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Modified Chitosan Forms for Cr (VI) Removal

Şerife Parlayici and Erol Pehlivan

Abstract

The forms of utility in the wastewater treatment of chitosan-based adsorbents acquired from natural substances have attracted numerous attentions in recent years. The use of chitosan modified adsorbents for removal of the chromium has aroused great interest. When chitosan-based modified adsorbents are considered, they have got large amount of an amino ($-NH_2$) and hydroxyl ($-OH$) functional groups. Such adsorbents display that they have high activity and therefore they may be extensively utilized in wastewater treatment plants to cast off chromium. In this chapter, the utility outcomes of chitosan-based substances will be explained after applying different parameters to remove Cr (VI) from the aqueous surrounding with the information obtained the use of batch adsorption systems. Application of various chitosan-based adsorbents for Cr (VI) removal application will be demonstrated in a detailed way and they will be discussed within the textual content.

Keywords: adsorption, chitosan, Cr (VI), modification

1. Introduction

There is an increasing demand for new materials of natural origin to remove metal ions which include chromium from industrial liquid waste. Many researchers have evaluated and implemented the possibility of the usage of renewable-based materials to get this element. Cellulose, starch, pectin or crusted shell waste such as chitin and chitosan (Cts), which are polysaccharides as a class of natural macromolecules. They're exceedingly bioactive substances in the removal of water pollutants and are commonly derived from marine crustaceans and agricultural raw substances or by-products [1, 2].

There are thousands of different chemicals, physical and biological processes occurring between the solid adsorbent surface and the adsorbate. In the adsorption process, the active interactions occurring at the adjacent intermediate surfaces between a solid adsorbent and certain toxic metal solution and the changes in its concentration between both phases stand out. Biopolymers can be thought of as a polymer that we are used to (such as proteins, lignin, polysaccharides, chitin, chitosan, cellulose and hemicellulose) and originate from living organisms in nature. These polymers are often found in sources of carbon origin and are mostly derived from carbohydrates. Origins of some biopolymers are shown in **Figure 1**.

There have been numerous articles on chitin and Cts in recent years and it is more directed towards applications of these polymers and their modification. Some biological activities exhibited through such polymers, specially Cts and its derivatives which include biocompatibility, biodegradability, low toxicity, mucousness

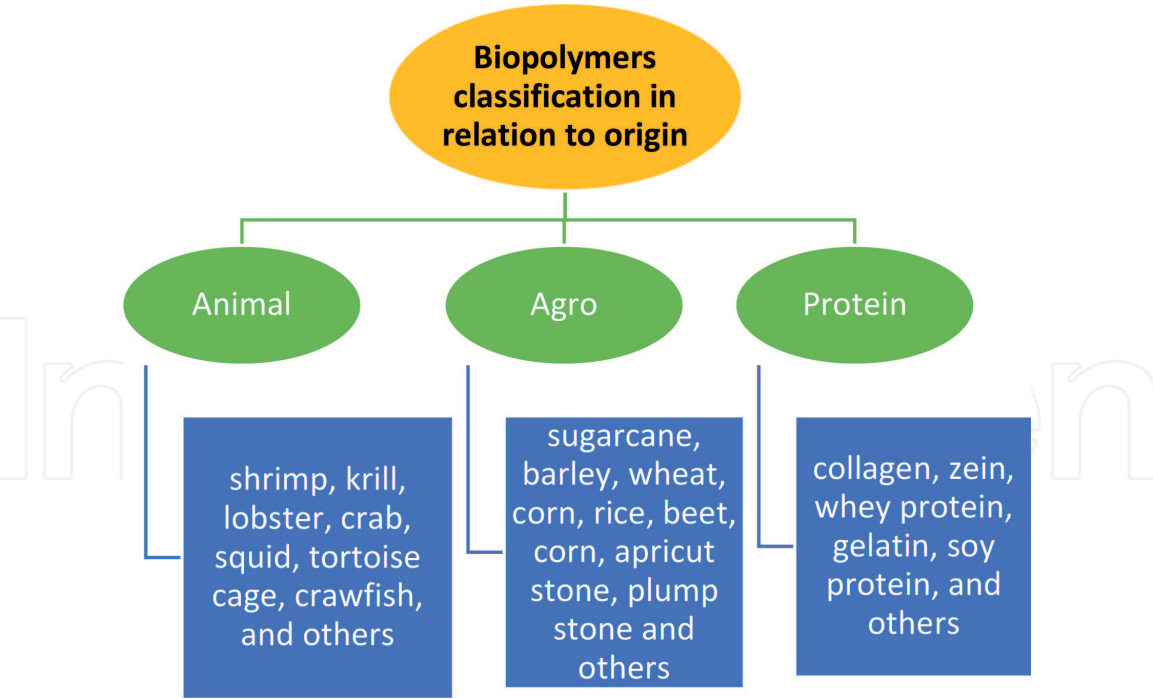


Figure 1.
Biopolymer classification: Animal, agro, and protein origins.

and antimicrobial activity have attracted interest in medicine, pharmacy, biomedical and health-related applications [1, 3, 4]. Numerous Cts-based materials were produced such as nano and microparticles, gels, sponges, films and membranes [4]. They have created an efficient field of application for drug delivery, wound healing and tissue regeneration applications.

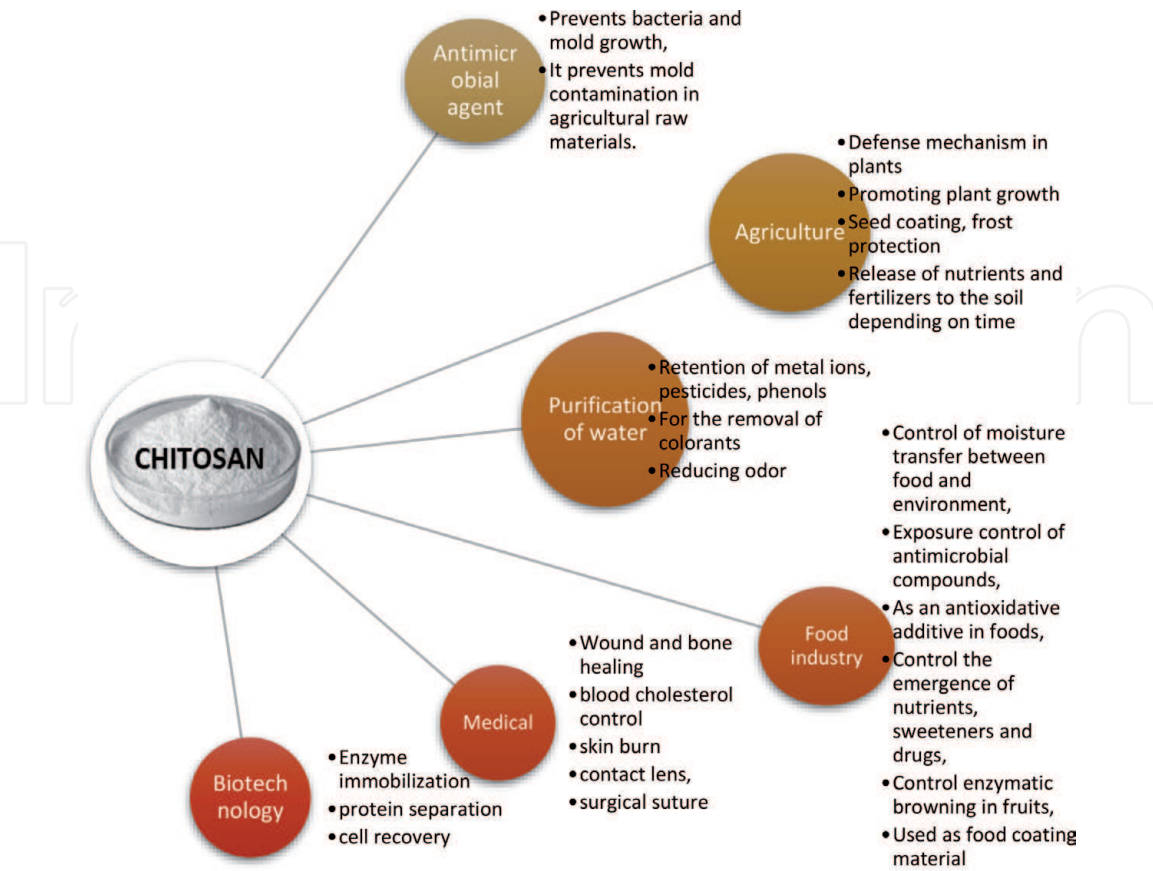


Figure 2.
Field of application of Cts.

The biggest advantage of chitin and Cts is that they are a renewable resource and an environmentally friendly natural biopolymer. With these features, it has been used in many different sectors in recent years. Cts attracts more attention compared to chitin because it is commercially available and can be used in many forms. Application areas of Cts can be listed as pharmacy (controlled drug release), medical (bandage), wastewater treatment, biotechnology, cosmetics, food, textile and agriculture (**Figure 2**).

2. Chitosan

2.1 Sources of chitin and chitosan

Chitin is usually found in nature in seaweeds, protozoa (flagellates, amoebic ciliates, etc.), selenterals, mollusks, arthropods, bacteria, fungi, insects and some plants. The richest sources of chitin are; crab, shrimp, lobster and crayfish shells. Chitin biopolymers of animal origin are mainly found in animals. Chitin is the most considerable polysaccharide on the planet. Due to its strong hydrogen bonds and high crystal property of its cohesive structure forces, chitin is an insoluble substance in normal solvents, including water and organic matter [5]. Cts is abundant in marine or terrestrial animals such as crustaceans, insects, mollusks and fungi [6] without a backbone, such as various insects and marine diatoms. Commercial production of Cts by alkaline hydrolysis by extracting chitin from shrimp shell waste has been carried out by a group scientist [3, 6].

2.2 Chitosan production

Cts is obtained from chitin. Rouget became aware of Cts in 1859 while conducting experimental activities on deacetylated forms of chitin [7]. Cts is obtained from waste shrimp and crab shells from the seafood industries by chemical methods in industrial processes around the world [4]. Basic structure properties of Cts are related to its molecular weight and degree of deacetylation. The crystallinity of Cts is important in classifying its particle size, moisture and ash content, which is based on its surface morphology properties. The solubility, antibacterial, polycationic character, biocompatibility and bio adhesiveness of Cts are the basis that define the Cts structure and application areas [8, 9].

Chemical modifications of Cts have been extensively described in recent studies. Cts contains the reactive amino ($-NH_2$) and hydroxyl ($-OH$) groups in its structure and can very easily be converted into new modified forms. The presence of amino groups in the Cts matrix (deacetylation degree) in macromolecular chains indicates that Cts has a polycationic property in acidic aqueous solutions. The protonation of amino groups in the polymer structure seriously affects the structure of macromolecules in solutions, and it is known that the structure behavior may be managed through changing the pH or ionic strength of the solution it is in.

Cts production is carried out by two basic methods, chemically and biologically. Classically, the chemical method is the method in which physical and chemical methods are used together. Chemical method; the isolation of the chitin is carried out by removing other substances in the shell. The procedures for this can be grouped under four main steps:

1. Preparation of shells.
2. Demineralization (removal of minerals).

3. Deproteinization (removal of proteins).

4. Decoloration (removal of pigments). These stages are given in **Figure 3**.

Biological methods are processes that can be examined under several headings. Cell cultures of various organisms such as *Mucor rouxii*, *Phycomyces blakesleeanus* are used in the microbial synthesis of Cts. The product obtained is developed by adding *Aspergillus niger* to the culture medium. Thus, this production mechanism also leads to the deacetylation of the Cts. Cts is obtained at the end of the 96-hour incubation period [10]. As a biological method, the use of proteolytic enzymes such as pepsin, trypsin, protease, proteinase and papain in protein removal can be counted [11]. Today, many other polymers used in industry are produced synthetically. Synthetic polymers have limited biocompatibility and biodegradability compared to Cts, a natural polymer.

2.3 Resolution of chitosan

Chitin is insoluble in dilute acids and many organic solvents. Because it is a semi-crystalline polymer and has a large amount of intramolecular and intermolecular hydrogen bonds in its structure. The effect of changes in the N-acetyl-D-glucosamine and D-glucosamine groups on solubility is shown in **Figure 4**.

The solubility concerning chitosan in a range of solvents and its polycationic properties are essential for the advent of chitosan derivatives and the use of them in many different applications. Many different factors are taken into account to control the solubility of Cts in aqueous solutions. These are the result of applying certain parameters such as temperature, alkali concentration, type and

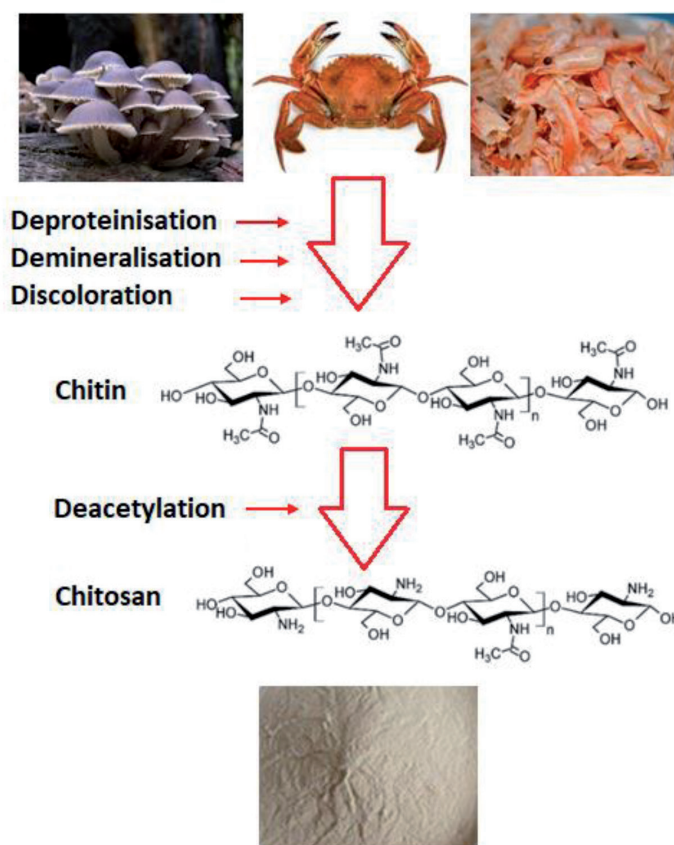


Figure 3.
General steps for chitin and Cts production.

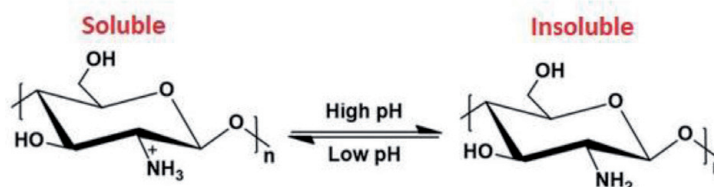


Figure 4.
 Nature of Cts below its pK_a .

concentration of acid, pH, deacetylation time, previous treatments applied to chitin isolation and chitin particle size, etc. Cts is regarded as a strong base as it has amino groups with a pK_a value equal to 6.3. Cts dissolves easily in dilute acid solutions below pH 6.0. It is a reality that the amino groups in the chitosan structure have significantly changed its charged state and its properties. H^+ ions present in low pH solutions protonate the NH_2 groups of Cts and causes the formation of $(NH_3)^+$. Thus, Cts has a polycationic biopolymer structure. This situation turns Cts into a very easily soluble polyelectrolyte in acidic medium. The most functional amine groups of Cts are protonated in low pH buffer solution. On the other hand, Cts amines are transformed to deprotonated form as the pH rises above 6 and the polymer loses its charge and becomes insoluble in basic solutions [12, 13]. The soluble–insoluble transition forms at its pK_a value between pH 6.0 and 6.5. The soluble and insoluble situation of Cts in aqueous media occurs pK_a valued around pH between 6 and 6.5. pK_a is considered to be significantly dependent on the degree of N-acetylation, hence Cts solubility varies depending on the deacetylation method applied [14]. Acetic formic, formic acid, lactic acids and organic acids are the most commonly used solvents. They can easily dissolve Cts as it is easily converted into quaternary nitrogen salts in aqueous solution at low pH values [15]. Cts, on the other hand, can be easily dissolved in some solutions (formic acid, acetic acid, etc.) at $pH < 6$ due to its cationic structure. Considering the best solvents, it has been found that it is the formic acid from which solutions are obtained in aqueous systems containing 0.2–100% formic acid. 1% acetic acid solution around pH 4.0 has been applied as the most utilized solvent in the Cts applications [15]. Likewise, Cts is very easily soluble in hydrochloric acid and dilute nitric acid solutions, however insoluble in sulfuric and phosphoric acids. These acids are not shown since they can break the chitosan polymeric chains promoting depolymerization. Cts is very difficult to break up in organic solvents, for example, dimethylformamide and dimethyl sulfoxide. Its solubility in the acidified polyol is generally very excellent [15, 16].

2.4 Cross-linkers used for chitosan cross-linking

Cts is soluble in both organic and mineral acids. This is a limiting parameter for industrial applications in wastewater treatments. By using different chemical reagents in the cross-linking process, the structure of Cts is strengthened mechanically and chemically (**Figure 5**). The chemical modification of Cts can be done for two purposes:

- a. To prevent the dissolution of the polymer when metal adsorption or metal desorption is performed in acidic solutions,
- b. To increase the metal adsorption properties (increase in adsorption capacity or increase in adsorption selectivity).

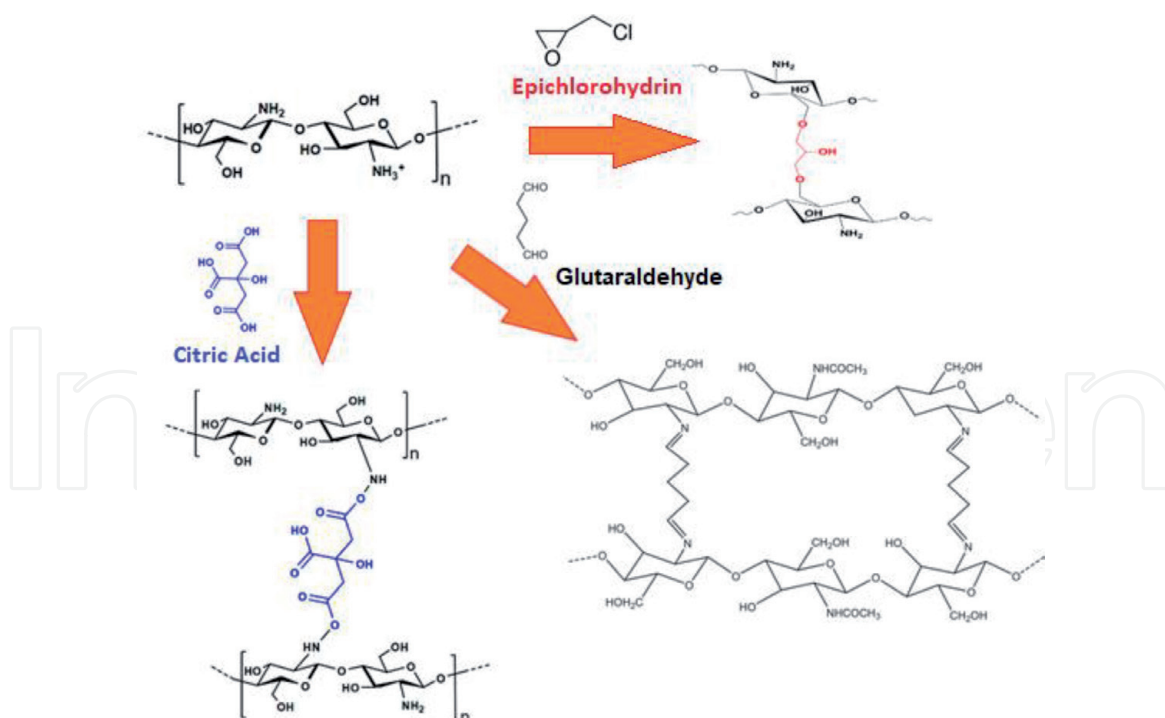


Figure 5.
Schematic representations of the cross-linking reaction of Cts with cross-linking agents.

The modifications carried out in the structure of Cts are aimed to further improve its biological and chemical properties and to change its solubility in the solvent or aquatic environment to be used. The behavior of Cts chains in diluted acids has been studied and at higher ionic strength or lower pH values, amino groups will undergo a higher protonation. In these cases, the macromolecules have been found to behave more like stiff rods [17, 18]. Cross-linking process can be applied by the reaction of Cts with different crosslinking agents such as glutaraldehyde, epichlorohydrin, polyethyleneimine etc. (**Figure 5**). Today, there are many activating agents and newly developed methods. Glutaraldehyde is widely used crosslinking agent because it is cheap and very effective crosslinker. Glutaraldehyde, a linear 5-carbon dialdehyde, is transparent and colorless [19]. It is an oily liquid with a pungent odor that can be dissolved in water, alcohol and organic solvents in all proportions. Chemical stability may be enhanced through chemical procedures which include crosslinking with glutaraldehyde for utility in a chemically acidic environment (**Figure 6**). By means of developing new bonds between Cts chains, the polymer is proof against dissolution even in strong solutions such as hydrochloric acid solution. In addition, the reality that Cts includes amine groups is an essential factor in being a good adsorbent. It is possible to observe an increase in the adsorption

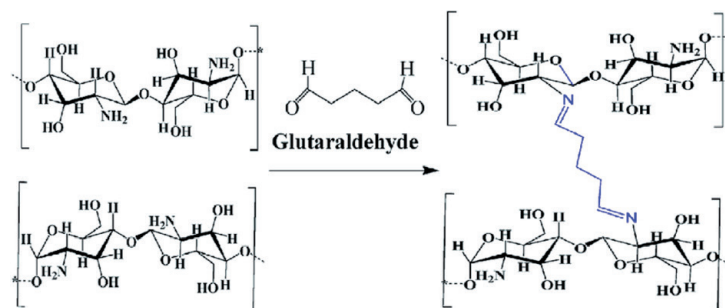


Figure 6.
Schematic representation of the cross-linking reaction of Cts with glutaraldehyde [20].

capacity by increasing the amine groups. The most important advantage of glutar-aldehyde is the presence of suitable amino groups that perform the binding on Cts surfaces [21, 22]. Adding cross-links to the structure of Cts gives it a solid three-dimensional structure. To form cross-linked Cts, chemicals with a wide variety of groups are used to form the cross-link structure. Condensation reaction resulting from the reaction between an aldehyde function and a primary amine group from the Cts chain. It quickly joins the matrix structure of Cts.

There may be the opportunity to apply mono-functional reagents (epichlorohydrin) by opening the ether group for grafting to an amine function through the Schiff base reaction, which is likewise capable of react, at the same time the chloride group then interacts with different functional groups or other amines. Tri-polyphosphate is also selected as a possible cross-linking agent, which may be used to prepare Cts gel beads by its coagulation and neutralization impact.

3. Adsorption of Cr (VI) using chitosan-based materials

3.1 Toxicity of chromium

The toxicity of chromium compounds varies according to the pH, temperature and oxidation step. Cr (VI) ions are much more toxic than chromium (III) (Cr (III)) in terms of toxicity [23, 24]. EPA's threshold limit value is 10 times lower than Cr (III). When Cr (VI) solution mixes with seawater, it prevents some aquatic plants from photosynthesis, reduces reproduction in fish and can cause fish death. Cr (VI) causes burns in human body, in case of contact, causing irritation, wounds and ulcers on the skin and respiratory tract [25]. Sensitivity to Cr (III) and Cr (VI) causes allergic reactions, redness in the eyes and nose, itching and rash. Taking Cr (VI) with the digestive system can cause ulcers, necrosis and death in the stomach and intestines. The recommended Cr (VI) limit in drinking water is 0.05 ppm [26, 27]. One of the most important effects of Cr (VI), which is a very oxidizing substance, is that it causes lung cancer [28, 29].

3.2 Removal of hexavalent chromium

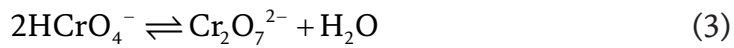
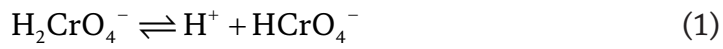
Chromium pollution is especially caused by chrome plating, automotive, leather and paint industry wastes [18]. Traditional refining methods used for chromium refining are not highly efficient, and these techniques require large amounts of chemicals and energy. Because they are costly, their use is impractical. Adsorption has superior properties in these aspects. In chromium treatment, the ability to use many different sources as adsorbents, such as plants, animal materials and various microorganisms, are easy to obtain, they can be produced by cheap and simple methods, regeneration ease and high removal efficiency are the features that make the adsorption approach preferred [23, 30].

Chemical precipitation, microfiltration, ultrafiltration, flotation, reduction, dialysis, membrane technologies, chelating, ion exchange, evaporation, solvent extraction, reverse osmosis, and adsorption can be listed among the methods used for dechroming of industrial wastewater [20]. In the selection of these methods, the acidic or basic character of the wastewater, the target envisaged for removal and recovery, the type and concentration of the chromium compound in the waste, the cost, chemical and energy consumption, the management of the waste generated by treatment and the removal efficiency should be taken into consideration.

The pH of the aqueous chromium influences the surface charge of the modified adsorbent, the degree of ionization and the adsorbate species. Depending on

the current pH, the Cr (VI) waste solution can be found in dichromate ($\text{Cr}_2\text{O}_7^{2-}$), chromate (CrO_4^{2-}) and hydrogen chromate (HCrO_4^-) forms. According to the pH of the Cr (VI) in aqueous solution varying ion types are given (**Figure 7**). HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ are the dominant species on the experimental concentration and these are the dominant components at a low pH. When the pH is excessive, CrO_4^{2-} is the dominant component of Cr (VI), so the initial solution pH is an important parameter for the adsorption of chromium. Electrostatic attraction forces between positively charged adsorbent surface groups and anionic Cr (VI) types occurs. This is particularly more common because Cr (VI) are present as oxyanions (HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-}) in solution phase. Positively charged adsorbent surface groups are formed as a result of the formation of both protonation or quaternization of the groups on the adsorbent matrix.

The equilibrium among the various Cr (VI) species may be represented by using Eqs (1), (2) and (3).



A few other parameters affecting the adsorbent capacity; solution pH, equilibration time, temperature of solution, coexisting ions and adsorbent dosage concentration.

3.3 Application of various chitosan form for Cr (VI) removal

Cts modifications can be by physical methods or by chemical methods in which crosslinking or gridding of functional groups is performed. Cts can form perfect gels in the membrane, bead, capsule or different forms thanks to its ability to dissolve in organic acids and to combine with polyionic compounds. Four different methods are used to create Cts gels. These are solvent evaporation method, neutralization method, cross-linking method and ionotropic gelation method. Among these methods, the neutralization method is the main method used in the preparation of spherical Cts beads of different sizes and pore properties. It is carried out by

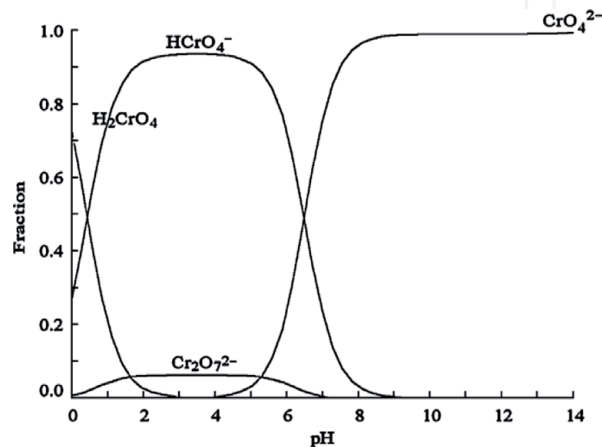


Figure 7.
Chromium speciation as a function of pH.

dropping Cts solution into NaOH and ethanol solution drop by drop. Since Cts is not soluble at high pH values, the drops become solid due to polymer precipitation.

The chelating property of Cts enables it to retain various metal ions. Cts is a polymer that has a wide range of uses in the removal of heavy metals from wastewater systems, in the food industry, in the encapsulation of drugs that need to be released slowly or overtime, in cosmetics, agriculture, pulp and paper industry to have all these properties. Cts, a poly N acetyl glucosamine, contains cationic amino and polar hydroxyl groups, which are chemically reactive groups attached to the glucosamine chain it carries. These groups support immobilization methods such as adsorption and covalent bonding. Amino capability qualifies Cts for a lot of chemical reactions inclusive of quaternization, grafting, alkylation and reaction with carbonyl compounds. The presence of the hydroxyl group lets in Cts to form hydrogen bonding together with polar atoms, grafting, crosslinking, and some chemical reactions inclusive of O-acetylation [31].

Recently, more composite materials containing modified Cts used in chromium removal have been reported. Eliodório et al. investigated the synthesis and characterization of Cts functionalized with three different ionic liquids and their application in Cr (VI) waste treatment [28]. Amino groups in Cts are significantly effective in the adsorption mechanism, especially when protonated at acidic pHs. Besides, intermolecular interaction is also effective. This phenomenon will increase the cationic ability on the Cts surface, facilitating the adsorption of negative groups via electrostatic interaction and improving the elimination of Cr (VI) (**Figure 8**). At acidic pHs, there has been a strong protonation of the amine groups that gave the Cts surface a positive character. Thus, the electrostatic attraction force between this positively charged surface and negatively charged anion (HCrO_4^-) will boom and this could motive the increase of adsorption of Cr (VI).

Parlayıcı and Pehlivan inspect the adsorption of chromium ions on Cts doped with multiwalled carbon nanotubes (Cht-MWCNT) [32]. Under optimum

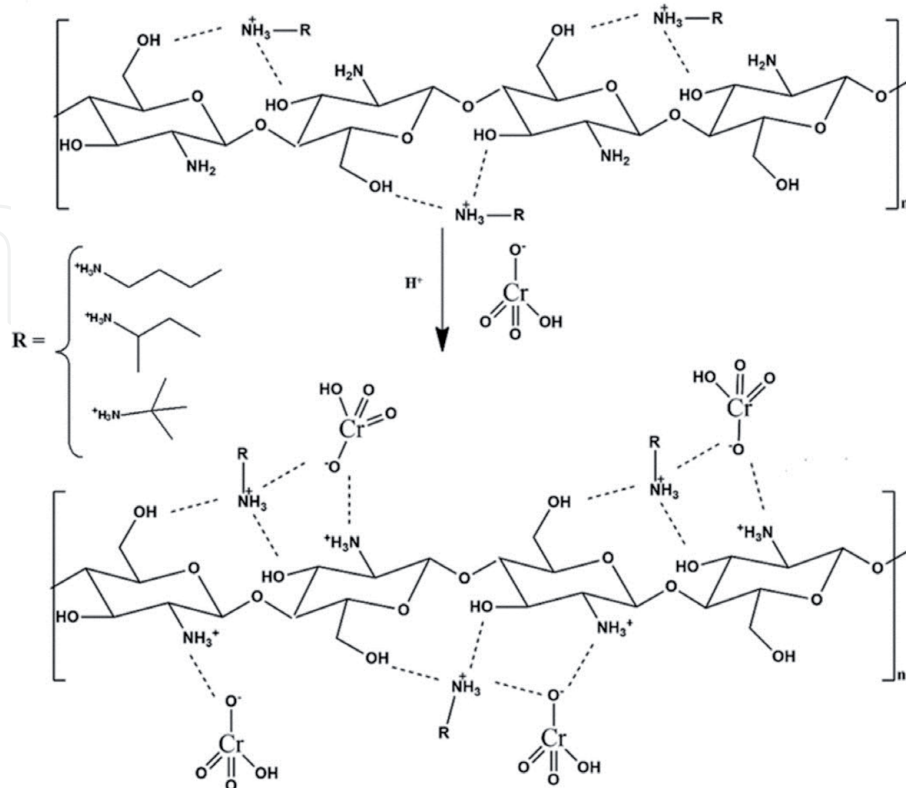


Figure 8.
 Adsorption mechanism of chromium hexavalent [28].

situations, maximum adsorption capacity of Cr (VI) determined by using Langmuir model have been improved 26.14 mg/g. When carbon nanotubes (CNT) is examined, carbon atoms are allotropes of carbon that have an aromatic surface while in a sp^2 -type hybridization rolled together like a tubular system (1D system) [33]. The structural properties of the CNT's surface permit because of an intense together with solids having organic molecules through non-covalent forces, for example, hydrogen bonding, π - π stacking, electrostatic forces, van der Waals forces and hydrophobic interactions. Moreover, the CNT structure allows the incorporation of one or more chemicals functional groups and they can build selectivity and stability of the subsequent framework. The chemical functional groups may be anchored to CNT surface through functionalization or purification processes [34]. This carbon allotrope structure is an interesting nanostructure that harbors remarkable electronic and mechanical properties that are directly dependent on chirality and diameter. Its excellent properties combined with unusual morphology make it extremely attractive for some many practical applications in wastewater systems; for example, with the improvement of solid composite materials for ideal adsorption, high impact ability, selectivity and productivity [35].

Cts-humic acid-graphene oxide (Cts-HA-GO) composite was produced (**Figure 9**) and the removal of toxic Cr (VI) ion from aqueous solutions was

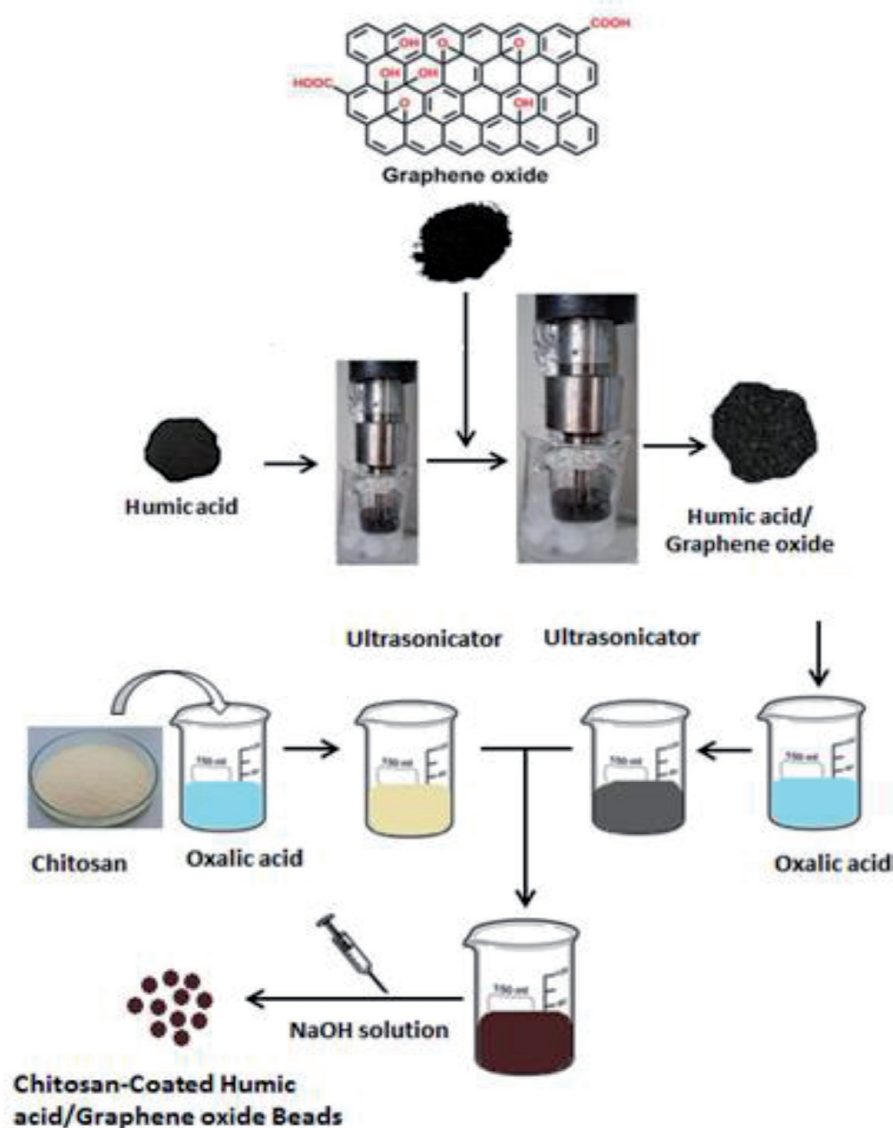


Figure 9.
Preparation of Cts coated humic acid/graphene oxide composite beads.

studied by batch equilibration technique [27]. The percentage adsorption was 85.28% by using 200 ppm Cr (VI) and 2 g/L composite. Maximum adsorption of Cr (VI) ion has occurred at pH 2 value as 83.64 mg g^{-1} .

Graphene oxide (GO)-based adsorbents are very useful substances because of the presence of functional groups on the surface of imparted for the duration of the oxidation of graphite. The presence of those groups is taken into considered best adsorbent for the use of graphene oxide for metal ion chelation because they show off hydrophilic properties due to hydrogen bond. Some other exciting magnificence adsorbents is GO-based adsorbent, mainly due to the plentiful -OH , -COOH and -C=O functional groups on their surface imparted throughout oxidation of graphite. The presence of such groups makes GO an ideal adsorbent for metal ion chelation and outstanding hydrophilic properties owing to hydrogen bonding [36].

Humic acids (HA) are a principal component of humic substances, which are the significant constituents of soil, peat and coal. It is a perplexing combination of various acids containing carboxyl and phenolate groups so that the mixture acts functionally as a dibasic acid or, occasionally, as a tribasic acid. There are functional groups in the HA structure. These consist of various types of carboxylic (COOH), phenolic hydroxyl and carbonyl (C=O) structures. HAs have an extraordinary effect on metal adsorption as they have carboxyl and phenolic -OH groups that interact with various metal ions [37]. The carboxyl groups, which render the polymers negatively charged at neutral pH values, are in particular effective in complexing metal ions in aqueous solution.

Cts consists of a crystal phase and a non-crystalline (amorphous) phase [38]. Crystalline Cts molecules are in the form of layers and are tightly held by intra-layer hydrogen bonds (**Figure 10**). Fenton reaction was used to increase the Cr (VI) adsorption capacity of Cts [24]. With the Fenton modification, Cts both efficiently adsorbed Cr (VI) and converted it to less toxic Cr (III) over a wide pH range as a result of layer formation defined by a sandwich model. The highly reactive $\text{HO}\cdot$ destroyed the hydrogen bond in the Cts structure, and Fe^{3+} ions were chelated with the Cts biopolymer. After Fenton modification, HCrO_4^{4-} entered the gap in the Cts structure and was adsorbed in the newly formed adsorption sites. The adsorption process of Cr (VI) using the Fenton modified Cts, adsorption isotherms of Freundlich were investigated and the adsorption capacity exceeded 120 mg/g .

Cellulose and lignin-based adsorbents are the most basic biopolymer widely used for toxic metal removal from wastewater. Cellulose exhibits natural qualities such as strength, reward, biodegradability, non-toxicity, and mechanical stability. However, cellulose is an odorless water-soluble linear polymer covalently bonded in its structure by the monomeric units of b-D-anhydroglucopyranose C1-C4 b-glycosidic bonds [39]. Due to its water solubility, it has some drawbacks in terms of being used as an

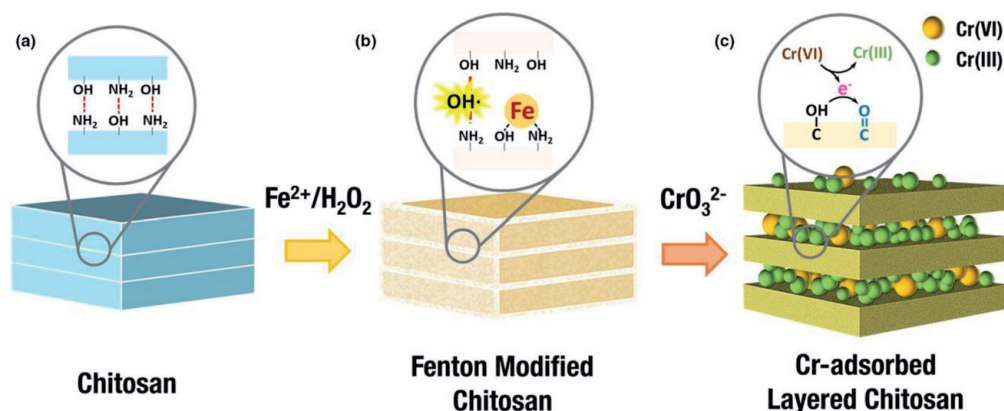
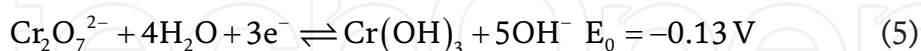
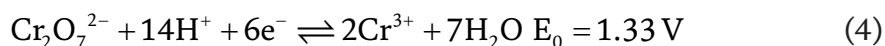


Figure 10.
 The adsorption of Cr (VI) onto the Fenton modified Cts by a sandwich model [24].

adsorbent in the raw structure; thus, it is made more suitable for adsorption applications by applying various functionalization techniques. Abundance, low cost and availability of various functions groups in agro-based byproducts (hydroxyl, carboxyl, carbonyl etc.) like shells, barks, straws, stem and seeds, they attract the attention of researchers to explore potential applications in the removal process of toxic metals from wastewater. These substances have the small surface area and their low stage of adsorption performance in wastewater treatment limits their implementation among their ordinary state. Valorization of agricultural waste in adsorption processes is an environmentally friendly approach for wastewater treatment studies. Parlayıcı and Pehlivan reported the preparation of glutaraldehyde crosslinked Cts coated Rosehip (*Rosa canina*) seed shell (Cts/RS) capsules to evaluate the adsorption of Cr (VI) ions from aqueous solution [40]. The data were fitted to the Langmuir adsorption isotherm. The maximum capacity of Cts/RS was determined as 34.13 mg/g.

Black sesame (*Sesamum indicum* L.) seed pulp (BSSP) and Cts (Cts)-coated black sesame seed pulp bead (Cts-BSSP) composite were produced (**Figure 11**) and tested to remove hexavalent chromium (Cr (VI)) during the adsorption process [23]. BSSP is an agricultural waste that has no economic value. After reaching equilibrium time, the Cr (VI) removal capacity was calculated as 31.44 mg/g for Cts-BSSP and 18.32 mg/g for BSSP. The results indicated the feasibility of using Cts-BSSP as adsorbents for the removal of Cr (VI) from aqueous medium.

Let us talk about the synergy in adsorption and reduction during removal of Cr (VI) from aqueous media by natural adsorbents. Anionic Cr (VI) is adsorbed onto protonated solid adsorbent surfaces preferentially by electrostatic bonding or anion exchange. When the strong redox nature of Cr (VI) is examined, it causes the adsorbent surface to oxidize while it is reduced to Cr (III). If the aqueous medium has acidic conditions and the presence of electrons is large, this further catalyzes the reduction. Heteroatoms such as; O, N and S in the adsorbent structure carry these electrons, making Cr (VI) easier to reduce. In the case of Cr (VI) adsorption, the chelation mechanism is very touchy to pH in the attachment of the metal by the adsorbent and it is generally found that no adsorption happens at low pH. Therefore, a simple change in the pH of the solution medium can reverse the adsorption reaction completely.



It has been determined that there are two feasible reduction mechanisms in the removal of Cr (VI) from aqueous solutions (Reaction 1 and Reaction 2). In mechanism I indicates that Cr (VI) will be reduced to Cr (III) in acidic conditions at some stage in adsorption. Mechanism II is an indirect reduction. Adsorbed Cr (VI) species take electrons from an adjoining location of the adsorbent mass to facilitate the reduction. Besides, reducing agents such as ferrous iron, zerovalent iron, and iron composites have also been used [29].

The physicochemical properties of Cts can be improved by making a stronger structure, especially by making a composite by chemical modification or the inclusion of some strengthening agents. New adsorbents can also be formed by integrating into the Cts matrix with composite materials that allow continuous capture of toxic materials [41]. Clay mineral has a long enchanting history of metal-binding capacity while being used independently or combined with other natural polymers. Clay-biopolymer composites show excellent potential and high efficiency for the removal of chromium from aqueous solution. Parlayıcı prepared Cts coated perlite

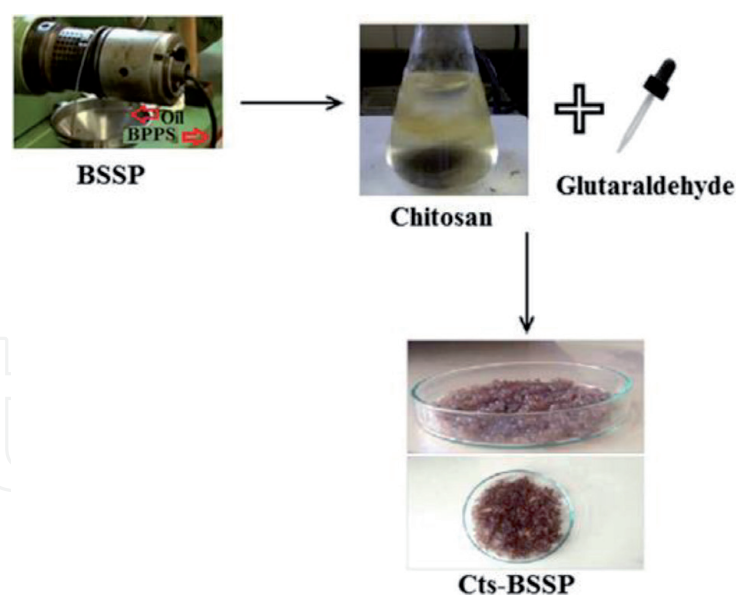


Figure 11.
Preparation of Cts-coated black sesame seed pulp beads (Cts-BSSP) [23].

composite beads (**Figures 12 and 13**) and investigated systematically the process parameters influencing the adsorptions of Cr (VI) ions [30].

Jiang et al. synthesized magnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Cts}$ (MFSC) biopolymers successfully by a simple cross-link method assisted and evaluated them for Cr (VI) removal [21]. The maximum adsorption capacities reported were 336.7 mg g^{-1} . Chitosan was successfully coated with inert substrate perlite and prepared as spherical beads. In this modified form of chitosan, it exhibits two types of accessory mechanisms to remove Cr (VI) from the aqueous environment, one of which is electrostatic interaction and the other is a procedure involving reduction (**Figure 14**).

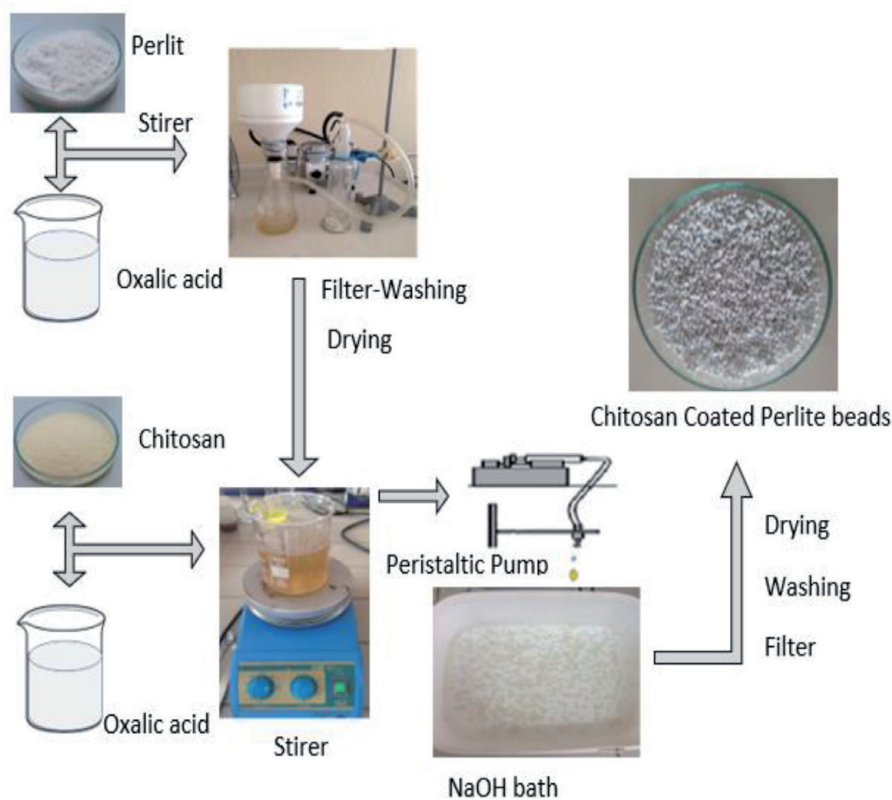


Figure 12.
Preparation of Cts coated perlite beads.

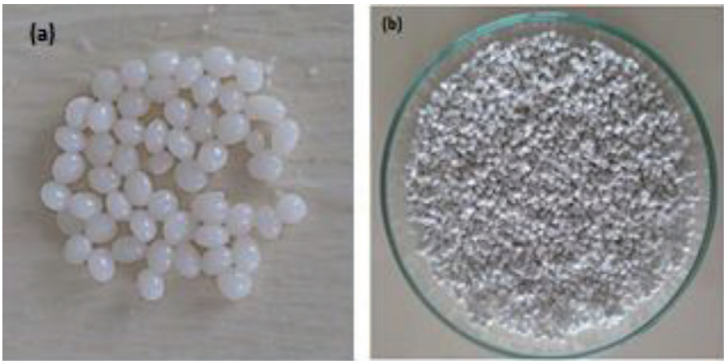


Figure 13. Photograph images of Cts coated perlite beads (a) wet beads (b) dry beads.

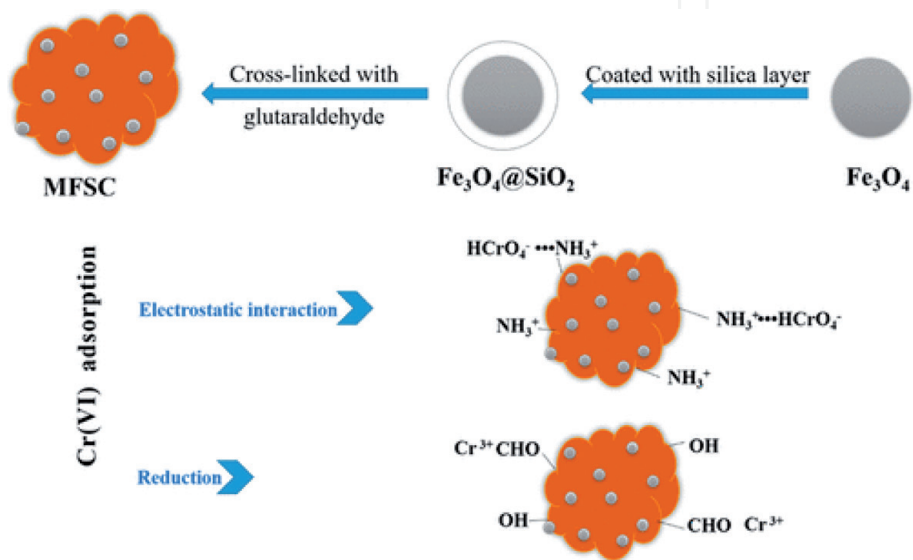


Figure 14. Adsorption mechanisms involved in adsorption of hexavalent chromium onto $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Cts}$ (MFSC) biopolymers [21].

4. Conclusion

The main purpose of this article was to review some Cts based modified composite adsorbents for the adsorptive removal of Cr (VI). Most adsorbents used for longer in its pristine form, but with few changes carried out. Superior properties of adsorbents can be achieved by functionalizing and converting them into composite forms. The layers are formed by using different levels of polymers. Some of these layers are made up by different adsorbents, eg. Humic acid/graphene oxide, MWCNT/Cts, nanoparticle/Cts and Cts/perlite. Graphene oxide, nanoparticles and silica are known to have high surface areas, while biomass such as black sesame seed pulp and chitosan exhibit low surface area, but contain abundant functional groups. Cross-linking or modification is very effective in functionalization of adsorbents.

Features and development history together chromium toxicity, sources, removal mechanism from the aqueous medium, latest trends in composite adsorbent synthesis and preparation were discussed at length. The interpretation of the Cr (VI) removal mechanism summarized in the text. It is possible to reach higher capacities to determine the appropriate conditions in studies with composite adsorbents. The adsorption of Cr (VI) alone electrostatically is not sufficient. If Cr (VI) is considered to be suitable for strong oxidation, it can be removed from the aqueous environment by finding sensitive electrons from the groups in Cts-based adsorbents to transform into Cr (III) form. Heteroatoms such as O and N responsible for

donating electrons are found in almost every Cts-based adsorbent structure. The removal mechanism of adsorbents is also affected by surface chemistry and physical properties in the Cr (VI) elimination process. Their high surface area properties, usability, porosity and cost effectiveness play an important role in increasing the capacity of the Cts-based adsorbent for Cr (VI) removal in wastewater. The modified adsorbents together with Cts for Cr (VI) removal have been shown to possess high capacities and they can be economically used in wastewater treatment units. By using Cts modified adsorbent, a faster and more efficient process will be provided to remove Cr (VI) for water treatment applications.

Conflict of interest

The authors declare no conflict of interest.

Notes

The authors declare no competing financial interest.

Abbreviations

Cts	Chitosan
MWCNT	Multiwalled Carbon Nanotubes
CNT	Carbon Nanotubes
GO	Graphene Oxide
HA	Humic Acids
RS	Rosehip Seed Shell
BSSP	Black sesame (<i>Sesamum indicum</i> L.) seed pulp
MFSC	Magnetic Fe ₃ O ₄ @SiO ₂ -Cts

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