# A review : Removal of heavy metal ions using modified Chitosan

Nur Yusaerah, AR. Sella Auliya, Wahyu Setya Rini, Ganden Supriyanto\* and Handoko Darmokoesoemo

# Department of Chemistry, Faculty of Science and Technology, Airlangga University, 60155, Indonesia

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#### ABSTRACT

Chitosan and its modifications have received great attention over the past few years due to its application as an environmentally friendly adsorbent against various heavy metal ions from industrial waste. Chitosan can remove and adsorb heavy metals because of the active groups -NH<sub>2</sub> and -OH which are highly reactive, can chelate, and base. Chitosan is soluble in acid, so the use of chitosan directly as an adsorbent will be less effective. This is because in an acidic area it will reduce the amine group which is an active group capable of binding with metal ions, so that chitosan can increase resistance to acids and increase the stability of chitosan. Modification of chitosan is carried out by impregnation, crosslinking and grafting with respect to pH, temperature, contact, adsorbent mass, and initial metal ion concentration. The optimal results of the modified chitosan were characterized using FTIR, XRD, SEM, and desorption tests to see the adsorption efficiency. Modification of chitosan into composites by combining two methods is the best method, namely the cross-linking method continued grafting because the two active sides of modified chitosan, which can increase the adsorption of chitosan in binding heavy metal ions. The adsorbent based on chitosan and its modification allows better adsorption of heavy metal ions.

Key words : Removal, Heavy metal ions, Chitosan, Modified chitosan.

# Introduction

Heavy metal pollution from wastewater as a byproduct of the production process continues to increase along with the progress of the industry because these heavy metals function as raw materials, additives and catalysts. The cause of heavy metal ion pollution usually comes from the input of water contaminated by industrial and mining wastes, as well as burning fossil fuels. Industrial wastewater contains heavy metals which can harm human health (Marie *et al.*, 2017) and can have a direct or accumulated effect on the food chain even though the concentration is very low (Gao *et al.*, 2016).

Heavy metals are one of the most dangerous species, due to their toxic properties. Heavy metals such as cobalt, mercury, copper, zinc, chromium, cadmium, lead, nickel, arsenic, etc. can enter water (directly or indirectly) through various industries, such as fertilizer, mining, painting, batteries, and paints or textiles (Mojiri *et al.*, 2016; Igberase *et al.*, 2016; Xu *et al.*, 2018). Heavy metals are toxic, nonbiodegradable, and exist in various oxidation states for long periods in the environment. Therefore, it is important to remove heavy metal ions from wastewater contaminated with heavy metals before discharge to the environment (Mojiri *et al.*, 2016).

Various technologies have been developed to

overcome the problem of heavy metals (Zhao *et al.*, 2016; Liu et al., 2019). Heavy metal ions in general are often separated by chemical means (Kyzas et al., 2017) such as ion exchange (Wang et al., 2014; Sansuk et al., 2016; Kolodyñska et al., 2017) and precipitation with certain chemicals to be precipitated as hydroxides (Ginting and Anggraini, 2016; Arora, 2019). Conversely, the physical separation of metal ions for these metal ions such as coagulation or flocculation (Heffron et al., 2016), osmosis (Alshahateet et al., 2014; Li et al., 2015), membrane filtration (Li et al., 2013; Perreault et al., 2015; Lee et al., 2016; Li et al., 2017; Shariful et al., 2017) and photodegradation (Tan, et al., 2017; Zhang et al., 2017) tends to be less stable thermal and mechanical, requires a relatively long time, and the adsorption capacity and selectivity are low (Yin et al., 2017). During the separation process, each method has its own advantages and disadvantages in terms of technical, economic and associated impacts.

Adsorption is an efficient technique used to remove odors, organic pollutants, and industrial inorganic heavy metal ions from wastewater (Badawi et al., 2017). This adsorption process is more advantageous because the process is easy and inexpensive, easy to operate, efficient, stable (Deng et al., 2017), can adsorb heavy metals quickly even in low concentrations, and the absence of toxic side effects (Yin et al., 2017; Massoud et al., 2018; Moreira et al., 2019; do Nascimento et al., 2018; Jaafari and Yaghmaeian 2019; Londono-Zuluaga et al., 2019) with influencing factors such as the type of adsorbent used, contact time, pH and weight. Therefore, an alternative processing or separation of heavy metals is used using an adsorption process (Ali et al., 2016; Zhang et al., 2018).

In general, a good adsorbent has the advantages of high adsorption capacity and selectivity, good stability, easy access, low cost, environmentally friendly, and easy regeneration (Reddi *et al.*, 2017; Wang and Zhuang, 2017). Chitosan is an interesting polysaccharide to be explored regarding its application in removing heavy metals due to its availability in nature and special properties such as biocompatibility, biodegradability, non-toxicity, and metal ion chelation (Igberase *et al.*, 2017; Shariful *et al.*, 2017; Canas *et al.*, 2016). Therefore, chitosan has received special attention as an effective adsorbent for the adsorption of heavy metal ions from heavy metal contaminated waste (Vakili *et al.*, 2019).

Chitosan can remove heavy metals in industrial

waste because of the active groups -NH<sub>2</sub> and -OH which are highly reactive, can chelate, and are alkaline (Kyzas et al., 2017; Igberase and Osifo, 2015; Liao et al., 2016; El-Magied et al., 2018; Wu et al., 2018; Ren et al., 2019). Chitosan will exchange protons that are owned by heavy metals with electrons that are owned by nitrogen. However, chitosan is acid soluble which hinders the development of its application. This is the weakness of chitosan which can be overcome by chemical or physical modification of its molecule (Zhao et al., 2014). Modification of chitosan is done physically or chemically to make chitosan performance better (Rahayu and Khabibi, 2016). In recent years, a number of chitosan derivatives have been synthesized through physical and chemical modifications to improve flexibility, stability, susceptibility of chitosan to dissolving in acidic media, and its adsorption capacity.

The modification process that can be carried out on chitosan is by impregnation, crosslinking, and grafting. Impregnation has been performed using tricapry methyl ammonium (Ranjbari et al., 2020), dodecyl triphenyl phosphnium (Pascu et al., 2020), aluminum hydroxy (Yang et al., 2020), and ZnCl, (Kahu et al., 2017). Modification of chitosan is done to form an adsorbent that has high resistance to acid which can be done by crosslinking and grafting (Ramirez et al., 2020). Grafting and crosslinking are two common methods for improving the chemical properties of chitosan. Crosslink is a linkage of macromolecular chains to one another by adding a cross-linking agent. Chitosan is cross-linked such as using formaldehyde (Atangana, 2019), glyoxal (Mirabedini et al., 2016; Igberase and Osifo, 2019), gluteraldehyde (Atangana and Oberholster, 2019; Hiu, 2020; Bui et al., 2020; Atangana et al., 2020; Altun, 2020), epichlorohydrin (Yan et al., 2018), tripolyphosphate (Dong et al., 2016; Nitsae et al., 2016; Kong et al., 2017; Giraldo et al., 2017; Babakhani and Sartaj, 2020), ethylene glycol diglycidyl ether (Tsai et al., 2015), through covalent bonds that do not dissolve or break under extreme conditions such as in concentrated acids or in concentrated bases because they are more chemically stable. However, crosslinking can reduce the adsorption capacity because it uses part of the chitosan functional group. Therefore, a modification by grafting was used ie the addition of an additional functional group to the main frame (Zheng et al., 2016).

Although the decrease in the density of the amine groups on the adsorbent surface due to the cross-

linking results can reduce the reactivity of chitosan against metal ions, this can be compensated for by the active group of the crosslinking agent. In addition to cross-linking, to increase functional group density and expand the application of chitosan, chitosan modification can be done by attaching a functional group of different monomers or polymers to the active site of chitosan which is called the grafting method. This method is useful for increasing the adsorption capacity and selectivity of chitosan. Graft copolymerization can be carried out using various methods to increase amino acid density, including the ceric-induced graft copolymerization method, conventional grafting based on oxidation-reduction reactions, grafting with a-ray waves, electron beam, and grafting with microwave (Purwanto et al., 2013). Several studies on heavy metal adsorption with grafted chitosan are polyaniline (Vafakish and Wilson, 2020), poly (acrylic acid) (Maleki et al., 2015; Zhang et al., 2017; Zhang et al., 2019), poly (acrylamide) (Saleh et al, 2017), maleic acid (Zhuang et al., 2017), and poly (ethylenimine) (Yusof et al., 2019). Therefore, in this review article we will discuss adsorbent based on chitosan which can be modified to improve its adsorption performance which allows for better adsorption of heavy metal ions.

#### Modification of chitosan

#### Modification of chitosan by impregnation

Chitosan can be modified by adding other adsorbents such as silica, zeolite and activated charcoal. The presence of hydroxyl and amine groups causes chitosan to be chemically modified easily. Impregnation means the total saturation of certain substances. Modification of chitosan through impregnation or immobilization processes can be carried out using activating groups such as sulfate and humate to produce modified chitosan.

The results of impregnation of chitosan with various activating substances have been carried out such as with humic acid (Negm *et al.*, 2015). The immobilization process involves the main functional groups of humic acid -COO<sup>-</sup> and chitosan -NH<sub>2</sub>, where the main functional groups of chitosan which are activated in acidic solution will undergo protonation to produce a positive charge and the main functional groups of humic acid which are activated with a base will be deprotonated to produce a negative charge. The difference in charge between the two active sites allows electrostatic interactions to occur. This interaction can be seen in Figure 1.

The surface of Figure 1. impregnation of chitosan with humic acid (Negm *et al.*, 2015), chitosan acts as a buffer for humic acid molecules, which initially have an irregular shape which changes to a linear shape according to the chitosan surface, so that the immobilized active site of humic acid becomes more open. Thus, the number of active sites in immobilized humic acid increases so that the ability to adsorb metal cations will increase. The data on chitosan modification by impregnation using various compounds are shown in Table 1.

#### Modification of chitosan by crosslinking

Crosslinking is bonds that connect one polymer chain to another. Crosslinkers are compounds that have low molecular weight with more than two hydroxyl groups or amine groups. The cross-linking of chitosan can be carried out with one or more different cross-links to improve various properties such as the degree of development, the efficiency of removing certain pollutants, and increased selectivity (Kosheleva *et al.*, 2019).



Fig. 1. Impregnation of chitosan with humic acid (Negm et al., 2015)

Adsorbent Type	Reference
Chitosan-tannic acid	(Massoud <i>et al.</i> , 2018)
Chitosan-methyl trioctyl ammonium chloride	(Ranjbari <i>et al.,</i> 2020)
Chitosan-stanic chloride	(Kahu et al., 2017)
Chitosan-glycine	(Basu <i>et al.</i> , 2019)
Chitosan-diethylene triamine	(Mahfouz <i>et al.</i> , 2015)
Chitosan- thiourea	(Zhu et al., 2016)
Chitosan-thiosemicarbazide (TSCS)	(Ahmad et al., 2016)
Chitosan-ethylene diamine tetraacetic acid (EDTA)	(Labidi <i>et al.</i> , 2016)

Table 1. Modification of chitosan by impregnation

One of the modification of chitosan with cross linking is by using tripolyphosphate (TPP) (Babakhani and Sartaj, 2020). TPP is used as a crosslinking agent because this compound is a polyanion which reacts electrostatically with chitosan. The amine groups in chitosan interact with TPP which has a negative charge with ionic bonds to form cross bonds. The cross-link structure of chitosan and TPP is shown in Figure 2. Data on the modification of chitosan by cross-linking using various compounds are shown in Table 2.

# Modification of chitosan by grafting

Modification of chitosan with crosslinking provides a solution to its weakness because chitosan becomes insoluble in acidic media. However, this cross-linking process is known to have a low binding capacity in heavy metals because the chitosan amine



Fig. 2. The structure of the crosslinked chitosan. (a) Chitosan-TPP; (b) Chitosan-EDGE; (c) Chitosan-Glu

Table 2. Modification of chitosan by crosslinking

Adsorbent Type	Reference
Chitosan-TPP	(Babakhani and Sartaj, 2020)
Chitosan-ethyleneimine	(Lv et al., 2016)
Chitosan- diethylene triamine pentaaacetate	(Bhatt <i>et al.</i> , 2016)
Chitosan-trimesic acid	(Bhatt et al., 2017)
Chitosan-silicone	(Sshi <i>et al.</i> , 2016)
Chitosan-gluteraldehyde	(Chen and Wang, 2016; Nagireddi et al., 2017)
Chitosan-epichlorohydrin	(Li <i>et al.,</i> 2015)



Fig. 3. The structure of chitosan-TPP grafted acrylic acid.

group is involved in the reaction process. Therefore, grafting to improve the adsorption performance is important (Fang *et al.*, 2018).

Modification of chitosan by grafting is carried out by attaching a functional group of different monomers or polymers to the active site of chitosan such as acrylic acid. The goal is to increase the density of functional groups and expand the application of chitosan. Acrylic acid is used as a monomer for grafting because it has a double bond that allows copolymerization of grafting to occur (Zhang *et al.*, 2019). The structure of the grafted acrylic acid chitosan-TPP bond is shown in Figure 3. Data on grafted chitosan modification using various compounds are shown in Table 3.

# Removal heavy metal ions using modified chitosan

Chitosan with its active site is played by the N atom from the amine group  $(-NH_2)$  and the O atom from the hydroxyl group (-OH). Both of these atoms have free electrons which can bind protons or metal ions freely to form a complex. The lone pair interaction on the O atom is stronger than the lone pair interaction on the N atom, so that the N atom tends to do-

Tab	le 3.	Modi	fication	of	chitosan	by	grafting
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nate the lone pair more easily than the O atom. However, when chitosan is modified it is possible that the two active groups of chitosan will bind to metal ions. The amine group in chitosan will provide two free electrons to form covalent bonds with metal ions. In addition, there is also a breaking reaction of the H atom in the hydroxyl group, which causes O<sup>-</sup> to ionically bond with the metal ion.

The adsorption process is a complex process with the adsorption process scheme can be seen in Fig. 4.



Fig. 4. Schematic of the heavy metal ions adsorption process

In general, the interaction between modified chitosan and heavy metal ions can be seen in Figure 5.

The lone pair of this N atom will then bind to the metal ion, like the following reaction:

$$\text{R-NH}_2 + \text{H}^+ \rightarrow \text{R-NH}_3^+ \tag{1}$$

The reaction (1) above shows the protonation and deprotonation of the amino groups in chitosan. When chitosan is added to a metal ion solution, the following reactions may occur:

$$R-NH_2 + M^{2+} \rightarrow R-NH_2M^{2+} \quad .. (2)$$

Adsorbent Type	Reference
Chitosan-aniline	(Vafakish and Wilson, 2020)
Chitosan-poly (glycidyl methacrylate)	(Kosheleva et al., 2019)
Chitosan-poly (acrylic acid)	(Lim et al., 2017)
Chitosan-hydroxy ethyl methacrylate	(Vijayasri and Tiwari, 2019)
Chitosan-dimethyl acrylamide	(Perez-Calixto et al., 2016)
Chitosan-PEGMA	(Kongkaoroptham et al., 2019)
Chitosan-HEMA	(Elbarbary and Ghobashy, 2017)



Fig. 5. The interaction between modified chitosan and heavy metal ions

 $R-NH_3^+ + M^{2+} \rightarrow R-NH_2M^{2+} + H^+$  .. (3) R is a component other than the  $-NH_2$  group in chitosan and M is a metal.

When reaction (2) takes place, the free electrons from the N atom interact with the metal ion. Reaction (3) has the same mechanism as reaction (2), although the -NH<sub>2</sub> group of chitosan has changed to become positively charged due to receiving H<sup>+</sup> ions from the environment. The interaction between metal ions and N atoms in reaction (2) is stronger than the bond between H<sup>+</sup> ions and N atoms in reaction (3) (protonation of amino groups). This is because the strength of the electrostatic interaction between the lone pair of the N atom and the metal ion is stronger than the electrostatic interaction between the lone pair of the N atom and the proton H<sup>+</sup> (Sutirman *et al.*, 2016).

#### Heavy metals

#### Lead (Pb)

Lead (Pb) has an atomic number of 82 with an atomic weight of 207.20 g/mol. Pb is a type of heavy metal that is often referred to as lead. Pb is very dangerous for living things because it is carcinogenic, can cause mutation, decompose in a long time and its toxicity does not change.

Pb can pollute the air, water, soil, plants, animals, and even humans. The entry of Pb into the human body can be through food from plants that are commonly consumed by humans such as rice, tea and vegetables. Pb metal is found in waters both naturally and as a result of human activities. The critical limit or threshold for Pb metal in waters as a result of industrial waste is 0.01 ppm (WHO, 1995). This metal enters the waters through the crystallization of Pb in the air with the help of rainwater. In addition, the corofication process of mineral rock is also one of the pathways for Pb to enter the waters. If this metal enters the human body it can cause poisoning. Pb poisoning will cause symptoms such as a metallic taste in the mouth, black lines on the gums, vomiting, personality changes, paralysis, and blindness. Other symptoms of poisoning include anemia and albuminuria. Acute poisoning can lead to death (Atangana, 2019).

#### Cadmium (Cd)

Cadmium (Cd) is a chemical element in the periodic table which has the symbol Cd with atomic number 40, atomic weight 112.4 g/mol. CD can be found in plating wastewater, the ceramic industry, photographic products, the pigment industry, the chemical synthesis industry, and can be found in the soldering process washing wastewater. The human body does not need Cd in its function and growth, because Cd is very toxic to humans.

Cd in wastewater is generally limited to a concentration of less than 0.1 ppm (WHO, 1995). Acute poisoning will cause gastrointestinal symptoms and

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kidney disease. The clinical symptoms of Cd poisoning are very similar to those of ordinary glomerulonephiritis. Only in the advanced phase of Cd poisoning are spinal softening and fractures found. Symptoms are back pain, fractures, high blood pressure, kidney damage, and influenza-like symptoms (Babakhani and Sartaj, 2020).

# Copper (Cu)

Copper (Cu) is a heavy metal having an atomic number of 29 and an atomic weight of 63.55 g/mol in the metallic form it has a reddish color, but is more often found in the form of bonds with other ions such as sulfates so that it has a different color than pure copper metal. Cu has a threshold range of 2 ppm (WHO, 1995). Cu is actually necessary for the development of the human body. However, in high doses it can cause gastrointestinal symptoms, kidney, liver, vomiting, headaches, weakness, anemia, and even death. In low doses it causes abrasiveness, color, and corrosion of pipes, fittings and kitchen utensils (Ali *et al.*, 2016).

# Zinc (Zn)

Zinc (Zn) is an element with the symbol Zn, has an atomic number of 30, and an atomic mass of 65.37 g/mol. Zn is a metal that has fairly reactive characteristics, is bluish-white, fades when exposed to air vapor, and burns when exposed to air with bright green flames. Zn can react with acids, bases, and non-metal compounds.

Zn with a threshold in waters for contaminants with industrial waste is 5 ppm (WHO, 1995). The

body requires Zn for metabolic processes, but at high levels, it can be toxic. In water, it will feel choked and can cause vomiting symptoms (Atangana, 2019). Zn is also used in various types of industries such as paints, rubber products, cosmetics, pharmaceuticals, floor coatings, plastics, printing, ink, batteries, textiles, electrical equipment, as a chemical, and also for metal galvanizing, especially for coating iron and steel from corrosion.

#### Factors affecting adsorption

# pН

The pH at which the adsorption process occurs shows a great influence on the adsorption itself. This is because the hydrogen ion itself is strongly adsorbed, in part. After all, pH affects ionization and hence the adsorption of some compounds. The NH, group in chitosan is the main reactive group



Fig. 6. The results of pH optimization test using chitosanglu grafted EDTA (Igberase and Osifo, 2020).

<b>Table 4.</b> List of pH optimization of several types of adsorbents and adsorbates usin	g modified	chitosan
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Adsorbate	pH Test Range	Optimum pH	Reference
Pb (II)	2-8	5	(Igberase <i>et al.,</i> 2017)
Cd (II)		6	
Cu (II)		5	
Zn (II)		6	
Cu (II)	4-8	6,5	(Reddi <i>et al</i> , 2017)
Pb (II)	2-8	5,7	(Igberase and Osifo,
Cd (II)		6,0	2019)
Cu(II)		5,7	
Zn (II)		5,9	
Pb (II)			
Cd (II)			
Cu (II)			
Zn (II)	3-8	5	(Giraldo <i>et al.,</i> 2017)
	Adsorbate Pb (II) Cd (II) Cu (II) Zn (II) Cu (II) Pb (II) Cd (II) Cu(II) Zn (II) Pb (II) Cd (II) Cd (II) Cu (II) Zn (II)	Adsorbate pH Test Range   Pb (II) 2-8   Cd (II) 2-8   Cu (II) 4-8   Pb (II) 2-8   Cd (II) 4-8   Pb (II) 2-8   Cd (II) 3-8	Adsorbate pH Test Range Optimum pH   Pb (II) 2-8 5   Cd (II) 6 6   Cu (II) 5 7   Zn (II) 6 6,5   Pb (II) 2-8 5,7   Cd (II) 6,0 6,0   Cu (II) 5,7 7,7   Zn (II) 5,7 7,7   Zn (II) 5,9 7,9   Pb (II) 2-8 5,9   Cd (II) 5,9 7,9   Pb (II) 2-8 5,9   Zn (II) 3-8 5

for metal ion adsorption. Although, OH groups can also contribute to adsorption. The pH value has a different effect on metal adsorption into the chitosan adsorbent. For most metals, the adsorption capacity of the adsorbent increases with increasing pH but can fall at very high pHs (Yu *et al.*, 2016; Sargin and Arslan, 2015).

Similar results were observed for the adsorption of Cd(II) and Pb(II) to PGC (Karthik and Meenakshi, 2015). Increasing the pH from 2 to 6 the adsorption capacity increases and the optimum for both metal ions is at pH 6. As for the adsorption of Cd(II) using TPP cross-linked chitosan with a pH range of 4-8, the optimum at pH 7 (Pal and Pal, 2017). The chitosan-g-PMAm crosslinking pH 2-6 for the adsorption of Cu(II) and Cd(II) was optimum at pH 4 and 5 (Sutirman et al., 2018), respectively. Chitosang-itationic acid for Pb(II) adsorption with the optimum pH range 1-6 at pH 5 (Ge et al., 2017). Lower pH is unfavorable for adsorption due to electrostatic repulsion between heavy metal cations and protonated chitosan, as well as the completion of adsorption between H<sup>+</sup> and metal ions to form chitosan (Pakdel and Peighambardoust, 2018). At pH close to neutral, absorption can occur via chelation on -NH<sub>2</sub> or -OH groups (because Lewis bases donate electron pairs) and metal ion groups providing empty orbitals (because Lewis acids accept electron pairs (Vakili et al., 2019). PH optimization data of several types of adsorbent and adsorbate using modified chitosan are shown in Table 4.

#### Temperature

The temperature at which the adsorption process occurs will affect the speed and amount of adsorption that occurs. The adsorption rate increases with increasing temperature and decreases with decreasing temperature. However, when adsorption is an exothermic process, the degree of adsorption increases at lower temperatures and decreases at higher temperatures. The effect of temperature on the adsorption efficiency using chitosangluteraldehyde grafted amino benzoate is shown in Figure 7.

Several other studies also found that the adsorption capacity of Pb (II) using CS-g-IA increased from 25 to 65°C, and was found to be optimum at 45°C. The temperature increase accelerates the binding of metal ions until it reaches the optimum temperature (Kyzas *et al.*, 2014). The adsorption of Pb(II), Cd(II)

and Zn(II) on CEA was studied at five temperatures (25–65 °C) (Maleki *et al.*, 2015). The results showed that the adsorption capacity slightly increased with increasing temperature. The results were similar for the adsorption of Cd(II) and Zn(II) to CSTU with a temperature range from 20 to 40 °C and the optimum temperature was observed at 30 °C (Monier and Abdel-Latif, 2012). Lalita *et al.* (2017) adsorbed Cu(II) ions using chitosan-g-isopropylacrylamide to obtain the optimum temperature at 30°C.

The increase in adsorption at higher temperatures is due to the strengthening of the interaction between the metal ion and the active site. In addition, higher temperatures will also affect more particle mobility and reduce the viscosity of the liquid. Conventionally, the adsorption process takes place in two processes, namely fast diffusion and slow complexation. The increase in temperature will not only accelerate the diffusion rate of metal ions from the solution to the adsorbent surface, but also accelerate the complexation of metal ions with adsorbent functional groups (Wu *et al.*, 2018; Gupta *et al.*, 2019; Hadiani *et al.*, 2019; Noormohamadi *et al.*, 2019; Xu *et al.*, 2019).



Fig. 7. Effect of temperature on adsorption efficiency using chitosan-glu grafted amino benzoate (Igberase *et al*, 2017).

#### Contact time

Contact time is something that really determines the adsorption process. The contact time allows the diffusion and adhesion of the adsorbate molecules to take place better.

Increasing the contact time, the more adsorbed

metal ions. However, at a certain time the number of metal ions adsorbed decreases because part of the active surface of the adsorbent has bonded with the metal. At a certain time limit, there is an equilibrium state where the adsorbent is unable to absorb the metal or the adsorbent surface is saturated. The effect of contact time on adsorption efficiency using chitosan-gluteraldehyde grafted ethyl acrylate is shown in **Figure 8**.



Fig. 8. Effect of contact time on adsorption efficiency using chitosan-gluteraldehyde grafted ethyl acrylate (Igberase *et al.*, 2019).

Shankar et al. (2014) also observed that the adsorption efficiency of Cu(II) using CS-g-AN increased with increasing contact time, and the maximum removal was observed at 360 minutes. The Cu (II) adsorption study used CS-gPAA with contact time from 0 to 180 minutes (Sugashinia and Begum, 2013), and the results showed that the adsorption capacity increased rapidly with an increase in contact time from 0 to 20 minutes and the adsorption equilibrium at the contact time of 15 minutes. Aliabadi et al. (2013) investigated the effect of contact time on the adsorption of Pb(II), Cd(II), Cu(II) and Ni(II) using CS / PEO, and their results showed that more than 80% of the total metal ion adsorption occurred in The first 60 minutes and then it reaches adsorption equilibrium after about 120 minutes.

The effect of contact time on the adsorption of Pb(II), Cd(II), Cu(II) and Zn(II) metal ions using cross-linked chitosan gluteraldehyde grafted ethyl acrylate shows that increasing contact time will increase the interaction time between the active sites in the adsorbent and the ion. metal in solution which in turn increases metal ion uptake (Okoli *et* 

*al.*, 2017). It is observed that 40 minutes is sufficient to reach equilibrium for all metal ions. Adsorption is faster at the start of the adsorbent interaction with metal ions because the available sites for the binding of metal ions are more, but becomes slower until equilibrium is reached because the binding site has been covered with metal ions causing repulsion with increasing time (Igberase and Osifo, 2020). With increasing contact time, more metal ions are absorbed. It can be seen from the optimum contact time for Pb(II), Cd(II), Cu(II), and Zn(II) at 40 minutes and has reached the equilibrium point (Atangana, 2019).

# Initial adsorbate concentration

The effect of the initial metal concentration on the adsorption process is usually investigated to determine the dependence of the initial metal ion concentration in the aqueous phase and the metal adsorption capacity of the adsorbent. The absorption of metal ions depends on the initial concentration and will increase with the increase in the initial concentration. The effect of the initial adsorbate concentration on the adsorption efficiency using chitosangrafted polyaniline is shown in Figure 9.



**Fig. 9.** Effect of initial metal ion concentrations on adsorption efficiency using chitosan-grafted polyaniline (Igberase and Osifo, 2015).

The lower the initial metal ion concentration, there is sufficient binding site for Pb(II) and Cd(II). At higher concentrations, there is a greater driving force to adsorb metals, but the amount of Pb(II) and Cd(II) is quite high compared to the available adsorption sites (Igberase and Osifo, 2015). Adsorption of Cu(II) using CS-MMT with various variations in the initial concentration of adsorbate (60, 70, 80, 90, and 100 ppm) has an adsorption capacity that continues to increase with an increasing initial concentration of the adsorbate (Ngwabebhoh *et al.*, 2016). Therefore, the adsorption percentage of heavy metal ions is highly dependent on the initial ion concentration and decreases as the initial ion concentration increases.

# Adsorbent Mass

The adsorbent mass greatly affects the metal ion adsorption process from the adsorbent. The use of adsorbent mass also greatly affects the adsorption capacity. The higher the adsorbent mass, the more likely metal ions will be adsorbed, and the adsorption capacity will decrease. The decrease in adsorption capacity is caused by the presence of active adsorbents which have not all bonded to the adsorbate. The effect of the adsorbent mass on the adsorption of Cd (II) is shown in Figure 10.



Fig. 10. Effect of adsorbent mass on adsorption of Cd(II) (Babakhani and Sartaj, 2020).

Figure 10. Shows the effect of the adsorbent mass on the adsorption of Cd(II) ions using TPP crosslinked chitosan. It can be seen from the graph that the percentage of metal adsorption increases with increasing dose. This can be attributed to the increase in the number of absorption sites available for metal adsorption. This observation is the result of the increasing presence of available adsorption sites for the interaction of Cd(II) and chitosan. However, the adsorption capacity experienced the opposite, decreasing from 101.1 mg/g to 43.9 mg/g as the adsorbent mass increased. The decrease in adsorption capacity is due to the presence of active adsorbents which have not all bound to the adsorbate (Babakhani and Sartaj, 2020).

Adsorption of Cu(II), Cd(II) and Pb(II) using EDCMS with adsorbent mass from 0.5 to 1.5 g (Ren et al., 2013). The results showed that the adsorption efficiency increased rapidly with an increase in the mass of the adsorbent from 0.5 to 1.0 g, but the adsorption capacity did not have a significant change in the range of 0.5 to 1.0 g and then decreased drastically. Similar studies for the adsorption of Cd(II) and Pb(II) to GXCS were studied with the adsorbent mass varying from 1.5 to 6.5 g (Igberase and Osifo, 2015). The result is that the adsorption capacity increases sharply from 1.5 to 4.5 g then reaches equilibrium. Salah et al. (2014) found that the adsorption of Cd(II) increased rapidly with increasing nHAp dose, which could be due to the increase in available adsorption sites.

#### Adsorption kinetics and thermodynamics

#### Adsorption kinetics

Pseudo-first-order and Pseudo-second-order models were used to adjust the kinetic data. Recent studies have shown that a Pseudo-second-order kinetic model provides a better fit for adsorption data.

This Pseudo-first-order model study aims to describe the adsorption in the liquid-solid phase using the Pseudo-first-order kinetics model as presented in Equation (1).

$$\frac{dq_t}{d_t} = kp_1(q_t - q_t) \tag{1}$$

This equation was formulated by Lagergren, 1898, who proposed that the kinetics equation had been used to describe the adsorption of adsorbate from an aqueous solution. The linear form of the pseudo-order one kinetics model as proposed by Lagergren is presented in Eq. (2)

$$ln\left(q_{e}-q_{t}\right) = lnq_{e}-kp_{1}t \qquad ..(2)$$

where  $q_e$  is the number of metal ions adsorbed at equilibrium (mg/g), qt is the number of metal

Table 5. The Adsorption kinetics model of Zn(II) and Pb(II) ions

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Kinetics Model	Metal Ions	R <sup>2</sup>	Slope	Intercept	k <sub>s</sub>	$q_e$
Pseudo-first-orde	Zn(II)	0,9814	0.0779	9,126	0,967	0,0834
	Pb(II)	0,9382	0,0668	11,250	0,914	0,0802
Pseudo-second-order	Zn(II)	0.9960	20,19	4,239	11,717	0,0890
	Pb(II)	0,9687	31,48	3,276	8,828	0,0760

ions adsorbed at time t (mg/g);  $kp_1$  is a constant of first-order (min<sup>"1</sup>) and t is time (min). Linearity between the two parameters  $ln (q_e-q_t)$  and t is therefore expected, provided that the adsorption process follows first-order kinetics. Figure 11. shows the Pseudo-first-order kinetic model and the R<sup>2</sup> values are 0.9383 (Pb(II)) and 0.9814 (Zn(II)).



Fig. 11. Pseudo-tirst-order kinetics model of Pb (II) and Zn (II) Ions using formaldehyde crosslinked chitosan (Atangana, 2019)

The Pseudo-second-order kinetics model uses equation (3)

$$\frac{t}{q_t} = \frac{1}{k_s q_s^2} + \frac{1}{q_s} t \qquad ...(3)$$

where t is time (minutes),  $k_s$  is the rate constant of the second-order Pseudo-second-order kinetic model (g/mg/min), and  $q_e$  is the equilibrium ion concentration (mg ion/g adsorbent). The t/q<sub>t</sub> plot gives the linear form of this equation if the adsorption follows the Pseudo-second order model according to Figure 12. As shown in Table 5, and can be calculated from the slopes and intersections of the plots.

Yan et al. (2012) reported that the Pseudo-second-



**Fig. 12.** Pseudo-second-order kinetics model of Pb(II) and Zn(II) ions using formaldehyde crosslinked chitosan (Atangana, 2019)

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order model is more appropriate for describing the behavior of the adsorption kinetics for Cu (II) ions to MCM. Similar conclusions were observed in other studies, based on adsorption kinetic studies of Cu(II) ions with initial concentrations ranging from 10 to 40 mg/L (Sikder *et al.*, 2014). Karthik and Meenakshi (Karthik and Meenakshi, 2015) found that the adsorption of Pb(II) and Cd(II) to PGC followed Pseudo-second-order kinetics.

#### Thermodynamics

Gibbs energy ( $\Delta$ G), enthalpy ( $\Delta$ H), and entropy ( $\Delta$ S) are thermodynamic parameters in the adsorption process which are determined using Equations 4, 5, and equation 6 as follows:

$$\Delta G = H - \Delta S \qquad \dots (4)$$

$$Kc = \frac{q_e}{c} \qquad .. (5)$$

$$\ln \mathrm{Kc} = \frac{\mathrm{S}}{\mathrm{R}} - \frac{\mathrm{H}}{\mathrm{RT}} \qquad .. (6)$$

where Kc, qe, Ce, R, and T are the equilibrium constant, the amount of metal adsorbed by the adsorbent at equilibrium (mol/g), the concentration of metal equilibrium in solution (mol/L), the gas constant (8.314 J/mol K), and temperature (K). By plotting the graph of ln Kc against 1/T, the values of  $\Delta$ H and  $\Delta$ S can be estimated from the slopes and points of intersection. The thermodynamic parameters obtained are given in Table 6.

Positive  $\Delta$ H and  $\Delta$ S values indicate that the reaction is endothermic. The negative value  $\Delta$ G implies the spontaneous nature of the adsorption process. The decrease in  $\Delta$ G value with increasing temperature indicates that the adsorption process is more spontaneous at higher temperatures. In general, the free energy change for physisorption is between 20 and 0 kJ/mol, but for chemisorption, it is in the -80 to -400 kJ/mol range. The  $\Delta$ G values obtained are within the range of the physisorption mechanism (Maleki *et al.*, 2015). The same result was also found in the research of Babakhani and Sartaj (Tsai *et al.*, 2015) with a negative  $\Delta$ G value which indicated the spontaneous nature of Cu (II) adsorption using TPP cross-linked chitosan.

#### Characterization of modified chitosan

# pH<sub>PZC</sub> (Point Zero Charge)

Characterization of  $pH_{PZC}$  is to adjust the pH at the point of intersection of the X axis at line 0. Done by

Metal Ions	ΔH	ΔS	R <sup>2</sup>		Δ	G	
				T(K)			
				298	308	318	328
Pb(II)	135.5	81.4	0.991	-24.1	-24.9	-25.7	-26.5
Cd(II)	10.1	8.3	0.986	-2.4	-2,5	-2.6	2,7
Zn(II)	85.3	85.3	0.954	-98.9	-102.3	-105.6	-108.9

Table 6. Thermodynamic parameters of the adsorption of Pb(II), Cd(II), and Zn(II)

varying the initial pH and then looking for  $\Delta pH$ , which is the difference between the initial pH and the final pH after several treatments. Then from the  $\Delta pH$  data a graph will be made of the X axis and Y axis. At the intersection of the X axis line 0 which is called  $pH_{PZC}$ . The amount of  $pH_{PZC}$  in a sample is different because it is treated with different treatments.

*Point Zero Charge* is the point where the surface functional groups of acids or bases no longer contribute to the pH value of the solution. The  $pH_{PZC}$  as shown in Figure 13. was found to be around 4.6 and 4.2 for chitosan and PGCB respectively. A similar observation was reported for chitosan-tripolyphosphate beads which is about 4.0 (Ngah and Fatinathan, 2010). The decrease in the  $pH_{PZC}$  value obtained for PGCB was caused by grafting, because the hydrogen ions present on the bead surface after grafting were released into the solution, thus lowering the pH. Furthermore, adsorption of cations will be advantageous at pH values higher than pH<sub>PZC</sub>, and adsorption of anions at pH values lower than  $pH_{PZC}$ . As for the modification of chitosan with chitosan-glu grafted ethyl acrylate, it was found that the  $pH_{PZC}$  of the adsorbent was 3.8 (Igberase *et al.*, 2014) as shown in Figure 14.

#### FTIR Spectroscopy (Fourier Transform Infrared)

When a material is exposed to electromagnetic



**Fig. 13.**  $pH_{PZC}$  of chitosan and modified chitosan (Igberase and Osifo, 2015)

wave radiation, energy absorption will occur by atoms or molecules of the material. A compound can absorb electromagnetic wave radiation at a certain wavelength, depending on the structure of the compound. FTIR (Fourier Transform Infrared) is an infrared spectroscopy method that is equipped with Fourier transforms to analyze the spectrum results. The spectroscopic method used in FTIR is the adsorption method, which is a method based on differences in the absorption of infrared radiation.



**Fig. 14.** pH<sub>PZC</sub> of chitosan and chitosan-glu grafted ethyl acrylate (Igberase *et al.*, 2014)

The FTIR spectrum of unmodified chitosan showed a strong peak width at 3434 cm<sup>-1</sup> which was attributed to the overlap between the -NH<sub>2</sub> and -OH stretching vibrations and the hydrogen-bonding of the polysaccharide. The same is true for the modifi-



Fig. 15. FTIR spectrum of chitosan and chitosan-glu grafted PMAm (Igberase *et al.,* 2017)

cation of grafted ethyl acrylate chitosan which is 3449 cm<sup>-1</sup> as shown in Figure 16.



Fig. 16. Spectrum FTIR (a) chitosan, (b) CEA, (c) CEA-Zn (Maleki *et al.*, 2015)

The characteristic peak of the symmetric and asymmetric -CH<sub>2</sub> groups can be observed at 2923 cm<sup>-1</sup>. This clearly shows the absorption peak of the chitin portion of the chitosan at 1649 cm<sup>-1</sup> (C-O stretch). The peaks at 1423 cm<sup>-1</sup> and 1380 cm<sup>-1</sup> were associated with C-N bond stretching and C-H deformation, respectively, while the peaks at 1080 cm<sup>-1</sup> were associated with C-O strain vibrations.

Meanwhile, the chitosan-g-PMAm cross-linking spectrum showed a significant variation in intensity and peak shift. The absorption peak at 3439 cm<sup>-1</sup> was due to the typical strain vibrations of the -OH and -NH<sub>2</sub> groups (Igberase *et al.*, 2017). This slight change in peak intensity with respect to chitosan indicates that a large amount of NH<sub>2</sub> / OH in chitosan is involved in the cross-linking and grafting reactions.

The new peak at 1731 cm<sup>-1</sup> is caused by the vibrational C-O strain of the aldehyde. The presence of this group may result from unreacted glutaraldehyde tips or self-polymerization. In addition, a peak at 1636 cm<sup>-1</sup> indicates a C-O stretch. This shift in frequency compared to chitosan is due to the inclusion of MAm, which further confirms grafting. The spectrum also shows the peaks referring to the C-N stretching vibration at 1120 cm<sup>-1</sup> and 1023 cm<sup>-1</sup> (Gupta *et al.*, 2019).

As for Figure 16. for Figure b, the peak located at  $1074 \text{ cm}^{-1}$  which is fixed to the C-O stretch bond remains unchanged, before and after modification. The peak intensities in Figure c are in the range of 3449, 1700, and 1074 cm<sup>-1</sup> decreasing, which may be due to the involvement of the corresponding OH, C=O and C-O functional groups in the adsorption of Zn<sup>2+</sup> ions from solution (Maleki *et al.*, 2015).

#### XRD (X-Ray Diffraction)

Characterization with XRD was carried out to determine the crystalline phase of a material by determining the lattice parameters and crystal structure and to obtain the size of a crystal. The basic principle of XRD is to diffract the light that passes through the crystal gap.

The crystallinity of chitosan and modified chitosan was tested by XRD instrument. The crystalline nature exhibited by chitosan prevents some functional groups from binding successfully with metal ions (Igberase and Osifo, 2015). Figure 14. illustrates the diffraction of CS (chitosan), CCS (gluteraldehyde cross-linked chitosan), and GCCS (gluteraldehyde cross-linked chitosan and grafted EDTA). We have observed a general feature of  $2\theta = 20^{\circ}$ , which corresponds to 110 chitosan fields, this is because it is possible to modify chitosan and still retain some of its properties. As a result, there is an increase in intensity from about 852 to 1054 a.u when chitosan is cross-linked with glutaraldehyde



Fig. 14. XRD (a) CS; (b) CCS; (c) GCCS (Igberase and Osifo, 2020)

and this may be due to the fact that the chitosan amine group is involved in the cross-linking process. When the cross-linked chitosan was grafted with EDTA the intensity was reduced to about 751 a.u, this observation may be due to the fact that the crystal chain had decreased during the grafting process (El-Magied *et al.*, 2018). Likewise, the modification of chitosan with iodate (CS-I) shows that  $2\theta =$  $20^{\circ}$ , the XRD pattern of CS-I composites after Pb(II) adsorption shows some additional crystal peaks associated with Pb(II) adsorption as shown in Fig. 18.



Fig. 18. XRD (A) Chitosan (B) CS-I before adsorption of Pb(II) (C) CS-I after adsorption of Pb(II) (Gedam and Dongre, 2015)

# SEM (Scanning Electron Microscopy)

SEM was used to determine themorphological structure surface of the modified chitosan.



Fig. 19. SEM chitosan and chitosan *grafted* PAA (a5000x,b30,000x) dan CS-g-PAA(c5000x,d 30,000x) (Lin *et al.*, 2017)

Based on the SEM analysis of Figure 19., chitosan and CS-g-PAA, it is clear that chitosan displays a smooth and non-porous surface. In contrast, the surface of CS-g-PAA is clearly rough and porous, providing a large surface area for adsorption purposes because it can be absorbed into the modified chitosan pores. The same results were obtained from the CS-PEI-GLU shown in Figure 20.



Fig. 20. SEM (a) CS and (b) CS-PEI-GLU (Yusof *et al.*, 2019)

SEM of CS shows a smooth and even surface. There was an irregular and rough surface with visible pores for CS-PEI-GLU. These pores allow for more adsorption sites to be adsorbed as they can diffuse into CS-PEI-GLU (Yusof *et al.*, 2019).

# TGA (Thermographic Analysis)

Characterization with TGA aims to determine the graph of heat addition to a particle mass. Heat is added periodically. A plot of wt% against tempera-



Fig. 21. TGA of XB, XXB and GXXB (Igberase et al., 2017)

ture was carried out to see the thermal stability of chitosan, chitosan-glu, and chitosan-glu grafted ethyl acrylate which is shown in Figure 21.

The weight loss in chitosan is thought to come from the depolymerization and decomposition of the acetylated and deacetylated adsorbent units where the breakdown of chitosan is not crosslinked (Hao *et al.*, 2016). The weight reduction in chitosanglu and chitosan-glu grafted acrylic acid was in accordance with the removal of surface water, depolymerization and decomposition of the acetate adsorbent unit and the deacetylation and decomposition of crosslinked chitosan respectively (Omorogie *et al.*, 2016).

Figure 22. It can be seen that CS is lower than CS-DEO. This shows that the cross-linking reduces the weight loss of chitosan at high temperatures, and the thermal decomposition of chitosan is increased by cross-linking treatment. This could be due to the newly formed bonds between the chains of chitosan molecules which cross-link the molecules and cause an increase in the decomposition temperature (Vakili *et al.*, 2019).



Fig. 22. TGA (a) CS and (b) CS-DEO (Vakili et al., 2019)

#### **BET-BJH**

The size of the surface area (BET) and pore size (BJH) can be identified through BET-BJH characterization. By knowing the structure of the chitosan

Table 7. Results of the BET-BJH analysis

nanoparticle synthesis results through previous characterization, chitosan nanoparticle samples can be characterized by BET as shown in Table 7. (Gedam and Dongre, 2015).

It can be seen that the surface area of the I-CS adsorbent BET is smaller than pure chitosan. Therefore it can be concluded that I-CS physisorption for Pb (II) ion is limited and chemosorption is the main adsorption mechanism due to the active binding site for Pb (II) ion (Gedam and Dongre, 2015). As the analyzed pore diameter size also increases after modification, the clogged pores will become micropores, resulting in a decrease in surface area and total pore volume.

As a comparison, the BET surface area of CS-Dt is greater than that of Dt, which confirms that the CS adhering to the Dt surface increases the specific surface area of CS-modified Dt. Meanwhile, the mean pore diameter of CS modified Dt was higher than that of crude Dt due to modification (Yang *et al.*, 2020). Given the large specific surface area and porous structure of the CS modified Dt, it can provide more adsorption sites and is a good adsorbent.

Table 8. Results of the BET-BJH analysis

Sampel	BET (m <sup>2</sup> /g)	Pore diameter (nm)
Dt	19.303	9.998
CS-Dt	148.251	5.185

#### Desorption and reusability

Desorption or regeneration of adorbent is an important parameter in evaluating the efficiency of an adsorbent. Regeneration is defined as the rapid recycling or recovery of used adsorbents or adsorbents that have been used using technically feasible and economically feasible methods.

Low-cost is an important factor in the process of synthesis adsorbent. Therefore, regeneration of the used adsorbent is very important to remove contaminants from waste. Modified chitosan regeneration can give many advantages, such as: (i) recovery of pollutants, (ii) reuse of adsorbents, (iii) reducing costs, (iv) reducing secondary waste, and (v) identifying adsorption mechanisms. Currently, HCl,

Adsorbent	BET $(m^2/g)$	v <sub>total</sub> (cm <sup>3</sup> /g)	$v_{micro}(cm^3/g)$	v <sub>meso</sub> (cm <sup>3</sup> /g)	Pore diameter (nm)
CS	3.5	4.582	4	5.82	5.23
CS-I	0.87	2.126	1.18	9.46	9.77



Fig. 16. Scheme procedure regeneration of adsorbent chitosan

NaOH,  $H_2SO_4$ ,  $HNO_3$ , EDTA, and DPTA solutions as eluents have been widely used for the modified chitosan desorption process.



Fig. 17. Desorption of heavy metal ions with modified chitosan (Igberase and Osifo, 2019)

HCl was used as a desorption agent for Cd(II) and Pb(II) ions using cross-linked chitosan gluteraldehyde grafted polyaniline, 98.94% and 97.5% for each metal with five cycles (Ren *et al.*, 2019). The use of HCl can also be seen in the desorption of Pb (II), Cu (II), Ni (II), and Cd (II) ions using glyoxal grafted diethylenetriamine cross-linked chitosan. The results obtained indicate that there is no significant change in the desorption efficiency. A loss of 0.0% in mass was observed in the third cycle, which may be due to the use of HCl on the metalloading adsorbent resulting in opening of pores for subsequent adsorption (Igberase and Osifo, 2019). Similar reports presented 4-aminobenzoic acid grafted on epichlorohydrin to remove metal ions in batch systems (Sargin and Arslan, 2015). As for using  $\text{HNO}_3$  with the same adsorbent for the desorption of Pb (II) and Cd (II) ions, the decrease did not change significantly even after the third cycle for Pb(II), while the Cd(II) ion decreased significantly with increasing number cycle up to the third cycle (Ngah and Fatinathan, 2010).

# Conclusion

Chitosan as adsorbent has received considerable attention from researchers due to its specific characteristics such as low cost, excellent adsorption performance, biocompatibility and eco-friendly, biodegradability, and bioactivity. To improve the adsorption performance of chitosan, impregnation, crosslinking and grafting methods were used to obtain modified chitosan. This modified chitosan has many advantages, such as the absence of secondary pollution, easy regeneration, and strong bonding ability for heavy metal ions, and its adsorption capacity for heavy metal ions is superior to conventional adsorbents. The adsorption of heavy metal ions using modified chitosan shows that functional groups on its surface are mostly responsible for binding heavy metal ions by electrostatic force or covalent bonds. The optimal results of the modified chitosan were seen by characterization using FTIR, XRD, SEM, and desorption to see the adsorption efficiency. The adsorbent based on chitosan and its

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modification allows for better adsorption of heavy metal ions.

The adsorption of heavy metal ions using modified chitosan has major advantages over conventional adsorbents as long as the following are considered: (i) the modified chitosan preparation method should be simplified and easily controlled, (ii) to find the optimal process parameters and obtain the maximum adsorption capacity of metal ions weight to the modified chitosan, (iii) more attention should be paid to developing environmentally friendly and multipurpose chitosan modifications; and (iv) greater effort in estimating production and application costs.

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