectivity, adsorbing both target pollutants and other substances. Modifying CS surface properties or introducing functional groups can enhance selectivity (Al-Jubouri & Holmes, 2020). Research should focus on effective methods for regenerating spent adsorbents without sacrificing adsorption capacity. Techniques like desorption using solvents, pH adjustment, and other strategies must be explored (Sajid, 2022).

Scaling up production of CS-based adsorbents can be hindered by high costs and limited availability. Investigating alternative CS sources, such as waste streams, can reduce production costs (Gao et al., 2021). Developing cost-effective synthesis methods and improving manufacturing processes are essential

Table 4. Advantage and Disadvantages of CS-Based Technologies.

PROPERTIES	ADVANTAGES	DISADVANTAGES
1. Adsorption capacity	CS-based adsorbents possess a high adsorption capacity due to amino and hydroxyl groups on CS facilitating effective adsorption of various contaminants, including heavy metals, dyes, and organic compounds.	CS-based adsorbents may have limited adsorption capacity compared to some other materials, depending on factors like CS molecular weight, degree of deacetylation, and contaminant nature.
2. Selectivity	CS-based adsorbents exhibit selectivity toward certain contaminants, making them suitable for specific applications. The functional groups on CS can form complexation or coordination interactions with targeted contaminants, enhancing selectivity. This makes CS-based adsorbents useful in treating wastewater or purifying drinking water.	The selectivity of CS-based adsorbents can sometimes be a disadvantage. While they may have a high affinity for specific contaminants, they may not be as effective for removing a broad range of pollutants. The selectivity of CS can limit its versatility in treating complex mixtures of contaminants.
3. Regeneration potential	CS-based adsorbents can be regenerated and reused, which is advantageous from an environmental and economic perspective. After adsorption, the contaminants can be desorbed from the adsorbent using appropriate desorption agents or techniques. CS reversible adsorption properties allow for multiple cycles of adsorption and regeneration.	The regeneration potential of CS-based adsorbents may vary depending on the adsorbent formulation and the nature of the contaminants. Some contaminants may strongly bind to CS, making their desorption challenging and reducing the effectiveness of regeneration. In such cases, additional treatment steps or harsh desorption conditions may be needed, impacting the adsorbent's longevity.
4. Cost-effectiveness	CS is derived from chitin, a naturally abundant biopolymer found in the exoskeletons of crustaceans such as shrimp and crab. The availability and low-cost nature of chitin make CS-based adsorbents relatively cost-effective compared to some synthetic adsorbents. This is particularly advantageous in large-scale applications.	Despite being cost-effective, the overall cost of CS-based adsorbents can be influenced by factors such as the degree of deacetylation, purification processes, and the need for regeneration. Additionally, their cost may increase if CS-based adsorbents require customization or functionalization for specific applications.

for large-scale implementation. Stability and durability require attention involving the exploration of composite materials, coatings, or encapsulation techniques (Issahaku et al., 2023). Real-world performance should be assessed through field trials and case studies in diverse environmental conditions to uncover practical challenges and limitations of CS-based adsorbents.

Conclusion and Future Perspectives

CS-based adsorbents offer significant promise for effectively addressing soil HM contamination. Their suitability arises from several advantageous characteristics. Firstly, CS-based adsorbents demonstrate a remarkable affinity for HM ions, such as Cd and As, achieved through chelation, ion exchange, and electrostatic interactions. This robust binding capacity ensures the efficient removal of these toxic elements from soil. Secondly, their substantial surface area and porous structure amplify adsorption capabilities, with functional groups on the CS surface providing numerous active sites for HM adsorption. Moreover, their natural origin minimizes ecological impact, with nonhazardous degradation products a critical consideration for soil remediation. The versatility of CS allows for the development of various modified forms and composite materials, further enhancing adsorption efficiency through methods like chemical treatments, cross-linking, blending with other materials, or nanoparticle incorporation. Additionally, CS-based adsorbents are easily synthesized and cost-effective

compared to alternatives, making them economically viable for large-scale soil remediation projects.

Future research endeavors have the potential to yield CS-based adsorbents with significantly enhanced adsorption capacities, thereby bolstering their efficacy in pollutant removal. The customization of CS surface properties to amplify its affinity for specific contaminants while mitigating interference from coexisting substances becomes paramount. Achieving selectivity proves indispensable for precise and efficient pollutant removal, especially within intricate matrices such as contaminated soil. The challenges associated with regeneration and reusability necessitate the development of effective methods that can restore adsorption capacity and stability post-pollutant binding. Exploring innovative techniques, including desorption utilizing alternative solvents or stimuli-responsive systems, offers a promising avenue to overcome these challenges. Simultaneously, addressing scalability and ensuring cost-effectiveness becomes pivotal for the widespread application of CS-based adsorbents, particularly in large-scale scenarios. Optimizing synthesis methods, spanning the choice of raw materials, reaction conditions, and manufacturing processes, holds the potential to deliver efficient and economically viable production methods. This comprehensive approach to research aims to enhance the environmental sustainability, ecological equilibrium, and economic feasibility of CS-based adsorbents across diverse applications and expansive geographical areas.

In conclusion, CS and its derivatives hold significant potential as promising adsorbents for the removal of Cd and As from soil. Their robust adsorption capacity, extensive surface area, porous structure, environmental friendliness, and adaptability render them promising candidates for sustainable soil remediation. Further research and optimization of CS-based adsorbents are essential to enhance their efficiency and practical applicability across various fields. By addressing adsorption capacity, selectivity, regeneration, scale-up, and biocompatibility challenges, researchers can unlock the full potential of CS-based adsorbents, thereby facilitating more effective and sustainable solutions for environmental remediation, health-care, and industrial processes.

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