Recent Advancements in Chitosan-based Adsorbents for Hexavalent Chromium Removal from Aqueous Media

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1 Graphical Abstract

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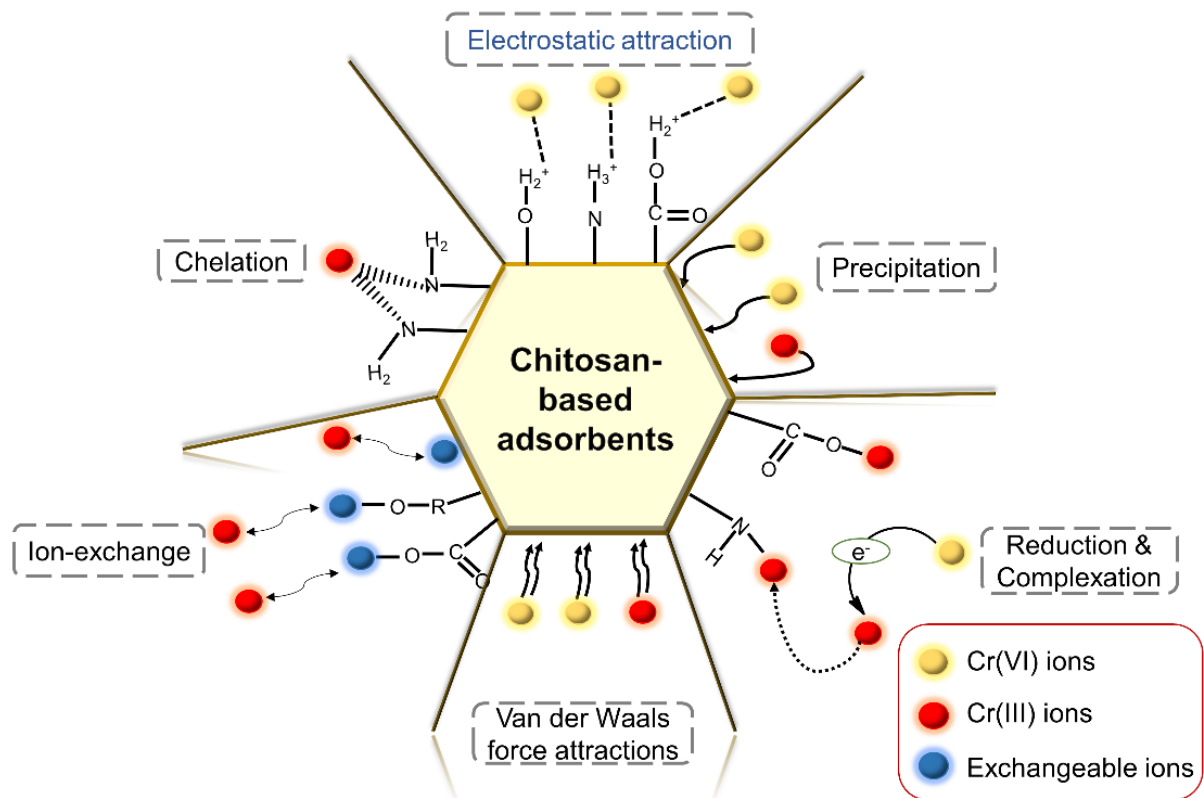
Abstract

Contamination of aqueous environments by Cr(VI) has become a matter of concern owing to its detrimental impacts on human health with its long-term exposure. Thus, effective treatment of adulterated aqueous media is critical in terms of the health and safety of humans together with flora and fauna. Currently, chitosan is considered an excellent adsorptive material for the remediation of Cr(VI) contamination owing primarily to its biodegradability, non-toxicity, abundance, and ability to modify its microstructure. The present review focuses on the up-to-date progression of chitosan-based sorbents that can be utilized in the mitigation of Cr(VI) oxyanions from aqueous media. This paper provides an overview of pristine chitosan along with recent advancements and insights into structurally and chemically modified chitosan. Chitosan has been chemically modified through cross-linking, grafting, and/or combination with other adsorptive materials to enhance its performance in Cr(VI) removal. Structurally modified chitosan-based hybrid materials that are commonly used in Cr(VI) removal include magnetic adsorbents, hydrogels, aerogels, and nano/microparticles. The sorption capacities of chitosan-based hybrid materials have varied from 27.25 - 357.14 mg g^{-1} depending on the type of adsorbent, dosage, initial Cr(VI) concentration, pH, and type of modification. Also, beneficial information through a compare-and-contrast of the effectiveness of the stated sorbent materials and their variants in the mitigation of Cr(VI) is provided. Furthermore, mechanisms of Cr(VI) removal by chitosan-based sorbents accentuating the main governing mechanism, electrostatic interactions are described and discussed. Desorption and regeneration studies are presented to assess the reusability of the chitosan-based adsorptive materials utilized in the mitigation of Cr(VI) contamination. Desorption studies reveal that sorption of Cr(VI) onto most of the chitosan-based adsorbents are fairly reversible with desorbed percentages above 60% with the usage of an efficient stripping agent. Through the literature survey of approximately 100 recently published papers, it could be evinced that chitosan-based adsorbents have proved to be an outstanding sorbent even if some challenges remain.

Keywords: Adsorption, chitosan, Cr(VI), hybrid materials, mechanism

1.0 Introduction

The degradation of the quality of water resources has become a significant source of concern for humankind for the last few decades. Recently, urbanization, population explosion, extensive agricultural activities, and industrialization have severely affected the quality of water resources (Ali et al., 2018, Basheer, 2018). Water resources are contaminated by numerous chemical pollutants including pharmaceuticals, heavy metals, persistent organic pollutants, dyes, and pesticides (Abdulrasool et al., 2021). Among the aforementioned pollutants, heavy metals gain prominence due to their high toxicity, bioaccumulation, and non-degradable properties (Hassaan et al., 2016, Wang et al., 2019a). Heavy metals, mainly Hg, Cd, As, Pb, and Cr, adversely affect the environment and human health when disposed into natural waters (Hsu et al., 2010). Amidst the heavy metals, chromium (Cr) draws special attention as a top-priority toxic metal (Duan et al., 2017). Primarily, Cr is available in the trivalent Cr(III) and hexavalent Cr(VI) forms. The carcinogenic and mutagenic properties of Cr(VI) cause more harmful effects on human health than its Cr(III) (Basha et al., 2008). The reason for that is that Cr(III) is less mobile than Cr(VI) (Zhang et al., 2018). Moreover, Cr(III) is considered a trace nutrient required for the human body for proper functioning. Because of the extreme toxicity of Cr(VI) to human health, the WHO mandates that the maximum levels present in drinking water should be less than 0.05 ppm (Nowruzi et al., 2020a). Speciation studies of Cr(VI) report its existence mainly in five ionic species, viz., H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, $HCr_2O_7^-$, and $Cr_2O_7^{2-}$ under various pH conditions. Cr(III) exists in at least five species depending on the pH values as Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$, and $Cr(OH)_4^-$ (Rakhunde et al., 2012, Kotaś and Stasicka, 2000).

Generally, Cr(VI) has an anthropogenic origin and infrequently occurs naturally (Pehlivan and Cetin, 2009). Primarily, Cr(VI) originated from the industrial sector. Some of the prominent sources of Cr(VI) pollution are textile, leather tanneries, electroplating, metal polishing, and the paint industry (Zhang et al., 2016, Preethi et al., 2019, Sankararamakrishnan et al., 2006). Natural occurrence of Cr(VI) in groundwater was detected in several parts of Greece with Cr concentration varying from 0.002- 0.1 ppm (Kaprara et al., 2015). A study revealed that the concentration of Cr(VI) before and after treatment (0.18 ± 0.01 and 0.08 ± 0.002 ppm) of the discharged tannery effluent in Bahi Dar Tannery, Ethiopia has exceeded the WHO permissible limits (Zewdu et al., 2018). The Cr(VI) concentration in the Buriganga River in Bangladesh varied from 0.01 to 3.54 ppm revealing high levels of contamination (Rahman et al., 2020). Hospital wastewater generated in Sri Lanka has been analyzed for Cr(VI) and it has varied around 0.01- 0.225 ppm exceeding the maximum tolerance limit (Kumarathilaka et al., 2015).

Owing to the high mobility and solubility of Cr(VI), it may cause liver dysfunction, diarrhoea, haemolysis, skin and mucous membrane irritant, and eczema apart from its carcinogenicity and mutagenicity (Pandey and Mishra, 2011, Kerur et al., 2021). Therefore, it is mandatory to treat the Cr(VI) contaminated effluents before being discharged into the environment mainly due to their toxicity and also to comply with the environmental regulations.

A wide variety of effluent treatment methods are employed for the elimination of hazardous heavy metals; reverse osmosis, flocculation/coagulation, bioremediation, membrane filtration, electrodialysis, photocatalysis, flotation, adsorption, chemical precipitation, and ion exchange (Ren

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et al., 2017). Amongst the above-stated techniques, at present, the adsorption technique has gained greater significance, mainly due to its simplicity, cost-effectiveness, the possibility of using a diversified variety of raw materials, eco-friendliness, and the possibility of regeneration of adsorbents (Zuo et al., 2021). The limitations of the adsorption technique are the dependence of the performance on the type of adsorbent, weak specificity, and low sorption capacity (Crini and Lichtfouse, 2019). The type of the adsorbent and its nature affect the efficiency of heavy metal adsorption from wastewater (Vakili et al., 2019a). Currently, the usage of a variety of sorbents in the remediation of toxic metal pollution, including Cr(VI), has been reported. In comparison with many adsorbents, chitosan has been considered an outstanding candidate for the mitigation of Cr(VI) from effluents (Habiba et al., 2017, Karthik and Meenakshi, 2014, Zhang et al., 2016). As a result of the advantageous properties of chitosan, which include low cost, easy availability, non-toxicity, macromolecular structure, specificity, biodegradability, biocompatibility, versatility, presence of numerous adsorption sites, and excellent adsorption capacity have caused comprehensive studies in the field of effluents (Vakili et al., 2014a). Amino (-NH$_2$) and hydroxyl (-OH) functionalities in chitosan provide strong binding sites for various heavy metals including Cr(VI) (Baroni et al., 2008). Properties of chitosan such as hydrophilicity, stability in acidic media, mechanical resistance, and many more can be further enhanced by performing modifications (Vakili et al., 2018).

In the last few decades, the focus of researchers has inclined more toward the modification of chitosan to enhance the Cr(VI) contaminant removal (Yu et al., 2013). Recently, the trend has shifted toward the production of chitosan-based hybrid adsorptive materials through approaches like cross-linking, grafting, magnetic modifications, and many more (Yu et al., 2017, Yu et al., 2013). However, there is no record of an existing compilation of the recent developments of various types of modified-chitosan adsorptive materials for the Cr(VI) decontamination in aqueous media. Hence, a concise yet informative review is required to explore and comprehend the research findings on emerging types of chitosan-based adsorbents, and underlying mechanisms involved in Cr(VI) removal, desorption, and regeneration of the adsorbents. This review focuses on chitosan-based hybrid sorptive materials reported for the mitigation of Cr(VI) anions from the year 2003 to 2022. It is hoped that this paper will contribute to a deeper understanding of the following aspects: A highlight of chemical and structural modifications of chitosan-based adsorbents, a structured review on mechanisms of Cr(VI) uptake by chitosan-based adsorptive materials, a brief evaluation of desorption mechanisms of Cr(VI) from saturated adsorbents, and a summary of adsorbent regeneration methods that are being utilized.

2.0 Chitosan-based adsorbents

2.1 Pristine chitosan sorbent

Chitosan (poly-β-(1→4)-2-amino-2-deoxy-D-glucose) is a pseudo-natural bioactive polymer abundant in nature (Figure 1) (Zhang et al., 2019, Vakili et al., 2019b, Salih and Ghosh, 2017, Rinaudo, 2006). Chitosan which is available commercially is produced via partial alkaline N-deacetylation of chitin, the primary building unit of the crustaceans' exoskeleton including crabs and shrimps (Huang et al., 2018). The physicochemical characteristics of chitosan polymers are significantly affected by the degree of deacetylation, degree of polymerization, and molecular weight distribution (Schmuhl et al., 2004).
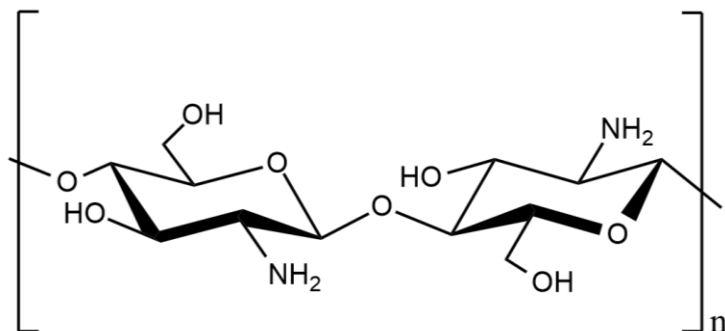
Figure 1: Structure of chitosan

Chitosan has been widely utilized as a sorbent for the remediation of toxic metal pollution as it has a high metal ion selectivity owing to the amino ($-NH_2$) and hydroxyl (-OH) functionalities in its structure that is capable of serving as chelating sites (Ismael et al., 2020, Feng-Chin Wu a, 2001). The amino groups present in chitosan can be increased by increasing the degree of deacetylation (Weska et al., 2007). These amino groups can form inter and intra H bonding which is responsible for the structural and physicochemical properties of chitosan. As a result, the polycationic character and solubility of chitosan are enhanced, broadening the applications of chitosan, particularly in Cr(VI) pollution remediation (Gupta, 2009). Hydroxyl groups in chitosan have resulted in high hydrophilicity which also aids in the remediation of anion-polluted water (Huang et al., 2018).

The zero-point charge of chitosan which is 6.3, is also significant in the sorption of Cr(VI) (Alvarenga, 2013). The uptake of the heavy metals including Cr(VI) on chitosan is highly pH-dependant. Hence, efforts have been made to assess the variation in the efficiency of sorption of Cr(VI) onto chitosan by altering the pH from 3 to 9 (P. Udaybhaskar, 1990). A study revealed that the uptake of Cr(VI) by chitosan is 90% at pH 3 given that the adsorbent dosage is 500 mg L^{-1} and the initial Cr(VI) concentration is 5 mg L^{-1}. Even though the removal would be more efficient below pH 3.0, it has been recorded that in particular conditions, a tendency of dissolution of chitosan could occur in low pH values as a result of strong electrostatic interactions between protonated amine functional groups (P. Udaybhaskar, 1990).

Despite the excellent Cr(VI) removal ability of chitosan, it has several limitations such as agglomeration tendency, low surface area, the tendency of dissolution in highly acidic media, swelling properties, and poor mechanical properties, restricting the usage of chitosan biosorbent in adsorption (Salih and Ghosh, 2017). In aqueous media, pristine chitosan shows a tendency for agglomeration and gel formation, making most of the hydroxyl and amino groups inaccessible for the binding of the Cr(VI) oxyanions (Nowruzi et al., 2020b). Moreover, the dissolution of chitosan in high acidic media is a consequence of the protonation of free amines present in its structure (Vakili et al., 2019b).

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2.2 Modified chitosan-based adsorbents

Many scientists have driven further advancements of novel chitosan-based adsorbents by supplying physical or chemical aid to enhance the intrinsic features of pristine chitosan leading to better removal of Cr(VI) (Salih and Ghosh, 2017, Chagas et al., 2019, Zhang et al., 2015). Recent advancements in Chitosan-based sorbents for the mitigation of Cr(VI) in water can be summarized under two main sections; structural and chemical modifications.
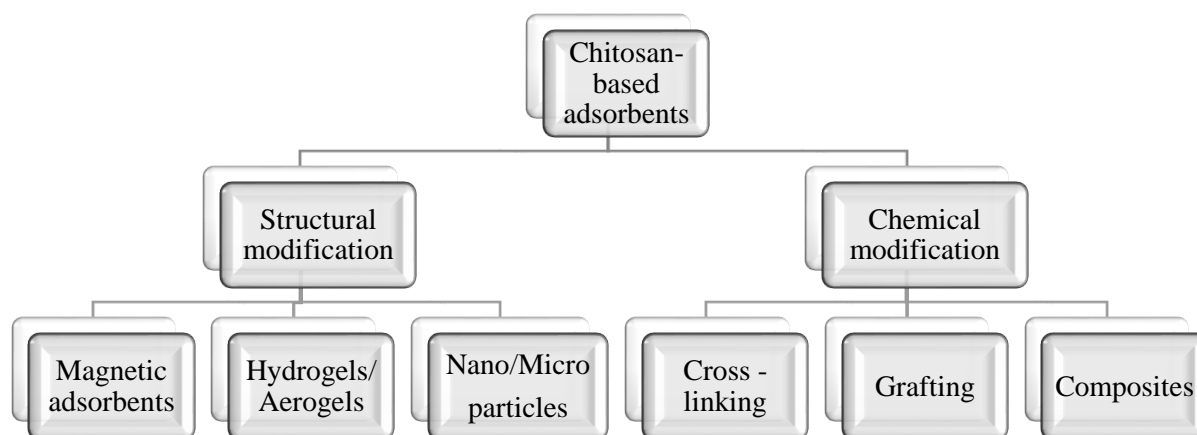
Figure 2: Modifications of chitosan sorbent

2.2.1 Structurally modified chitosan-based adsorbents

Magnetic adsorbents have the benefits of quick separation, comparatively low operational cost, and short treatment time (Xitong Sun, 2016). Most of the chitosan-based magnetic adsorbents when cross-linked or modified chemically have shown good reusability and enhanced Cr(VI) removal capacity (Zheng et al., 2019). As a result, magnetic nanocomposite adsorbents are among the most important nanocomposite sorbent materials. The blending of adsorption and magnetic properties, into a single composite permit for the creation of a magnetic adsorbent that could be used in Cr(VI) contaminant treatment (Tamjidi et al., 2019). Magnetic composites may be utilized in the sorption of contaminants, which can then be extracted from the medium with the aid of a magnetic separation technique that employs an external magnetic field (Tamjidi et al., 2019). Chitosan microspheres that encapsulated magnetic silica nanoparticles have shown a sorption capacity of 233.1 mg g^{-1} at pH 2.5 while poly (4-vinyl pyridine) decorated magnetic chitosan polymer has shown 344.83 mg g^{-1} (Xitong Sun, 2016, Zheng et al., 2019).

Hydrogels are cross-linked three-dimensional synthetic or natural polymers that are capable of adsorbing and retaining significant volumes of water (Wang et al., 2020). Hydrogels are considered hydrophilic gels that have a physically distinct three-dimensional structure and chemically reactive functional groups. Gels are capable of enhancing the diffusion mechanism and making the inner sites available for sorption. Because of their increased surface area, ease of fabrication, enhanced sorption capacity, recyclability, biodegradability, low cost, enhanced functionality, and solubility in organic solvents, hydrogels are a promising adsorbent material (Ozay et al., 2009). A cross-linker along with a monomer and an initiator is a necessary chemical

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for the hydrogel's synthesis (Darban et al., 2022). Cross-linkers, also known as cross-linking agents, stabilize the binding sites between the sorption target molecule and the functional monomer and thereby aid in the formation of a polymeric three-dimensional network (Darban et al., 2022). With cross-linking, hydrogels can be dissolved into a solution preventing swelling (Verma et al., 2017). The maximum adsorption capacity of chitosan-based hydrogel which is synthesized through the chemical cross-linking of N, N′- methylenebisacrylamide with radical chitosan, and polyacrylic acid is recorded as 93.03 mg metal g^{-1} dried hydrogel (Vilela et al., 2019). Aerogels are a type of porous gel material where the liquid portion is substituted with gas without shrinking its shape (Oves et al., 2021). The β-cyclodextrin/ chitosan/ hexamethylenetetramine aerogel beads that have been fabricated have shown increased mechanical properties and easy regeneration along with enhanced adsorption capacity (Wang et al., 2019b).

Chitosan micro/nanoparticles have also been employed in the decontamination of Cr(VI) polluted water. However, cross-linking has been necessary due to low acid stability (Dima et al., 2015). The high surface area to volume ratio and quantum size effects of nanoparticles have resulted in better adsorption capacity and kinetics. However, their agglomeration tendency and difficulty in separation after the adsorption process that has taken place have limited their usage. Magnetic nanoparticles may show a tendency of undergoing oxidation in air losing their magnetic properties (Huang et al., 2016). In a recent study, to overcome the aforementioned restrictions, Fe_3O_4@mesoporous-SiO_2@chitosan@polyaniline core−shell magnetic nanoparticles have been prepared and it has shown good Cr(VI) removal capacity along with excellent reusability (Zuo et al., 2021). Coating a magnetic core with SiO_2 protects it from acidic and oxidative conditions.

2.2.2 Chemically modified chitosan-based adsorbents

Recently numerous studies were performed to produce chemically modified chitosan-based adsorptive materials for the enhanced sorption of Cr(VI) through grafting, cross-linking, and combining with other sorbent materials. With the modifications, most of the chitosan-based adsorbents have proved to show enhanced performance in the mitigation of Cr(VI) oxyanions (Table 1).

Cross-linking

Major drawbacks of pristine chitosan which restricts its usage as a sorbent in Cr(VI) removal include poor stability in acidic media, sorbent swelling, and low mechanical strength (Jóźwiak et al., 2017). Chemical modifications are carried out to overcome those limitations of pristine chitosan. Cross-linking is a chemical modification method that is usually utilized in the fabrication of most chitosan-based adsorbents to improve the acid resistance, mechanical properties, prevention of swelling, pore size, and hydrophilicity of pristine chitosan (Vakili et al., 2018). Chitosan chains can be cross-linked with the aid of various chemicals to increase acid resistance (Vakili et al., 2018). Further, cross-linking lowers the crystallinity of chitosan-based adsorbents and it is preferred for Cr(VI) removal. The crystallinity of the sorbent influences the sorption capacity through the control of the diffusion properties and availability of inner functionalities. Cross-linking modification can disrupt the intra and inter hydrogen bonds formed in between the amino and hydroxyl functionalities in chitosan, leading to formation of disordered

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polymer chains and the sorbent becoming amorphous. As a result, inner functional groups are available for Cr(VI) uptake enhancing its adsorption capacity. The formation of bonds between chitosan chains via a reaction with a cross-linking agent is termed as cross-linking of chitosan (Jóźwiak et al., 2017). Cross-linkers have an essential role in the improvement of the Cr(VI) uptake efficacy of chitosan-modified adsorbents. However, the active functionalities of the adsorbent (i.e., hydroxyl and amino groups) that are available for the binding of the adsorbate, involve in cross-linking reactions which may decrease the accessible binding sites for the adsorbate. Hence, the cross-linking can result in lower uptake of Cr(VI) as well (Nishad et al., 2017). Therefore, cross-linking modification of chitosan is usually done in combination with some other chemical or structural modification method such as grafting, magnetic modification, and hydrogel formation to amplify the mitigation of Cr(VI) ions (Vakili et al., 2019b).

Choosing a desirable cross-linker and controlling the degree of cross-linking are crucial factors that should be considered in accordance with the sorbent used. The most used cross-linker in modifying chitosan-based sorbents which are used for the remediation of Cr(VI) contaminants is glutaraldehyde. Also, N, N' −methylene–bis-acrylamide, epoxy compounds, and epichlorohydrin have been used (Kyzas et al., 2013). Glutaraldehyde is a cross-linker that is widely used with chitosan-based adsorbents as it is cheap and has a low reaction time to produce chemically and thermally stable cross-links. The cross-linking reaction takes place between the amino groups of chitosan and aldehyde groups of glutaraldehyde to form a covalent imine bond through a Schiff reaction (Vanessa L. Gonçalves, 2005). Glutaraldehyde cross-linking has generally been followed by composite formation, grafting, or conjugation (Liu et al., 2015, Sankararamakrishnan et al., 2006, Singh et al., 2018). In N, N' −methylene–bis-acrylamide, the cross-linking reaction occurs between the amino group of chitosan and α, β-unsaturated ketone of N, N' −methylene–bis-acrylamide (Ismael et al., 2020). In contrast to most of the cross-linkers that react with the amino group of chitosan, epichlorohydrin links to the hydroxyl group of the chitosan. A carbon atom of epichlorohydrin reacts with the hydroxyl functionality of chitosan, causing the epoxide ring to rupture and the removal of a chlorine atom (Vanessa L. Gonçalves, 2005).

N, N' −methylene–bis-acrylamide has been recently used as a chitosan cross-linker in the presence of catalysts such as $FeCl_3.6H_2O$. The highest adsorption capacity obtained is recorded as 149.23 mg g^{-1} which is approximately four times that of pristine chitosan (Ismael et al., 2020). N, N' −methylene–bis-acrylamide has also been used in producing chitosan cross-linked poly(alginic acid) nano hydrogel adsorbent (Al-Muhtaseb and Sharma, 2016).

Epoxy compounds have also gained popularity due to their distinct properties, which differ from those of other cross-linkers in varied ways. In contrast to other cross-linkers like glutaraldehyde, epoxy compounds show the ability to interact with both hydroxyl and amine groups along with higher hydrophilicity and water solubility. Furthermore, epoxy groups have the ability to function as flexible joints in the cross-linking bridge owing to their oxygen arm while the carbon arm of the aldehyde groups in glutaraldehyde is rigid (Liu et al., 2022). Ethylene glycol diglycidyl ether and epichlorohydrin are two common cross-linkers with epoxy groups that have been previously reported; however, the low water solubility of both cross-linkers restricts their application (Vakili et al., 2018). Vakili et al., 2018 have used a diepoxy compound, 1,2:7,8-diepoxyoctane (DEO), as the cross-linker in producing cross-linked chitosan beads. Alkaline conditions cause the opening of epoxy rings, and cross-linkages are formed between the epoxy and amine/ hydroxyl groups of the chitosan bead structure (Vakili et al., 2018). Cross-linked chitosan-

DEO beads showed acid stability owing to the cross-linkages. They have found that the Chitosan-DEO beads have excellent sorption capacity, i.e., 325.5 mg g^{-1} at a pH of 2. It has also been recorded that at pH values above 5, the sorption of Cr(VI) anions was higher in unmodified chitosan beads than in the cross-linked chitosan (Vakili et al., 2018). As a result of cross-linkages between chitosan chains via bridging of DEO, it showed stability in deionized water, acetic acid solution (5% v/v), and 0.1M NaOH while chitosan beads were soluble in acetic acid solution. Enhanced acid stability is due to cross-linking of chitosan chains by bridging actions (Vakili et al., 2019b).

Sulphate has also been used as a chemical cross-linker to produce sulphate-cross linked chitosan for the mitigation of Cr(VI) contaminants. Pristine chitosan is soluble in most acids; however, it is insoluble in sulphuric acid and free amino groups are expected to react with sulphuric to produce corresponding salts. As sulphate is divalent, it forms inter-cross linkages between protonated amino groups of chitosan polymer chains. The maximum sorption capacity of sulphate cross-linked chitosan is reported as 156.85 mg g^{-1} in a comparatively short period of time (45 minutes) (Wang et al., 2019b).

Grafting

Sorption properties of chitosan towards Cr(VI) can be enhanced with the grafting of specific functionalities onto the chitosan skeletal structure. Owing to the numerous functional groups present in pristine chitosan chains, it is comparatively easy to graft new functional groups onto its skeleton (Thakur and Thakur, 2014).

Carboxyl groups have been grafted onto native chitosan. Alginic acid contains carboxylic acid groups with the capability of acting as an active binding site for heavy metals (Al-Muhtaseb and Sharma, 2016). Hydroxyl and amine groups of chitosan act as bases and provide active sites for the binding of alginic acid (Vakili et al., 2019b). Sulfur-containing groups are also grafted onto the chitosan backbone. Sankararamakrishnan et al., 2006 have increased the capacity of sorption of Cr(VI) onto a chitosan-based adsorbent modified through the grafting of a sulfur compound, the xanthate group. The newly formed chelating groups on the chitosan backbone cause an increase in the sorption properties (Sankararamakrishnan et al., 2006). Kyzas et al., 2013 evaluated the sorption capacity of the resultant product obtained by grafting poly(ethylene imine) chitosan powder followed by the cross-linking of epichlorohydrin. Due to the grafting, extra cationic groups (imino groups) have been added to the chitosan chain enhancing the Cr(VI) sorption capability of the adsorbent via even stronger electrostatic attractions (Kyzas et al., 2013).

Composites

Increased adsorption capacities of Cr(VI) removal have been achieved by combining chitosan with other materials such as clay minerals, carbonaceous materials, polymers, and inorganic materials. Furthermore, improved mechanical strength and chemical stability in low pH media was also achieved by the combination of chitosan with another material (Nowruzi et al., 2020b).

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A variety of clay minerals combined with chitosan have been used in several studies for the mitigation of Cr(VI) from aqueous media. Clay minerals have been a popular choice due to their ubiquitous nature, availability, inexpensiveness, and good mechanical and chemical stability (Singh et al., 2017, Kahraman, 2017, Yang et al., 2020). Most of the clay minerals are composed of a negatively charged surface which would result in the repulsion of Cr(VI) anions but combining it with chitosan causes charge reversal (Singh et al., 2017). Bentonite is a natural clay mineral that can be used conventionally in the mitigation of Cr(VI) due to its properties such as unique sandwich structure, availability, and mechanical and chemical stability (Feng et al., 2019). However, bentonite suffers from low adsorption and poor dispersion in water treatment (Yang et al., 2020). According to the literature, it can be deduced that combining chitosan with bentonite has not increased the adsorption capacity significantly even though it is higher than that of pristine chitosan or bentonite (Yang et al., 2020, Moussout et al., 2018). Literature records evince that the maximum adsorption capacity of a chitosan/bentonite composite at an optimum pH of 3 is 16.38 mg g^{-1} (Yang et al., 2020). Clay mineral, nontronite, has been used with chitosan and it has facilitated both sorption and reduction of Cr(VI). The amount of chitosan has been a significant parameter for the sorption and reduction processes (Singh et al., 2017). Rather than using clay minerals directly with chitosan, Organoclay (natural montmorillonite modified with quaternary ammonium salt) has also been used to enhance the uptake of Cr(VI) forming nanocomposites with chitosan. Maximum adsorption capacity has been recorded as 128.43 mg g^{-1} but it has other improved properties such as good regeneration ability and reusability (Kahraman, 2017).

Carbonaceous materials have been combined with chitosan for the decontamination of Cr(VI) and they have shown enhanced stability, mechanical strength, and specific area of the adsorbent. Carbonaceous materials combined with chitosan include carbon nanotubes, activated carbon, and graphene oxide. For instance, chitosan-modified multi-walled carbon nanotube composite has improved adsorption capacity in acidic media and the short time required for the efficient uptake of Cr(VI) oxyanions (Huang et al., 2018). Composites prepared using graphene oxide and chitosan have shown improved water solubility and dispersity. Conversely, due to the cationic nature of chitosan and the anionic nature of graphene sheets when dispersed in water, the available sites for Cr(VI) adsorption have been reduced. Hence, additional binding sites are usually grafted onto the adsorbent to enhance the elimination of Cr(VI) (Zhang et al., 2016, Ali, 2018). To increase the adsorption capacity, carbonaceous materials were combined with polymers along with chitosan. A polyvinyl alcohol/ chitosan/ activated carbon biocomposite has been prepared to remove Cr(VI) and its maximum adsorption capacity is recorded as 109.89 mg g^{-1} (Nowruzi et al., 2020b).

Polymer materials such as polypyrrole, polyaniline, and carboxymethylcellulose have also been used with chitosan in the mitigation of Cr(VI) (Yavuz et al., 2011). Carboxymethylcellulose is a natural polymer that favors sorption due to the presence of carboxyl and hydroxyl functionalities. However, both chitosan and carboxymethylcellulose show less stability and high hydrophilicity in acidic media. Thus, to overcome the aforementioned drawbacks, grafting, cross-linking, or combining with some other materials has been done. Chitosan combined with polypyrrole has shown enhanced adsorption of Cr(VI) and good reusability (Karthik and Meenakshi, 2014).

Inorganic materials such as metal oxides have been used with chitosan. Iron oxide has widely been used with chitosan for the mitigation of Cr(VI). Chitosan is capable of acting as a

dispersing and stabilizing agent enhancing the activity of iron oxides (Bauer and Knölker, 2015). γ- Fe_2O_3 magnetic nanoparticles and chitosan have also been used to prepare composites but with conducting polymers like polypyrrole to avoid self-agglomeration (Reis et al., 2021).

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Table 1: Comparison of adsorption capacities of several chitosan-based adsorbents in Cr(VI) removal

Adsorbent	Modification	Initial concentration (mg L^{-1})	Dosage (g L^{-1})	Optimum pH	Sorption capacity (mg g^{-1})	Ref
N, N'-methylene bis-acrylamide cross-linked chitosan	cross-linking	100	1	3	149	(Ismael et al., 2020)
Chitosan/organoclay bionanocomposites	composite	100	2	3	357.14	(Pandey and Mishra, 2011)
Chitosan/polyvinyl alcohol/activated carbon biocomposite	composite	60	0.8	2	109.89	(Nowruzi et al., 2020b)
Magnetic chitosan microspheres modified with 1,6-hexanediamine	magnetic adsorbent	10	0.1	3	208.33	(Yue et al., 2018)
Chitosan-1,2-cyclohexylenedinitrilotetraacetic acid – graphene oxide nanocomposite	cross-linking, combined with carbonaceous material, nanocomposite	25	2	3.5	166.98	(Ali, 2018)
Chitosan-iron oxide hybrid composite	combined with inorganic material	130	0.5	5	46.12	(Chagas et al., 2019)
Maghemite/chitosan/polypyrrole nanocomposites	combined with inorganic material, polymer	150	0.2	2	301.2	(Reis et al., 2021)
Bentonite/ cross-linked chitosan composite	cross-linking, combined with clay mineral	-	2	2	89.13	(Liu et al., 2015)
Titanium cross-linked chitosan composite	cross-linking, combining with metal ions	30	0.2	5	171	(Zhang et al., 2015)

Chitosan grafted graphene oxide nanocomposite	grafting, combining with inorganic material	50	2	2	104.16	(Samuel et al., 2019)
Chitosan nano-organoclay	combining with clay minerals	104	1.2	2	128.43	(Kahraman, 2017)
Cross-linked magnetic chitosan hydrogel film	cross-linking, magnetic hydrogel	15	1	4	27.25	(Mirabedini et al., 2016)

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3.0 Mechanisms of chromium removal

Researchers have considered the adsorption mechanism as a significant factor for the comprehensive understanding of the process of Cr(VI) removal onto different types of chitosan-modified adsorptive materials, and yet it has been a time-consuming and complicated task. Adsorption is a surface phenomenon that is a consequence of residual attractive forces of the adsorbent. The residual forces of the adsorbent's surface attract the adsorbate particles. Most of the research conducted on the uptake of Cr(VI) anions by chitosan-based sorbents has investigated the mechanisms of Cr(VI) removal and it has been discovered that in almost all the studies, Electrostatic interactions were the main governing mechanism. Additionally, Ion exchange, Chemical bonding (viz Chelation and Metal-ion complexation), Reduction, Vander Waals forces, and H bonding is also responsible for the Cr(VI) oxyanion uptake by chitosan-based adsorbents.

The pH is proven to be a crucial facet affecting the adsorption as it influences the speciation of Cr(VI) and surface properties of Chitosan-based adsorbents (Zhang et al., 2010). The Cr(VI) speciation is highly dependent on the pH of the media and its concentration (Pandey and Mishra, 2011). Cr(VI) is usually present as oxyanions in aqueous media: predominantly, $HCrO_4^-$ and $Cr_2O_7^{2-}$ are present at pH values between 0 and 6 approximately, while at pH value of about 4.5, CrO_4^{2-} emerges and reaches a maximum at a pH value of 8 or higher, and continue to remain at higher pH values (Kotaś and Stasicka, 2000, Ramsey et al., 2001, Rakhunde et al., 2012). In acidic pH values where $Cr_2O_7^{2-}$ and $HCrO_4^-$ are prominent, and the hydroxyl and amino functionalities of chitosan-based adsorptive materials are protonated and significantly incorporated with the adsorption of oppositely charged Cr(VI) oxyanions via electrostatic interactions (Eliodório et al., 2020b). The existence of a dual competition between OH^- and CrO_4^{2-} for binding sites, causes the weakening of the electrostatic interactions which may explain the lowering of the adsorption capacity at basic pH values (Zheng et al., 2019). The point of zero charge provides insight into the ability of the adsorbent to adsorb Cr(VI) anions. The pH at which the overall surface charge of the adsorptive material equals zero is termed the point of zero charge (pHpzc) (Nowruzi et al., 2020b). The pHpzc of unmodified chitosan is 6.3, and at about pH 4.3, 99% of the amino groups are protonated ($-NH_2^+$ or $-NH_3^+$) (Alvarenga, 2013). The adsorbent's charge becomes less positive as the pH rises. When the pH exceeds pHpzc, the surface becomes negatively charged, repelling anionic Cr species (Nowruzi et al., 2020b). With the lowering of the pH of the solution than the pHpzc, the surface of the adsorbent becomes positive, resulting in protonation of the amine functionalities on the chitosan backbone. As a consequence, the uptake of Cr(VI) ions occurs through electrostatic interactions (Pandey and Mishra, 2011). A recent study based on the uptake of Cr(VI) by trimethoxysilyl group terminated poly(1-vinylimidazole)-modified-chitosan composite, has recorded that the Cr(VI) uptake was pH dependant, indicating maximum removal at pH 3.5 and thereby increasing pH has resulted in lowering the removal efficiency (Islam et al., 2019). The amine and imidazole groups present on the composite are positively charged at low pH and above the optimum pH deprotonation of cationic groups was noted (Islam et al., 2019). In a recent work that studied the removal of anions of Cr(VI) by an adsorbent prepared by grafting poly(ethylene imine) onto chitosan powder, it was noted that the dominating mechanism of the sorption was electrostatic interactions, thus pH-dependent. Further, an increased number of cationic groups in the adsorbent was reported due to the grafting of extra cationic groups from poly(ethylene imine) onto chitosan, causing stronger adsorbate-adsorbent electrostatic interactions (Kyzas et al., 2013).

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In most of the Cr(VI) sorption processes of chitosan-based adsorbents, electrostatic interactions are often followed by complexation, reduction, or precipitation due to various modifications (Table 2). Research that was based on the uptake of Cr(VI) oxyanions onto chitosan engraved iron-lanthanum mixed oxyhydroxide material has suggested that the possible sorption mechanism is electrostatic attraction and chemical reduction. It suggests that heteroatoms may undergo complexation with Cr(VI) oxyanions, followed by the conversion of Cr(VI) ions to non-toxic Cr(III) form through reduction by acting as an electron donor (Preethi et al., 2019). Thus reduced Cr(III) ions will be released due to electronic repulsion between the Cr ion and the binding group. According to Dima et al., 2015, apart from electrostatic attraction and reduction, the amine groups act as active sites for the binding of Cr(III), forming complexes and triggering the precipitation of Cr(III) (Dima et al., 2015). According to research conducted by Pandey et al., 2011, on the sorption of Cr(VI) anions onto chitosan/clay nanocomposite, the mechanism is governed by electrostatic interactions, chemical reduction, and chelation. The hydroxyl and amino functionalities of chitosan are capable of involving in the chelation process of Cr(III). Some studies have recorded that the oxyanions of Cr(III) may adsorb onto chitosan-based adsorbents when hydroxyl and amino groups are protonated to $-NH_3^+$ and $-OH_2^+$ in acidic conditions through H bonding (Lili Ren, 2019, Rahim and Mas Haris, 2019). In a recent work by Sun et al., 2016, quaternary ammonium-modified magnetic silica nanoparticles encapsulated by chitosan microspheres were synthesized, and it has been recorded that uptake of Cr(VI) is mainly by ion exchange aside from electrostatic interactions due to the presence of quaternary ammonium salt ($R-N^+(CH_3)_3Cl^-$) (Xitong Sun, 2016).

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Table 2: Adsorbent- adsorbate interactions resulting in Cr(VI) removal

Adsorbent	Interactions	Functionalities	Influencing factors	Remarks	Ref
Chitosan/clay nanocomposite	Electrostatic attractions, Reduction, Chelation	amino, hydroxy, cloisite	pH, initial Cr(VI) concentration, adsorbent dosage, temperature	Endothermic process, therefore, adsorption increases with temperature.	(Pandey and Mishra, 2011)
Chitosan/polyvinyl alcohol/activated carbon composite	Electrostatic attractions	amino, hydroxyl, amides, carbonyl, carboxylic acid groups	pH, initial concentration, temperature, adsorbent dosage	With the increase in temperature, kinetic energy exceeds electrostatic attractions, reducing the Cr(VI) uptake	(Nowruzi et al., 2020b)
Chitosan/polypyrrole composite	Electrostatic attractions, Reduction	primary amine, hydroxyl, polypyrrole moieties	pH, initial concentration, adsorbent dosage		(Karthik and Meenakshi, 2014)
1,6-hexanediamine modified magnetic chitosan microspheres	Electrostatic attractions, Reduction	amine (NH/NH2) hydroxyl,	pH, initial concentration, temperature, adsorbent dosage	Cr(III) formed through reduction has been reabsorbed through supramolecular coordination.	(Yue et al., 2018)
Chitosan/ceramic alumina composite	Electrostatic attractions, H bonding, Vander Waals	amine, hydroxymethyl, carbonyl	pH, co-ion effect (such as sulfates, chlorides)	The effect of co-existing ions reduces efficiency due to anion competition for surface binding	(Boddu et al., 2003)
1,2:7,8-diepoxyoctane cross-link chitosan beads	Electrostatic attractions	primary amine, hydroxyl, amide, carboxyl group	pH, cross-linking temperature, contact time		(Vakili et al., 2018)
Cross-linked xanthated chitosan	Electrostatic attractions, Complexations		pH		(Sankararamakrishnan et al., 2006)

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Chitosan-1,2-cyclohexylenedinitrilotetraacetic acid – graphene oxide nanocomposite	Electrostatic attractions	amino, hydroxyl, carboxylic acid groups, epoxide functional groups	pH, the temperature of the adsorbate solution, adsorbent dosage		(Ali, 2018)
Staple microfibers based on chitosan	Electrostatic attractions, Reduction	primary amine, hydroxyl, amide	pH, temperature, adsorbent dosage		(Abdel-Mohsen et al., 2020)
Chitosan/ triethanolamine/Cu (II) composite	Electrostatic attractions, Physical interactions	amino, hydroxyl, acetyl, carbonyl	pH, temperature	High specific surface area resulting in physical adsorption	(Zhang et al., 2019)
Crosslinked chitosan– sericin conjugate	Electrostatic attractions, Reduction	hydroxyl, carbonyl, amide, amino	pH, co-ion effect, initial concentration		(Singh et al., 2018)
Diepoxyoctane -cross-linked chitosan beads	Electrostatic attractions	amino, hydroxyl	pH		(Vakili et al., 2019b)
Chitosan-based activated carbon	Electrostatic attractions	amino, hydroxyl, carbonyl	pH, adsorbent dosage		(Emamy et al., 2021)
Chitosan microspheres encapsulating magnetic silica nanoparticles	Ion exchange, Electrostatic attractions	quaternary ammonium groups, amino groups	pH	Adsorption was mainly due to quaternary ammonium groups (Ion exchange process)	(Xitong Sun, 2016)
Banana trunk fibers - reinforced chitosan bio composite film	Electrostatic attractions, Complexation (chelation)	amino, hydroxyl	pH, initial concentration, contact time		(Rahim and Mas Haris, 2019)
Chitosan-coated diatomaceous earth beads	Electrostatic attractions	hydroxyl, amine	pH, temperature, initial concentration, co-ion effect	Lower adsorption below pH 3 was explained by the formation of neutral H_2CrO_4 molecules.	(Salih and Ghosh, 2017)

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Chitosan engraved iron-lanthanum mixed oxyhydroxide material	Electrostatic attractions, Reduction	hydroxyl, amine	pH, contact time, co-ion effect		(Preethi et al., 2019)
Chitosan-based hydrogel	Electrostatic attractions	amide, hydroxyl, carbonyl	pH, initial concentration		(Vilela et al., 2019)
Cross-linked chitosan/bentonite composite	Electrostatic attractions	amino, hydroxyl	pH, contact time, initial concentration		(Liu et al., 2015)
Maghemite/chitosan/polypyrrole nanocomposites	Electrostatic attractions, Reduction, Chelation	amino, amide, carboxylic groups	pH, initial concentration, contact time	Polypyrrole chains acted as reducing agents	(Reis et al., 2021)
Chitosan-iron oxide hybrid composite	Electrostatic attractions, Reduction	amino	pH		(Chagas et al., 2019)
Reticulated micro/nanoparticles of chitosan	Electrostatic attractions, Reduction, Precipitation	amide, carbonyl, amine	pH, initial concentration	Cr(III) adsorbed through to amine groups, followed by its precipitation	(Dima et al., 2015)
β-cyclodextrin/ chitosan/hexamethylenetetramine aerogel beads	Electrostatic attractions, H bonding, Reduction, Complexation/Ion exchange	amino, hydroxyl	pH, co-ion effect, contact time		(Wang et al., 2019b)
Chitosan-based polymeric surfactants	Electrostatic attractions, Precipitation	amino, hydroxyl	pH, ionic strength, adsorbent dosage	Precipitation was noted at higher pH values than 5	(Lee et al., 2005)

4.0 Desorption and regeneration

The regeneration ability and reusability of the adsorptive material is a crucial element that is being considered when applying the adsorbent in Cr(VI) removal (Xitong Sun, 2016). It provides numerous information including economic competitiveness, reduction of secondary waste, and regeneration of the adsorbent. Nevertheless, utilization of most of the adsorbents in the heavy metal removal including Cr(VI) from aqueous media is severely limited by the low reusability of adsorbents (Wang et al., 2019b). Thus, analyzing the reusability of the adsorbent can be regarded as a significant consideration in research work. Desorption studies are vital to examine the reusability and regeneration of the adsorptive material along with the investigation of the recovery ability of adsorbed Cr(VI) (Yang et al., 2020).

The studies revealed that electrostatic interactions are the main governing mechanism in the sorption of Cr(VI) by chitosan-based adsorbents and it is heavily favored at a certain pH range over others. In contrast, it can be presumed that changing the pH will result in the desorption of Cr(VI) from chitosan adsorbents as well (Vakili et al., 2014b). Numerous reagents have been used to analyze the desorption process of Cr(VI) and regeneration of chitosan-based adsorbents, including NaOH, HCl, EDTA, and H_2SO_4 (Karthik and Meenakshi, 2014, Sankararamakrishnan et al., 2006, Dima et al., 2015). The most frequently used stripping agent is NaOH with various concentrations, as adsorption of Cr(VI) onto chitosan-based adsorbents is favored at acid pH, and desorption is tested by increasing the pH. Studies prove that a comparatively high regeneration capacity has been obtained in chitosan-modified adsorbents with the usage of an efficient stripping agent (Table 3). In a recent study, to evaluate the reusability of an aminated cross-linked chitosan bead, a 1.0 M NaOH solution was utilized (Vakili et al., 2019b). Cross-linked chitosan beads that have been aminated were successfully proven to be effective in three minimum sorption-desorption cycles without indicating a considerable reduction in adsorption capacity. But, in the last conducted adsorption-desorption cycle, adsorption capacity diminished to 192.3 mg g^{-1} (Vakili et al., 2019b). In research conducted by Sun et al., 2016, the sorption-desorption process of chitosan microspheres encapsulating magnetic silica nanoparticles was repeated for 10 cycles with a mixture of 0.3 M NaCl and 0.3 M NaOH as the stripping agent and the efficacy of desorption has been reported as 95.6% (Xitong Sun, 2016). To analyze the desorption of Cr(VI) from xanthated chitosan beads and flakes, distilled water, 0.01 M NaOH, 0.01 M EDTA, and 0.01 M HCl have been used (Sankararamakrishnan et al., 2006). Amidst the used stripping agents, both NaOH and HCl have shown 65% desorption. However, with the usage of HCl, the adsorbent has been sticky and deformed (Sankararamakrishnan et al., 2006).

NaOH can be considered an efficient desorbing agent as it converts protonated functional groups of chitosan-based adsorbents to their base forms which in turn suppress attachment of Cr(VI) oxyanions via electrostatic interactions (Zheng et al., 2019). The declination of desorption with the increased number of sorption-desorption cycles may be associated with saturation, inaccessibility of functional groups, partial desorption, inevitable mass loss, and the presence of relatively stable metal ion-adsorbent functional group complexes (Huang et al., 2013, Wang et al., 2019b). Also, During the regeneration cycles, the properties of the surface of the adsorbent may be affected by the strong oxidizing properties of Cr(VI) thereby reducing its adsorption capacity (Vakili et al., 2018). The reactivity of the binding sites

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of the adsorptive material may also be weakened due to the stripping agent, slightly decreasing the adsorption capacity in the latter sorption-desorption cycles (Huang et al., 2018).

Table 3: Re-usability of chitosan-based adsorbents utilized in Cr(VI) removal

Adsorbent	Conditions	Reagent used	Regeneration cycles	Desorbed percentage %	Remarks	Ref
chitosan/clay nanocomposite	pH 3, 100 ppm Cr(VI), 50 mg of Adsorbent, 120 rpm, 35 °C, contact time 150 min	0.005 M H_2SO_4	5	93.50		(Pandey and Mishra, 2011)
Chitosan/polypyrrole composite	-	0.5 M HCl, 0.1 M NaOH	4	62.50	In 0.5 M HCl, doping with chloride anions also led to the regeneration of the sorption sites.	(Karthik and Meenakshi, 2014)
Chitosan coat ceramic alumina biosorbent	flow rate – 2 mL min^{-1}, Bed volume – 30 mL, 25 °C (-0.5 °C)	0.1 M NaOH	-	-	column adsorption-desorption studies have been performed	(Boddu et al., 2003)
1,2:7,8-diepoxyoctane cross-linked chitosan beads	pH 2, 500 ppm Cr(VI), 20 mg of adsorbent, 160 rpm, room temperature	1 M NaOH	6	-		(Vakili et al., 2018)
Diepoxyoctane -cross-linked chitosan beads	pH 2, 200 ppm Cr(VI), 160 rpm, contact time 24 h, 25 °C	1.0 M NaOH	3	-		(Vakili et al., 2019b)
Magnetic silica nanoparticles encapsulated by chitosan microspheres	eluent volume 5 mL, contact time 2 h, 25 °C	a mixture of 0.3 M NaOH	-	95.6		(Xitong Sun, 2016)

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		and 0.3 M NaCl				
Maghemite/chitosan/polypyrrole nanocomposites	150 ppm Cr(VI), 2 mg of adsorbent, contact time 12 h	1.0 M NaOH	5	-		(Reis et al., 2021)
β-cyclodextrin/ chitosan/hexamethylenetetramine aerogel beads	pH 2, 20 mg of adsorbent dose, 100 ppm Cr(VI) contact time 24 h, 25 ºC	0.2 M NaOH	9	98		(Wang et al., 2019b)
Chitosan/bentonite composite	100 ppm Cr(VI), 50 mg of adsorbent, 160 rpm, contact time 5 h, 25 ºC	NaOH or HCl	-	60.1, 10.3		(Yang et al., 2020)
Sulfate-cross-linked chitosan	5 g of adsorbent	NaOH or H_2SO_4	10	--		(Kahu et al., 2014)
Poly(1-vinylimidazole)-modified-chitosan composite	3.5 pH, 150 ppm Cr(VI), 30 mg of adsorbent, 150 rpm, contact time 150 mins	0.1 M NaOH	5	--		(Islam et al., 2019)
Chitosan-modified multi-walled carbon nanotube composite	200 ppm Cr(VI), 500 mg of adsorbent, contact time 2 h, 30 ºC	0.1 M NaOH	5	98-100		(Huang et al., 2018)
Poly (4-vinyl pyridine) decorated magnetic chitosan biopolymer	pH 2, 500 ppm Cr(VI), 50 mg of adsorbent, contact time 24 h, 25 ºC	0.5 M NaOH	5	-		(Zheng et al., 2019)

Fe$_3$O$_4$@mesoporous-SiO$_2$@chitosan@poly aniline core−shell nanoparticles	pH 2, 100 ppm Cr(VI), 5 mg of adsorbent, 25 ºC	0.01 M NaOH	8	97.3		(Zuo et al., 2021)
Functionalized chitosan with butylammonium ionic liquids	175 ppm Cr(VI), contact time 2 h, 25 ºC	0.025 M NH$_4$OH	4	84.33 ± 4.87	NH$_4$OH weakens the sorbent-hydrogen chromate ion electrostatic attractions resulting in desorption	(Eliodório et al., 2020a)
Graphene oxide/chitosan composite	pH 2, 50 ppm Cr(VI) 25 mg of adsorbent, 160 rpm, contact time 90 min, 25 ºC	1 M NaOH	7	92.5		(Zhang et al., 2016)
Glyoxal cross-linked magnetic hydrogel film	-	0.1 M HCl	3	78.92	It does not harm the adsorbent due to strong glyoxal cross-linkages	(Mirabedini et al., 2016)
Chitosan-nanoclay composite	pH 2, adsorbent concentration 1.2 g L^{-1} 200 rpm, contact time 50 min, 30 ºC	H$_2$SO$_4$	5	93.4		(Kahraman, 2017)
Chitosan grafted graphene oxide nanocomposite	pH 2, 50 ppm Cr(VI), adsorbent dose of 2 g L^{-1}	1M NaOH	10	96		(Samuel et al., 2019)

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Titanium cross-linked chitosan composite	pH 5, 30 ppm Cr(VI), 20 mg of adsorbent, 150 rpm, contact time 12 h	0.5 M NaOH	3	99.3		(Zhang et al., 2015)

5.0 Future perspectives

Literature reveals that over the past ten to twenty years, significant research advancements have been achieved in chitosan-based adsorbents for the remediation of Cr(VI) from aqueous media, via novel improvements in the structure and function of pristine chitosan. However, some of the areas are yet to be addressed in the future. Most of the studies have been conducted under controlled circumstances in laboratory settings. Even though the adsorbents are highly efficient under controlled conditions, their performance could be low in real-world situations. Therefore, the research should be further extended to the application of the prepared adsorbents to analyze their performance in the actual world. Another major concerning area is scalability, i.e., the scope of the practical applicability of the adsorbent on large scale. Despite the fact that laboratory-scale adsorption studies have displayed effective results, it is mandatory to implement studies on large scale to understand the adsorption parameters such as adsorption capacity and possible optimum conditions such as pH and dosage. Also, the cost of the adsorbent preparation in large-scale usage should be considered. These factors aid in revealing the true potential of these hybrid adsorbents in Cr(VI) decontamination on an industrial scale. In addition, the co-ion effect on some of the prepared adsorbents has not been well reported. As the adsorption process has a weak selectivity in the removal of contaminants and real-world applications, other contaminants are present along with Cr(VI) ions, so it is necessary to study the co-ion effect. These areas may restrict the scope and possibilities of real-world industrial applications in the future.

6.0 Conclusion

Chitosan-based adsorbents can be considered promising options for the mitigation of Cr(VI) from aqueous media. The chitosan-based adsorbents are analyzed in two sections as structurally and chemically modified materials. Much of the research is focused on chemical modifications such as cross-linking, grafting, and combination with other adsorbents. Cross-linking, the most commonly used modification technique suffers from the possibility of lowering the available binding sites for Cr(VI) uptake, therefore cross-linking has been usually carried out with other chemical or structural modification techniques. It has been revealed that electrostatic interactions are the main governing mechanism in the sorption of Cr(VI) by chitosan-based adsorbents. Most of the compiled works that evaluated the reusability have indicated that most of the chitosan-based adsorbents have high regeneration ability over several sorption-desorption cycles. Hence, it can be inferred that chitosan-based adsorbents have reduced the drawbacks of pristine chitosan and can be utilized as an eminent adsorptive material that would aid in the mitigation of Cr(VI) from aqueous media.

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