

**Cross-linked chitosan-based adsorbents: a comparative review of recent chemical modifications and their mechanisms for the removal of heavy metals from wastewater.**

A report submitted as the examined component of the Project Module SXC390.

Gina McNaught

The Chemistry of Biopolymers

21 August 2024

*4982 words*

## Abstract

Chitosan is a highly useful, abundant non-toxic and versatile natural material derived from chitin, which is found in the shells of shrimp and crustaceans. Among various uses across industries, it's a feasible wastewater treatment and can be used as an adsorbent for heavy metals. It's polymeric chain has -OH and -NH<sub>2</sub> functional groups which can chelate metal ions and provide electrostatic interaction and make chitosan readily available for chemical modification.

Whilst chitosan is a useful adsorbent, drawbacks include low strength and instability in acid. Crosslinking somewhat resolves these issues; however, it uses vital functional groups that would otherwise provide adsorption sites. Therefore, further modification of chitosan including grafting and combining with other materials to improve adsorption of heavy metals.

This literature review covers recent modification of crosslinked chitosan. Common structures were found to be aerogels, hydrogels, beads and microspheres, nanoparticles, membranes and composites. General mechanisms of adsorption discussed are chelation, complexation, electrostatic interaction and ion exchange. The literature search methods included use of Google Scholar as well as more detailed searching using Scopus database where the keywords used were *cross linked*, *chitosan*, *heavy metals* and *wastewater* between 2019-2024.

The role of chitosan in the modified adsorbent was deduced to fall generally into use as a starting material, part of combined adsorbents, providing increased selectivity, and in some cases a negative effect towards adsorption. Among the most successful modifications were addition of 3-indoleacetic acid, multiple walled carbon nanotubes, acid activated bentonite clay, amidoxime functionalised polyacrylamide,  $\beta$ -cyclodextrin, 4-aminobenzoic acid, methionine-glutaraldehyde and iron and polyvinyl alcohol and alginate. Possible adsorption mechanisms leading to success were discussed. Further work considered selectivity and broad range adsorbents and suggested continued refinement in the work of selective adsorbents in the interest of acquiring the highest possible adsorption rates due to heavy metal toxicity.

(297 words)

## Abbreviations

<b>AAB</b>	acid activated bentonite
<b>ACD</b>	advanced chemistry development
<b>AEBI</b>	1-acrylamido ethyl-2-butyl imidazoline
<b>ALG</b>	alginate
<b>AM</b>	acrylamide
<b>AM/AO/AEBI-CTS</b>	acrylamide/ acrylonitrile/1-acrylamido ethyl-2-butyl imidazoline-chitosan adsorbent
<b>AO</b>	acrylonitrile
<b>Chi</b>	chitosan
<b>CLCh</b>	crosslinked chitosan
<b>CLCh/MWCNT/Fe</b>	crosslinked chitosan/multiple walled carbon nanotubes/iron adsorbent
<b>CMC</b>	carboxymethyl cellulose
<b>CS</b>	chitosan
<b>CsG</b>	chitosan glutaraldehyde crosslinked
<b>CsG@AAB</b>	chitosan crosslinked glutaraldehyde and acid activated bentonite adsorbent
<b>CTS</b>	chitosan
<b>CTSA</b>	chitosan glutaraldehyde crosslinked
<b>DUDMA</b>	diurethane dimethacrylate
<b>ECH</b>	epichlorohydrin
<b>FTIR</b>	Fourier Transfer Infrared Spectroscopy
<b>G/ECH-CS</b>	grafted (with 4-aminobenzoic acid) /epichlorohydrin – chitosan adsorbent
<b>GO</b>	graphene oxide
<b>IAA</b>	indoleacetic acid
<b>IAA-CTSA</b>	3-indoleacetic acid-chitosan crosslinked glutaraldehyde adsorbent

<b>MG</b>	methionine glutaraldehyde
<b>MG-Chi/Fe<sub>3</sub>O<sub>4</sub></b>	methionine glutaraldehyde- chitosan/ magnetic iron oxide adsorbent
<b>MWCNT</b>	multiple walled carbon nanotubes
<b>NTA</b>	nitriloacetic acid
<b>NTA- B-CD-CS</b>	nitrilotriacetic acid - $\beta$ -cyclodextrin – chitosan adsorbent
<b>PVA</b>	polyvinyl alcohol
<b>PVA/ALG/CS</b>	polyvinyl alcohol/alginate/chitosan adsorbent
<b>SA</b>	sodium alginate
<b>XPS</b>	X-ray Photoelectron Spectroscopy
<b>B-CD</b>	B-cyclodextrin

## **Table of Contents**

<b>Abstract</b>	ii
<b>Abbreviations</b>	iii
<b>Table of Contents</b>	v
<b>List of Figures and Tables</b>	vi
<b>Chapter 1- Introduction</b>	1
<b>1.1– Background</b>	1
<b>1.2 – Objectives</b>	3
<b>1.3– Scope</b>	4
<b>1.4 – Methodology</b>	4
<b>Chapter 2 – General structures and adsorption processes</b>	5
<b>2.1 – Common Structures</b>	5
<b>2.2 – Heavy metal acquisition</b>	5
<b>2.2.1 – Chelation and Complexation</b>	6
<b>2.2.2 – Electrostatic interactions</b>	8
<b>Chapter 3 – Chitosan’s contribution to heavy metal adsorption mechanisms</b>	11
<b>3.1 – An effective starting material</b>	11
<b>3.3– Combining adsorbents</b>	14
<b>3.4 – Increased selectivity</b>	15
<b>3.5 – Limitations</b>	16
<b>Chapter 4 – Effectiveness of chitosan</b>	17
<b>4.1 – Defining success</b>	17
<b>4.2 - Discussion of success</b>	20
<b>Chapter 5 – Conclusions and Further work</b>	35
<b>5.1 – Conclusions</b>	35
<b>5.2 – Further work</b>	35
<b>References</b>	36

## List of Figures and Tables

**Figure 1- Deacetylation of chitin to chitosan.** ACD/ChemSketch 1.2 (ACD/Labs, 2020)  
Adapted from Chopra and Ruhi (2016)

**Figure 2 – One possible example of complexation of Cu(II). Depicting square planar complex geometry with bidentate ligands, possibly from chitosan functional groups.**  
Created using Microsoft Word (2024). Adapted from Li *et al.* (2023)

**Figure 3 – Proposed square planar complexation of Cu(II) where amino groups from chitosan and carboxyl groups from additional material each contribute as monodentate ligands.** Microsoft Word (2024) ACD/ChemSketch 1.2 (ACD/Labs, 2020). Adapted from Fan *et al.* (2021)

**Figure 4 - Probable adsorption mechanism for Cu<sup>2+</sup> and Ni<sup>2+</sup> onto AM/AO/AEBI-CTS adsorbent.** (He *et al.*, 2021)

**Figure 5 – Diagram of  $\pi$ -cation interactions of the indole ring with U<sup>6+</sup>, which represents cationic UO<sub>2</sub><sup>2+</sup>, UO<sub>2</sub>OH<sup>+</sup> and (UO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub><sup>5+</sup> species present at pH 4-7.** (Wang *et al.*, 2022) Where R represents crosslinked chitosan which 3-indoleacetic acid is grafted to. Adapted from Wang *et al.* (2022)

**Figure 6 – Schematic overview of ion exchange, hydrogen bonding and van de Waals forces.** Microsoft Word (2024). Adapted from Li *et al.* (2017).

**Figure 7 – Overview of chitosan common uses. a) chitosan as an effective starting material: Cross-linked chitosan, and cross-linked chitosan with additional grafted materials and b) combining adsorbents: cross-linked chitosan combined with or added to other adsorbents.** Created using Screenshot of Microsoft Word (2024)

**Figure 8 - Depiction of theorised chelation of U(VI) by suggested improved preorganisation created by addition of glutaraldehyde crosslinked bridge.**  
ACD/ChemSketch 1.2 (ACD/Labs, 2020). Adapted from Igberase and Osifo (2019) and Wang *et al.* (2022)

**Figure 9- General diagram of core shell magnetic structures.** Adapted from Salehi *et al.* (2022)

**Figure 10– Capture of Cr(VI) species by CLCh/MWCNT/Fe adsorbent.**  
ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from Neto *et al.* (2019)

**Figure 11 - Depiction of theorised chelation of U(VI) by suggested improved preorganisation created by addition of glutaraldehyde crosslinked bridge.**

ACD/ChemSketch 1.2 (ACD/Labs, 2020). Adapted from Igberase and Osifo (2019) and Wang *et al.* (2022)

**Figure 12 – Representation of CsG@AAB adsorbent where ion exchange and complexation are shown as mechanisms of adsorption of Pb(II).** ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from El Kaim Billah *et al.* (2024)

**Figure 13 – Depiction of AM/AO/AEBI-CTS adsorbent and proposed complexation of Cu(II).** ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from He *et al.* (2021)

**Figure 14 – Schematic of NTA-  $\beta$ -CD-CS adsorbent and proposed mechanisms for capture of Hg(II).** ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from Usman *et al.* (2021)

**Figure 15 – a) chemical structure of the chitosan- methionine glutaraldehyde modification. b) overview of the adsorbent bead structure showing magnetic core and adsorbent outer shell of MG-Chi/Fe<sub>3</sub>O<sub>4</sub>.** ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from Salehi *et al.* (2022)

**Figure 16 – Structure of G/ECH-CS adsorbent and proposed complexation of Ni(II).** ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from Igberase *et al.* (2019)

**Figure 17 – Capture of Cr(VI) and Cr(III) species by CLCh/MWCNT/Fe adsorbent.** ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from Neto *et al.* (2019)

**Figure 18 – Plausible structure of PVA/ALG/CS adsorbent showing complexation and electrostatic interaction of Pb(II) and Cr(VI).** ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from Zhang *et al.* (2022)

**Figure 19 – Proposed donors for complexation of a range of different heavy metals by G/ECH-CS adsorbent.** ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from Igberase *et al.* (2019) and El Kaim Billah *et al.* (2024)

**Table 1 – Types of chitosan-based adsorbent structures**

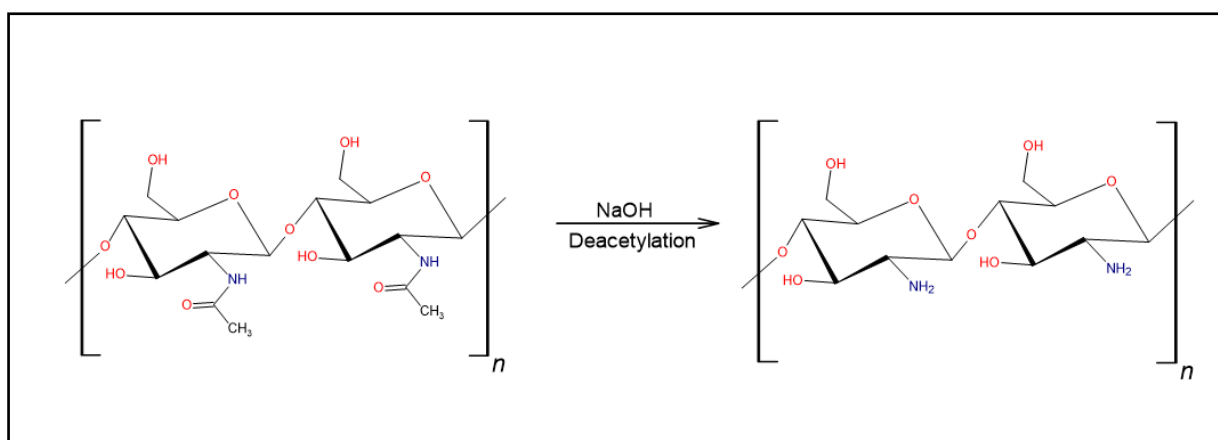
**Table 2 – Further uses of chitosan as a supporting adsorbent, chemically combined with other commonly used adsorbent materials**

**Table 3 – Compilation of most successful applications of modified crosslinked chitosan adsorbents for heavy metals in wastewater.**

## Chapter 1- Introduction

### 1.1 – Background

Wastewater from anthropogenic sources such as industrial and agricultural processes often contain undesirable substances including heavy metals, which can cause detrimental environmental effects and, in large quantities, be harmful to human life. In the treatment of wastewater, adsorbents are a useful material in removal of unwanted substances such as heavy metals. There is increasing drive to find natural materials and the use of biosorbents for this process is good. One example is chitosan (Contreras-Cortés *et al.*, 2019). Chitosan is a polycationic linear polymer derived, usually via deacetylation, from a natural material called ‘chitin’ which is extracted from crustacean shells like shrimp (Negm *et al.*, 2020). This process is shown in Figure 1 below.



**Figure 2- Deacetylation of chitin to chitosan.** ACD/ChemSketch 1.2 (ACD/Labs, 2020)  
Adapted from Chopra and Ruhi (2016)

Specifically, chitosan contains  $\beta$ -(1-4)-linked D-glucosamine and N-acetyl-D-glucosamine, distributed at random throughout its chain. It has various uses itself but a great platform for modification due to its functional groups, which is desirable due to chitosan’s low solubility in neutral and alkaline solutions. Along with its derivatives is considered highly versatile due to its bioactivities, being non-toxic, a low allergen, biodegradable as well as biocompatible (Cheung *et al.*, 2015). It has various medicinal, agricultural, technological and environmental applications and is used in the water industry for wastewater treatment. This ranges from general coagulation, removal of oil, pesticides, herbicides, dyes and heavy metals (Pal *et al.*, 2021).



Chitosan tends to chelate or bind with metal ions, and so is an effective material to remove heavy metals from wastewater. Specifically, the unprotonated NH<sub>2</sub> groups and OH groups can coordinate metal ions. The binding efficiency will be different depending on the amount of functional groups available within the chain, how long the chain is and other inter/intra molecular bonding present within the chitosan (Chopra and Ruhi, 2016 cited in Issahaku *et al.*, 2023). Therefore, modifications of chitosan can have varying effects on this process.

Chitosan has shown to be improved for adsorption when additional polymers or porous materials are combined with it, involving adding functional groups by grafting and by the process of cross-linking (Upadhyay *et al.*, 2021). Types of chitosan modifications include a huge range due to the high potential of reactive groups present such as an amino group, hydroxyl groups as well as glycosidic bonds and an acetamide group (Aranaz *et al.*, 2021).

Cross-linking involves the addition of a crosslink, a 'bridge', between different polymer chains. It is primarily used to increase strength as chitosan itself has low strength, affecting its ability to be reused. It can also increase chitosan's acid stability so that adsorbents can be insoluble in acidic conditions (Salehi *et al.*, 2022). The crosslink can form chemically or ionically. In chemical crosslinking, due to the 'crosslinker' reacting with functional groups on chitosan, it reduces adsorption capacity as less amine and hydroxyl groups are then available for chelation of metal ions but it is stronger than ionic. There are a few well known cross-linkers and different types of adsorbent structure overall (Upadhyay *et al.*, 2021).

## 1.2 – Objectives

- Introduce the chitosan biopolymer as an adsorbent material, its chemical structure and uses for wastewater treatment.
- Describe common structures of chitosan derivative used for adsorption and explain the chemical basis for removal of heavy metal from wastewater.
- Critically review the role of chitosan in adsorbent modification to improve the removal of heavy metal ions from wastewater
- Draw conclusions about the most effective derivatives of chitosan for removal of heavy metals from wastewater.
- Make recommendations for future research in the derivatization and application of chitosan for removal of heavy metals from wastewater.

### **1.3 – Scope**

This project reviews and critically evaluates recent chitosan-based adsorbents involving cross-linking. Looking at the contribution of chitosan to successful adsorption chemistry for potential use in wastewater treatment. Focusing on adsorption mechanisms and structural influences, detailed reflections are not considered for chemical synthesis, application in industry, environmental implications, chemistry of regeneration and economical/financial limitations although author awareness of these wider contexts is included herein.

Characterization is considered with a focus on significance of mechanism elucidation and not on specific analytical methods.

Many adsorption methods include the simultaneous removal of organic dyes; however, this project focuses solely on heavy metal removal. This review will focus almost exclusively on the chemical mechanistic successes involving modified chitosan, considering the contributions of chitosan to the adsorbent's successful qualities and the impact of additional materials and modifications.

### **1.4 – Methodology**

The Scopus database was searched using the Boolean terms “‘cross linked” AND chitosan AND “heavy metals” AND wastewater’ and was then refined this to include the years 2019-2024 to suit the ‘recent’ research scope of the paper.

A method was designed to screen for relevance to the scope of my project by checking the articles against my predefined inclusion criteria. That is, the article must focus on an adsorbent that is chitosan-based, or significantly employs chitosan, it must directly test removal of heavy metal ions, and the modifications must include the cross-linking of chitosan.

The analysis of credibility was furthered within this, and the Journal and author's reputation were taken into account, the sponsorship and possibly number of citations. Also, the quality of writing was considered as well as clarity and detail.

## Chapter 2 – General structures and adsorption processes

### 2.1 – Common Structures

Various physical structures of cross-linked chitosan-based adsorbents are summarised in Table 1 below, offering different characteristics effecting the porosity, strength and binding availability for heavy metal ions.

Table 1 – Types of chitosan-based adsorbent structures

Type of chitosan	Reference
Aerogel	(Huang <i>et al.</i> , 2019, Fan <i>et al.</i> , 2021; Wang <i>et al.</i> , 2022)
Hydrogel	(Pavithra <i>et al.</i> , 2021; Zhang <i>et al.</i> , 2022; Li <i>et al.</i> , 2023)
Beads and microspheres	(Contreras-Cortés <i>et al.</i> , 2019; Igberase <i>et al.</i> , 2019; Igberase and Osifo, 2019; Watwe and Kulkarni, 2021)
Nanoparticles	(Refaat <i>et al.</i> , 2020; Panahandeh <i>et al.</i> , 2021; Aghababi Beni <i>et al.</i> , 2021; Kaveh and Bagherzadeh, 2022; Salehi <i>et al.</i> , 2022; Zubair <i>et al.</i> , 2023)
Membranes	(Neto <i>et al.</i> , 2019; Liu <i>et al.</i> , 2020)
Composite	(Midya <i>et al.</i> , 2019; Atangana and Oberholster, 2020; Usman <i>et al.</i> , 2021; He <i>et al.</i> , 2021; Khan <i>et al.</i> , 2022; El Kaim Billah <i>et al.</i> , 2024)

Chitosan's hydroxyl and amine groups facilitate hydrogen bonding in water, making it hydrophilic. This is a useful characteristic for wastewater treatment as it can distribute well throughout the medium and have access to dissolved pollutants. The physical arrangement or structural modifications of chitosan can alter its physical strengths and weaknesses as an adsorbent, changing access to adsorbates, affecting reusability and ease of synthesis.

Structural modifications have significant impact on the feasibility of adsorbents but ultimately the chemical mechanisms of adsorption remain the same and are outlined next.

### 2.2 – Heavy metal acquisition

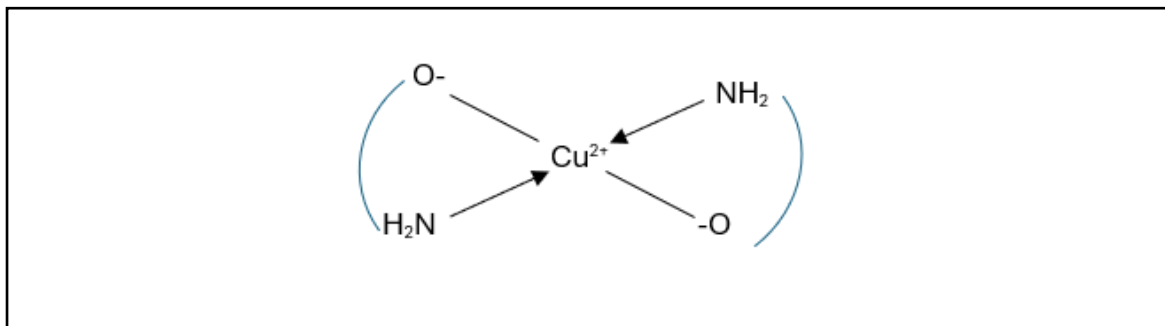
Mechanisms are often speculated and vary in degree of confidence between studies, with some using extensive analytical techniques to explain theories of binding to specific sites within the adsorbent, whereas others suggest more vaguely the various mechanisms at play.

Generally, mechanisms are found to be chelation, complexation, electrostatic interaction, cation- $\pi$  interaction, hydrogen bonding, van de Waals forces and ion exchange. Some aspects of these are explored below.

### 2.2.1 – Chelation and Complexation

Multiple analytical techniques are used including Fourier Transfer Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS) before and after adsorption.

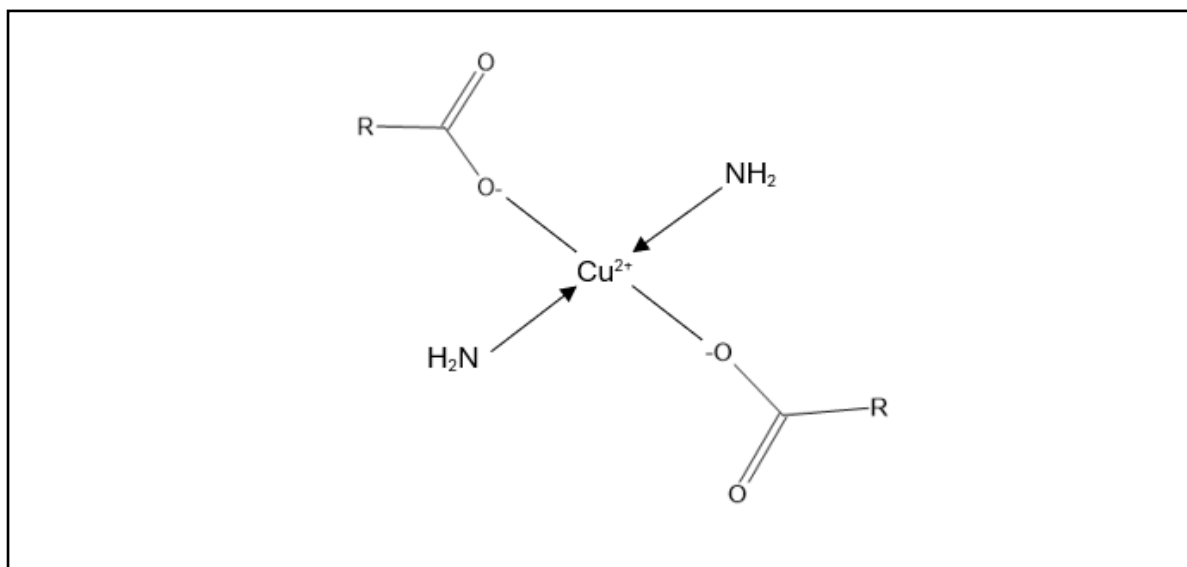
For the adsorption of copper, Li *et al.* (2023) found that nitrogen and oxygen atoms in functional groups of the adsorbent form a stable coordination complex with  $\text{Cu}^{2+}$  by sharing lone electron pairs. Cu(II) has the electron configuration  $[\text{Ar}] 3d^9$ , allowing the acceptance of the lone pair donation, and a four-coordinate complex is likely. This would result in a tetrahedral or square-planar complex (The Open University, 2024). Figure 2 below shows an example of such a complex.



**Figure 2 – One possible example of complexation of Cu(II). Depicting square planar complex geometry with bidentate ligands, possibly from chitosan functional groups.**  
Created using Microsoft Word, 2024. Adapted from Li *et al.* (2023)

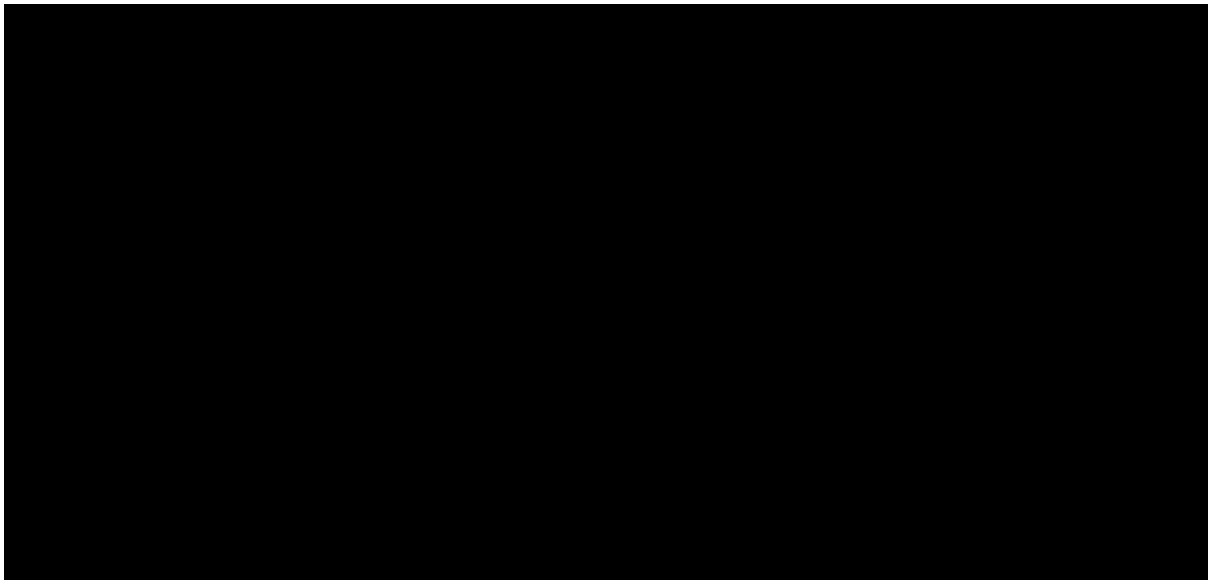
Another suggestion in this study is the formation of a proposed complex  $[\text{Cu}(\text{NH}_2)(\text{OH})_n.\text{H}_3\text{O}^+]$  (Li *et al.*, 2023).

Conclusions by Fan *et al.* (2021) supported the amine and hydroxyl oxygen chelation process described above, which were provided by chitosan, but offered additional carboxyl by their adsorbent, as a chelating group for  $\text{Cu}^{2+}$ . This was based on their FTIR analysis. XPS data showed the change in binding energy before and after adsorption of  $\text{Cu}^{2+}$  was highest for N and  $\text{NH}_2$  suggesting complexation by these groups were a significant contribution to the process (Fan *et al.*, 2021). Figure 3 below shows a proposed square planar complex with amine and carboxyl ligands.



**Figure 3 – Proposed square planar complexation of Cu(II) where amino groups from chitosan and carboxyl groups from additional material each contribute as monodentate ligands.** Microsoft Word (2024). ACD/ChemSketch 1.2 (ACD/Labs, 2020). Adapted from Fan *et al.* (2021)

He *et al.* (2021) also demonstrated, using a broad range of techniques, chelation by  $-\text{OH}$  and  $-\text{NH}$  groups towards  $\text{Cu}^{2+}$  by their adsorbent. Further to this, as a late row transition metal, Ni(II) has similar complexation characteristics as Cu(II) in that they both favour a four-coordinate complex, whereas Ni(II) has a  $d^8$  rather than  $d^9$  outer electron configuration. It's likely that mechanisms for the capture of Cu(II) would also be effective for Ni(II). This is evidenced by He *et al.* (2021) and depicted in Figure 4 below.



**Figure 4 - Probable adsorption mechanism for Cu<sup>2+</sup> and Ni<sup>2+</sup> onto AM/AO/AEBI-CTS adsorbent.** (He *et al.*, 2021)

In this depiction, as is largely the case in the literature, general groups are identified that may act as ligands towards either metal, rather than the portrayal of specific geometric complex formation. This is because the adsorption process is highly complex and may involve simultaneous, or various possible steps.

As well as copper and nickel, other heavy metals in d block follow similar reasoning in that the empty d shell orbitals can accept, as a coordinate bond, a lone pair from nitrogen-based ligands. In the literature covered here, these include cobalt, zinc, cadmium, and mercury. Based on this, it's likely that complexation contributes significantly to adsorption mechanisms for these metals. Chelation and complexation are also included as a process for the capture of uranium (Wang *et al.*, 2022), lead (El Kaim Billah *et al.*, 2024) and selenium (Zubair *et al.*, 2021).

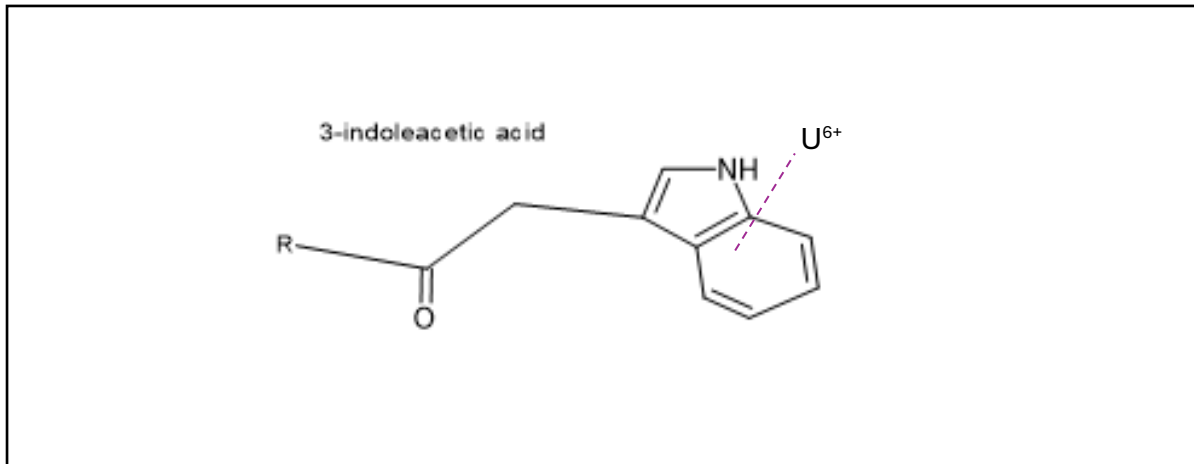
### **2.2.2 – Electrostatic interactions**

In the capture of Cr(VI) it is often seen that electrostatic interactions play an integral role. Watwe and Kulkarni (2022) found that protonation of chitosan's amino group under acidic pH conditions results in electrostatic attraction to Cr(VI) in the form of HCrO<sub>4</sub><sup>-</sup> anions. El Kaim Billah *et al.* (2024) depicted electrostatic attraction between NH<sub>3</sub><sup>+</sup> and HCrO<sub>4</sub><sup>-</sup> as well as NH<sup>+</sup> and HCrO<sub>4</sub><sup>-</sup>. Midya *et al.* (2019) and Zhang *et al.* (2022) also noted the integral role of electrostatic interaction in the capture of chromium species.

In a study by Zubair *et al.*, (2021) arsenic exists in its anionic form,  $\text{HASO}_4^-$ , and is thought to interact electrostatically with protonated  $\text{NH}_3^+$  groups in the adsorbent.

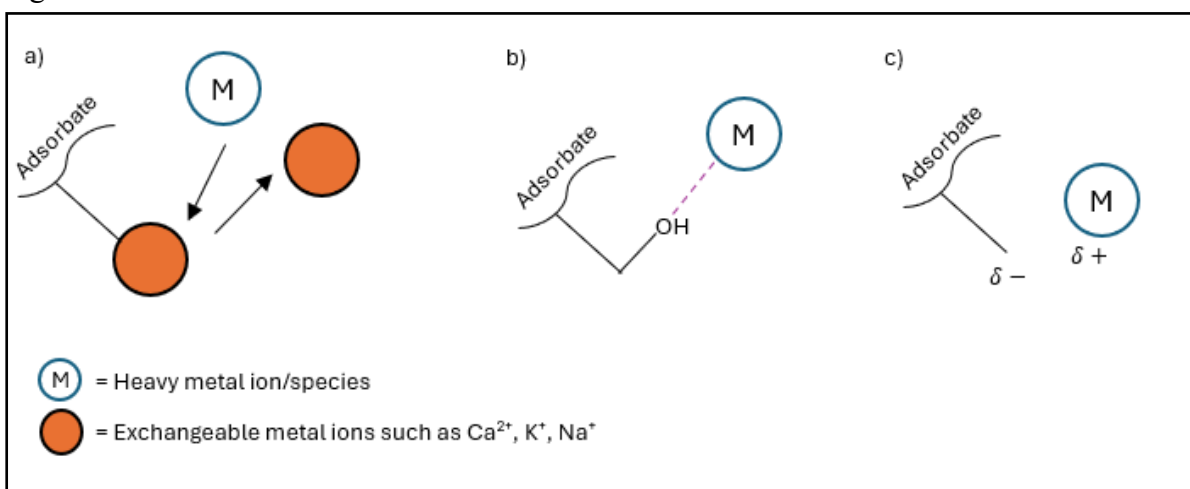
FTIR data by Wang *et al.* (2022) was used to conclude that binding and interactions with the indole ring, amide and amino groups were involved in the capture of Uranium, U(VI).

Notably,  $\pi$ -cation interactions between the indole ring from the adsorbent additional material and the metal ion as shown in figure 5 below.



**Figure 5 – Diagram of  $\pi$ -cation interactions of the indole ring with  $\text{U}^{6+}$ , which represents cationic  $\text{UO}_2^{2+}$ ,  $\text{UO}_2\text{OH}^+$  and  $(\text{UO}_2)_2(\text{OH})_2^{5+}$  species present at pH 4-7. (Wang *et al.*, 2022) Where R represents crosslinked chitosan which 3-indoleacetic acid is grafted to. Adapted from Wang *et al.* (2022)**

Further contributions to the adsorption of heavy metals includes ion exchange, hydrogen bonding and van de Waals forces between the adsorbent and the adsorbate as overviewed by figure 6 below.



**Figure 6 – Simplified overview of a) ion exchange, b) hydrogen bonding and c) van de Waals forces. Microsoft Word (2024). Adapted from Li *et al.* (2017).**

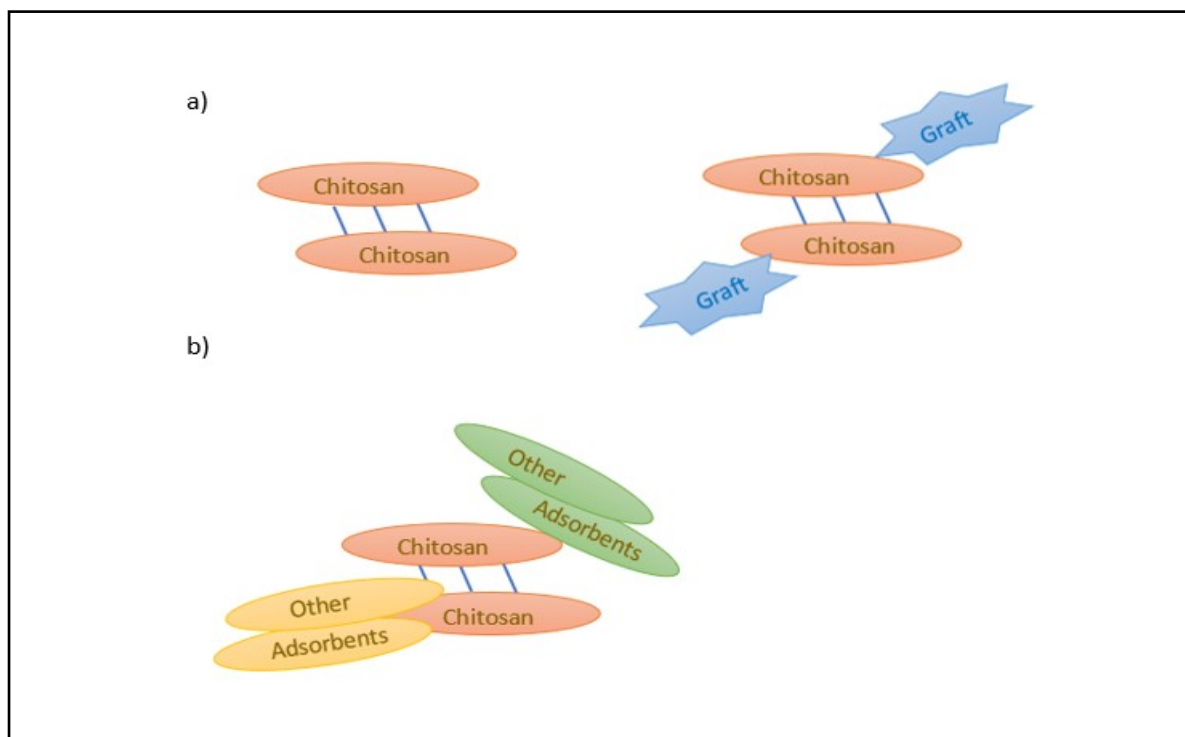


Although largely able to form complexes, copper was also found to involve electrostatic interaction and hydrogen bonding facilitated between amine and hydroxyl adsorbent groups and the copper ion (Li *et al.*, 2023). Also proposed are interactions between lead and deprotonated -COOH (Zhang *et al.*, 2022).

Generally, mechanisms exist simultaneously with complexity and uncertainty. Often, the main probable mechanism is elucidated by a combination of analytical data and reasoning. Not covered here are further physisorption mechanisms such as pore filling as most mechanisms were kinetically described as pseudo second order and fit chemisorption characteristics.

### Chapter 3 – Chitosan’s contribution to heavy metal adsorption mechanisms

Although chitosan’s uses cannot be definitively organised as each study brings its own unique approach and parameters, common themes can be identified in which chitosan is used in comparable ways. Figure 7 below simplistically overviews the different ways chitosan-based adsorbents can be comprised, varying in their complexity.



**Figure 7 – Overview of chitosan common uses. a) chitosan as an effective starting material: Cross-linked chitosan, and cross-linked chitosan with additional grafted materials and b) combining adsorbents: cross-linked chitosan combined with or added to other adsorbents.** Microsoft Word (2024).

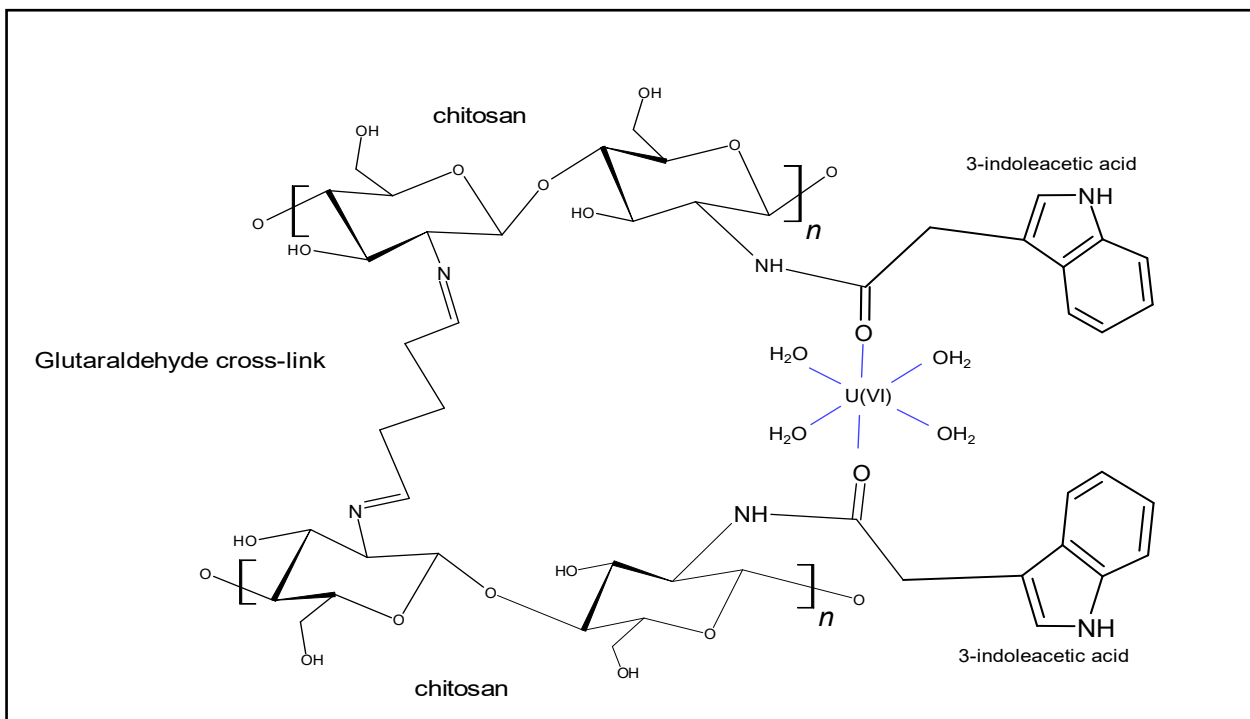
#### 3.1 – An effective starting material

Chitosan is sometimes used as a base material because it contains useful functional groups and can be stabilised with crosslinking. For example, Khan *et al.* (2022) used chitosan cross linked with glutaraldehyde to form an adsorbent film for the capture of Co(II). Chitosan was used because it contained many adsorption sites and the crosslinking provided mechanical strength and thermal stability. Similarly, Watwe and Kulkarni (2021) and Atangana and Oberholster (2020), used chitosan cross linked with glutaraldehyde in the form of adsorbent

beads, and a composite, to remove Cr(VI). Both showed the stabilising effect of the crosslinker; imine linkages created between chitosan and glutaraldehyde increased structural networking which resulted in increased stability in acid (Watwe and Kulkarni, 2021). The mechanism of adsorption by chitosan for Cr(VI) exhibited high efficiency for electrostatic interaction of  $\text{HCrO}_4^-$  with  $-\text{NH}_3^+$  groups of the adsorbent at low pH. Chitosan is unstable in acid conditions; a problem that was resolved by the crosslinking and increased network structure, allowing the adsorbent to work at low pH. (Watwe and Kulkarni, 2021)(Atangana and Oberholster, 2020).

Midya *et al.* (2019) used chitosan as a ‘backbone’ with diurethane dimethacrylate (DUDMA) crosslink (Midya *et al.*, 2019), combined with polyvinyl imidazole resulting in abundant amine, hydroxyl and carbonyl groups that could be easily protonated at acidic pH, providing an alternative medium for electrostatic interaction with the anionic Cr(VI) species.

In many cases, adsorbents start with chitosan, crosslinked for stability but include the grafting of materials that provide additional functional groups. This was the case for the capture of U(VI) as proposed by Wang *et al.* (2022). Chitosan aerogel (CTS) was cross linked with glutaraldehyde but further modified by grafting with 3-indoleacetic acid (IAA). Unlike the capture of Cr(VI), the adsorption mechanism was deduced to rely heavily on the addition of 3-indoleacetic acid, where complexation of U(VI) occurred via amide carbonyl, and further cation- $\pi$  interactions of U(VI) with the indole ring. (Wang *et al.*, 2022) Also key, is the glutaraldehyde crosslinker. Results showed that IAA-CTS, without crosslinking, only achieved 54% removal efficiency, compared to 94% when crosslinked, probably due to improved porosity and mechanical strength. (Wang *et al.*, 2022). It is also possible that the structural role of the crosslinker provides an appropriate degree of preorganisation to allow complexation of U(VI) via the carbonyl groups as depicted in figure 8.



**Figure 8 - Depiction of theorised chelation of U(VI) by suggested improved preorganisation created by addition of glutaraldehyde crosslinked bridge.**

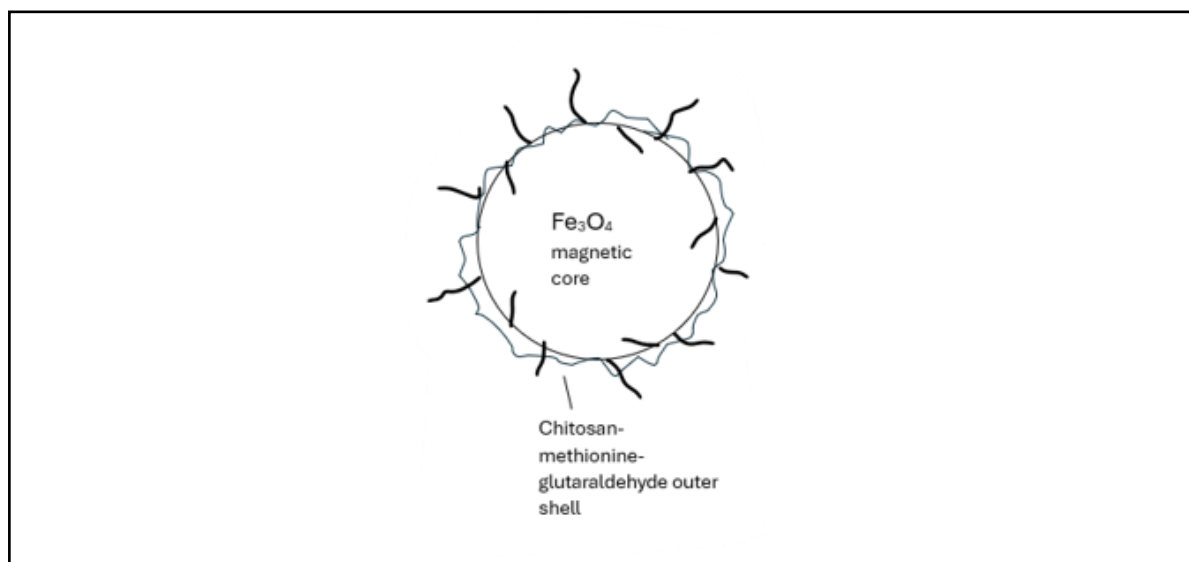
ACD/ChemSketch 1.2 (ACD/Labs, 2020). Adapted from (Igberase and Osifo, 2019) and (Wang *et al.*, 2022).

The variation in chitosan use can partially be attributed to the different mechanisms of adsorption for different heavy metal ions. In fact, the significance of the heavy metal ion, and furthermore speciation, influencing the adsorption mechanism can be explored when comparing Cr(VI) to Cu(II). Cr(VI) largely adsorbs by electrostatic interaction by protonated adsorbent species such as  $\text{-NH}_3^+$ , whereas chelation is more prevalent for Cu(II) (Fan *et al.*, 2021). At low pH for Cu(II) the protonated positive species of the adsorbent have the opposite effect repelling the cation which exists in a positive form (Fan *et al.*, 2021), unlike the oxyanionic species observed for Cr(VI). This highlights the effect of species distribution and pH in the different uses of chitosan to adsorb heavy metal ions.

Taking these contrasting results into account, it is interesting to explore chitosan's role as an adsorbent to capture both Cr(VI) and Cu(II) by Pavithra *et al.* (2021) where biomaterials chitosan, bentonite clay and orange peel were combined and grafted with polyacrylamide and networked using N,N'-Methylene bisacrylamide. Chitosan was used for its good chelating groups -OH and -NH<sub>2</sub> and improved by additional adsorbing materials. At lower pH, proton concentration is high, offering undesirable competition for metal cation chemical bonding with functional groups (Fan *et al.*, 2021). At higher pH, hydroxyl competition decreases electrostatic interactions between metal and adsorbent. At pH 4, adsorbance of approximately

80% efficiency was seen for each (Pavithra *et al.*, 2021). The combination of materials seems to provide a good balance for both Cr(VI) and Cu(II).

In some cases, chitosan has been chosen for its adsorbent groups and constructed to support magnetic material inside which aids removal from the water. The mechanism of adsorption is largely provided by chitosan functional groups and modifications offer key structural improvements for physisorption as well as some enhancement of chemical adsorption.



**Figure 9- General diagram of core shell magnetic structures.** Adapted from Salehi *et al.* (2022)

Salehi *et al.* (2022) and Panahandeh *et al.* (2021) employed magnetic  $\text{Fe}_3\text{O}_4$  with crosslinked chitosan where chitosan was part of a core-shell arrangement where it formed the shell of the bead structure, and the magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles formed the centre. Figure 9 shows this general arrangement. Similarly, the nanocomposite designed by Kaveh and Bagherzadeh (2022) was arranged such that chitosan was the outer layer and the magnetic iron the inner layer. In the capture of Cu(II), Pb(II) and Cd(II), chitosan was found to provide functional groups like  $-\text{NH}_2$  and crosslinking with methionine-glutaraldehyde improved mechanical properties, acid stability and the addition of chemical binding sites such as  $-\text{COOH}$ ,  $-\text{CN}$ , and  $-\text{S}$ - (Salehi *et al.*, 2022).

### 3.3– Combining adsorbents

Chitosan has also been used as a supporting material rather than a starting base. Combinations of adsorbents are summarised in table 2 below.

Table 2 – Further uses of chitosan as a supporting adsorbent, chemically combined with other commonly used adsorbent materials

Adsorbent addition to crosslinked chitosan	Heavy metal	Citation
Acid activated bentonite clay	Pb(II), Cr(VI)	(El Kaim Billah <i>et al.</i> , 2024)
Multiple walled carbon nanotubes and magnetic iron.	Cr(VI)	(Neto <i>et al.</i> , 2019)
Cellulose and polyvinyl alcohol	Cu(II)	(Li <i>et al.</i> , 2023)
Alginate and copper tolerant mycelium	Cu(II)	(Contreras-Cortes <i>et al.</i> , 2019)
Amidoximated chitosan crosslinked with imidazoline-functionalised polyacrylamide	Cu(II), Ni(II)	(He <i>et al.</i> , 2021)
Keratin with chitosan	Arsenic, selenium, chromium, nickel, cobalt, lead, cadmium, zinc	(Zubair <i>et al.</i> , 2023)
Chitosan and $\beta$ -cyclodextrin	Zn(II)	(Liu <i>et al.</i> , 2020).
Chitosan and polyvinyl alcohol* *Used as dynamic support for a seaweed based adsorbent.	Zn(II), Ni(II), Co(II)	(Aghababi Beni <i>et al.</i> , 2021)

### 3.4 – Increased selectivity

Zhang *et al.* (2022) found that the addition of chitosan greatly improved the specific adsorption of Cr(VI). When investigating the adsorption of polyvinyl alcohol/alginate (PVA/ALG) and PVA/ALG crosslinked with chitosan (PVA/ALG/CS) hydrogel beads for the removal of Pb(II), Cd(II), Cu(II) and Cr(VI), adding chitosan was found to alter the kinetic description of the adsorption indicating that mainly physisorption occurred. The favoured adsorption of Cr(VI) is attributed to increased -NH<sub>2</sub> sites (Zhang *et al.*, 2022). Differing to other studies, ALG based hydrogel had good adsorption towards Pb(II), and chitosan was added as an additional material. Whilst good for Cr(VI), this had drawbacks for the other metals as discussed below.

### 3.5 – Limitations

Interestingly, despite improving selective adsorption for Cr(VI), increase in chitosan concentration decreased the adsorption capacity for Pb(II), Cu(II) and Cd(II). Chitosan decreased the size of the pores within the hydrogel potentially reducing access for the larger heavy metals (Zhang *et al.*, 2022).

Huang *et al.* (2019) investigated the adsorption of Cr(VI) using an aerogel globule made from graphene oxide (GO) exfoliated with carboxymethyl cellulose (CMC) and micro crosslinked with chitosan. Despite many examples of chitosan providing active sites for adsorption of Cr(VI), chitosan's addition here resulted in a 38% decrease in adsorption capacity towards Cr(VI) compared with a pure GO aerogel. Although there were some improvements to structure, chitosan did not improve adsorption of the heavy metal (Huang *et al.*, 2019). The binding with GO may have used up more functional sites than it created towards capturing Cr(VI) resulting in the overall decreased adsorption.

Refaat *et al.* (2020) used cross linked sodium alginate (SA), and SA/chitosan to remove Pb(II) ions. The addition of chitosan did not improve adsorption. Crosslinking with chitosan changed the surface of the crosslinked SA from smooth to rough (Refaat *et al.*, 2020) perhaps reducing access for Pb(II) as proposed by Zhang *et al.* (2022).

Overall, chitosan's role in the adsorbance of heavy metals is complex and varied. It can largely be seen that for capture of Cr(VI) chitosan is effectively used for its functional group contribution to electrostatic interaction at low pH and in other cases the functional groups facilitate complexation. Whereas, for other heavy metals like U(VI) the complexation via additional materials is relied upon (Wang *et al.*, 2022). The most successful chitosan modifications are discussed next in chapter 4.

## **Chapter 4 – Effectiveness of chitosan**

### **4.1 – Defining success**

Success of an adsorbent was quantified with a relatively high adsorption capacity in ( $\text{mg g}^{-1}$ ), high selectivity for a particular heavy metal, or broad capability of adsorption. Unique findings were noted too. Some research did appear or claim to be of high success but lacked the quantitative evidence for comparison and so were not included in this summary. Table 3 below collates these key conclusions of success, which are further explored within this chapter; showing the composition of each adsorbent as well as the role chitosan contributed towards the removal mechanism for each.



Table 3 – Compilation of most successful applications of modified crosslinked chitosan absorbents for heavy metals in wastewater.

<b>Defining success criteria</b>	<b>Key conclusions</b>	<b>Adsorbent materials</b>	<b>Abbreviation</b>	<b>Chitosan's role</b>
Highest adsorption capacity per metal /mg g <sup>-1</sup>	847.5 for U(VI) (Wang <i>et al.</i> , 2022)	Chitosan crosslinked with glutaraldehyde, grafted with 3-indoleacetic acid.	IAA-CTSA	As starting material - structural
	449.3 for Cr(VI) (Neto <i>et al.</i> , 2019)	Chitosan crosslinked with glutaraldehyde combined with magnetic iron oxide doped multiple walled carbon nanotubes.	CLCh/MWCNT/Fe	As additional material
	452.78 for Pb(II) (El Kaim Billah <i>et al.</i> , 2024)	Chitosan crosslinked with glutaraldehyde and acid-activated bentonite clay.	CsG@AAB	As additional material
	190.7 for Cu(II) (He <i>et al.</i> , 2021)	Chitosan and amidoxime-functionalised polyacrylamide crosslinked with glutaraldehyde. Acrylamide, acrylonitrile, 1-acrylamido ethyl-2-butyl imidazoline chitosan.	AM/AO/AEBI-CTS	As additional material
	178.2 for Hg(II) (Usman <i>et al.</i> , 2021)	Chitosan crosslinked with glutaraldehyde and nitrilotriacetic acid crosslinked $\beta$ -cyclodextrin.	NTA- $\beta$ -CD-CS	As additional material

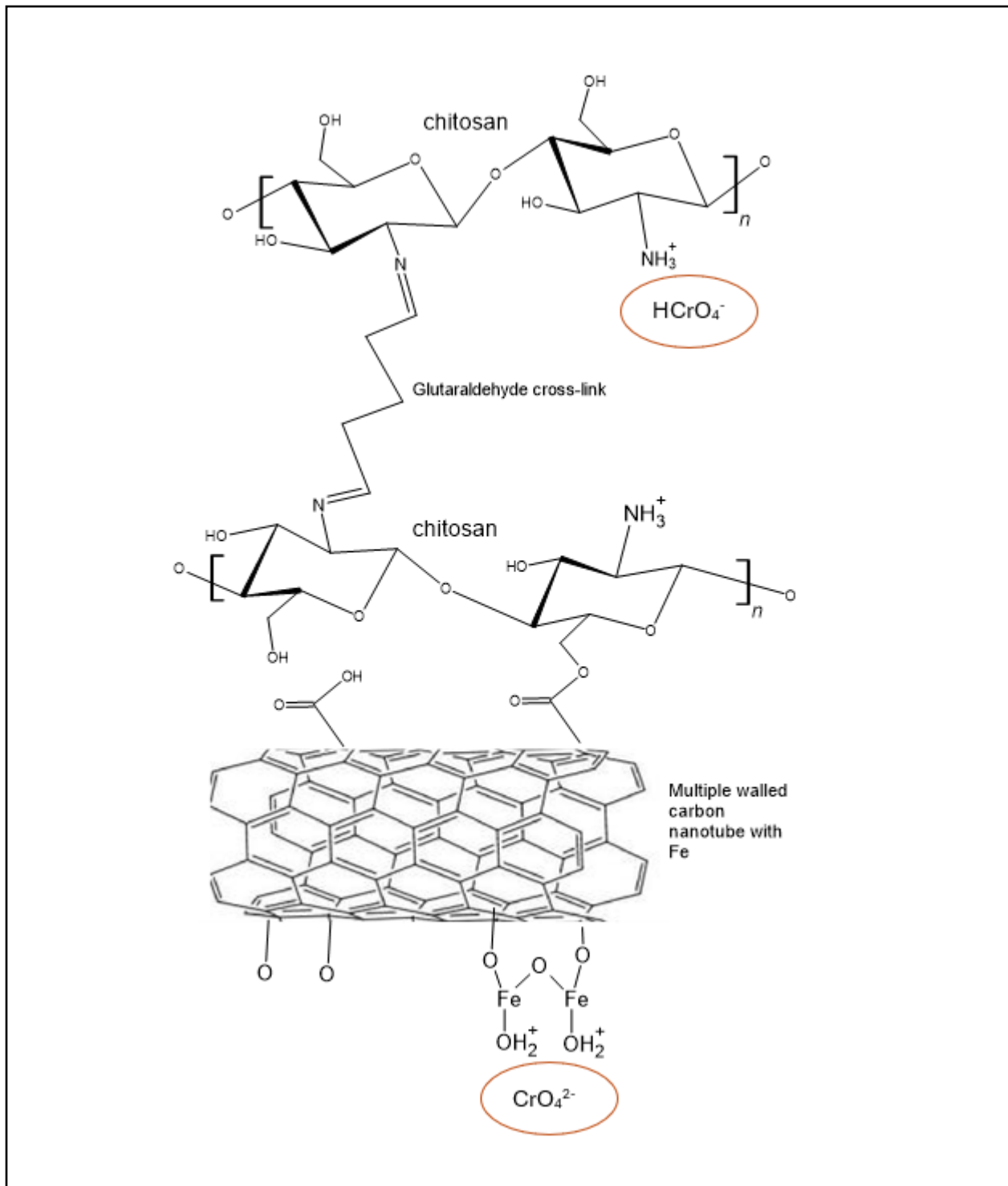
	163.9 for Cd(II) (Salehi <i>et al.</i> , 2022)	Chitosan crosslinked with methionine-glutaraldehyde and magnetic iron oxide.	MG-Chi/Fe <sub>3</sub> O <sub>4</sub>	As starting material
	155.21 for Ni(II) (Igberase <i>et al.</i> , 2019)	Chitosan crosslinked with epichlorohydrin, grafted with 4-aminobenzoic acid.	G/ECH-CS	As starting material
	66.25 for Cr(III) (Neto <i>et al.</i> , 2019)	Chitosan crosslinked with glutaraldehyde combined with magnetic iron oxide doped multiple walled carbon nanotubes.	CLCh/MWCNT/Fe	Contribution of adsorption sites
Displayed high selectivity	Capture of Cr(VI) by Zhang <i>et al.</i> (2022)	Chitosan with crosslinked blended polyvinyl alcohol and alginate.	PVA/ALG/CS	As additional material
Displayed a broad range of adsorption	Capture of Pb(II) Cu(II) Zn(II) Ni(II) Cd(II) successfully by Igberase <i>et al.</i> (2019)	Chitosan crosslinked with epichlorohydrin, grafted with 4-aminobenzoic acid.	G/ECH-CS	As starting material

## 4.2 - Discussion of success

### 4.2.1 - Adsorption capacity

Table 3 shows the highest adsorption capacity measured in  $\text{mg g}^{-1}$  per metal. Considering each heavy metal in turn, this section provides discussion and insight into the success by exploring the modification and proposed mechanisms resulting in the most successful derivatives of chitosan for heavy metal removal from wastewater.

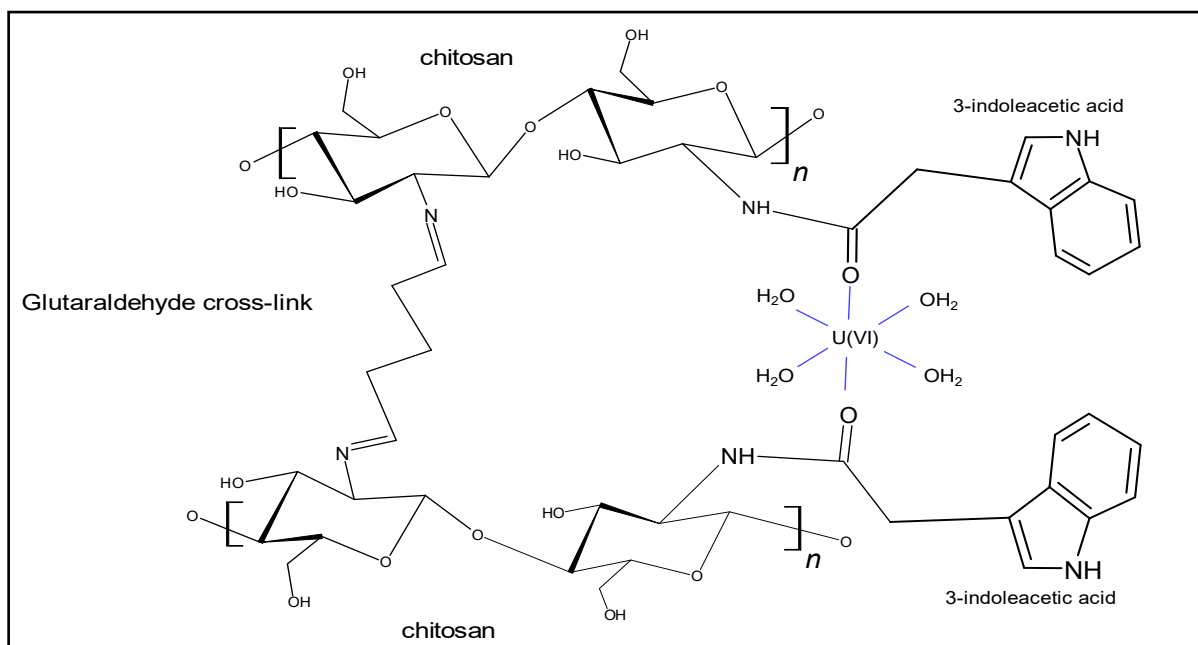
**Adsorption of Cr(VI):** Neto *et al.*, (2019) employed chitosan crosslinked with glutaraldehyde, combined with magnetic iron oxide doped multiple walled carbon nanotubes (CLCh/MWCNT/Fe) to capture Cr(VI). As figure 10 below shows, protonated  $\text{NH}_3^+$  groups can electrostatically interact with Cr(VI) in the form of  $\text{HCrO}_4^-$ . Figure 10 also depicts the proposed adsorption of Cr(VI) in the form of  $\text{CrO}_4^{2-}$  by  $-\text{OH}_2$  groups attached to the Fe-Multiple walled carbon nanotubes (Neto *et al.*, 2019). This could account for the high adsorption capacity of the adsorbent, as additional species of Cr(VI) are captured by further adsorption sites.



**Figure 10– Capture of Cr(VI) species by CLCh/MWCNT/Fe adsorbent.**

ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from Neto *et al.*, (2019)

**Adsorption of U(VI):** chitosan works well as a structural base where there is little evidence to show the use of functional groups in the adsorption of the heavy metal in this case. It is worth noting that this was the only study within the scope that tested for uranium. Figure 11 below shows how the addition of 3-indoleacetic acid is integral to the adsorption mechanism.

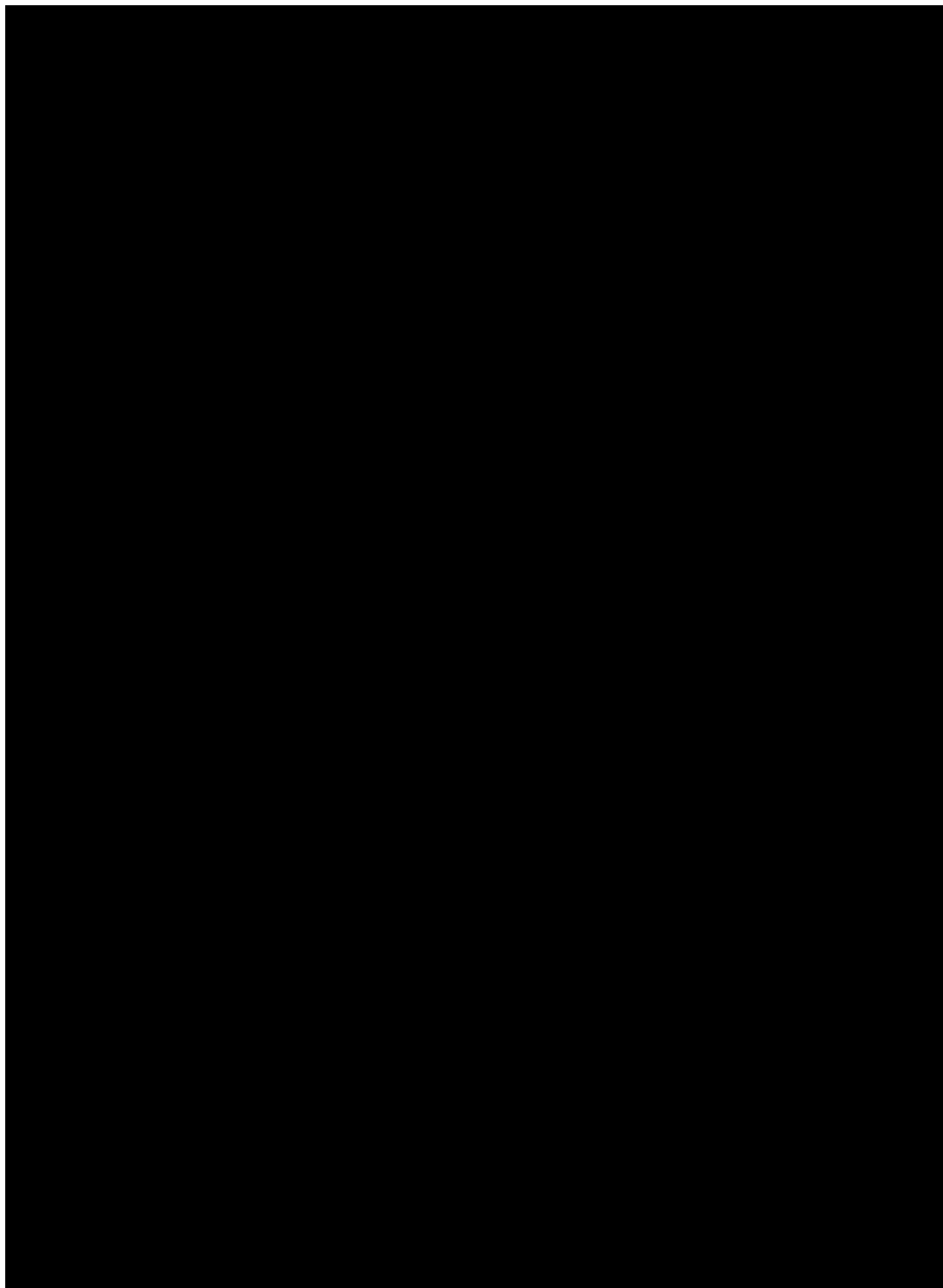


**Figure 11 - Depiction of theorised chelation of U(VI) by suggested improved preorganisation created by addition of glutaraldehyde crosslinked bridge.**

ACD/ChemSketch 1.2 (ACD/Labs, 2020). Adapted from (Igberase and Osifo, 2019) and (Wang *et al.*, 2022).

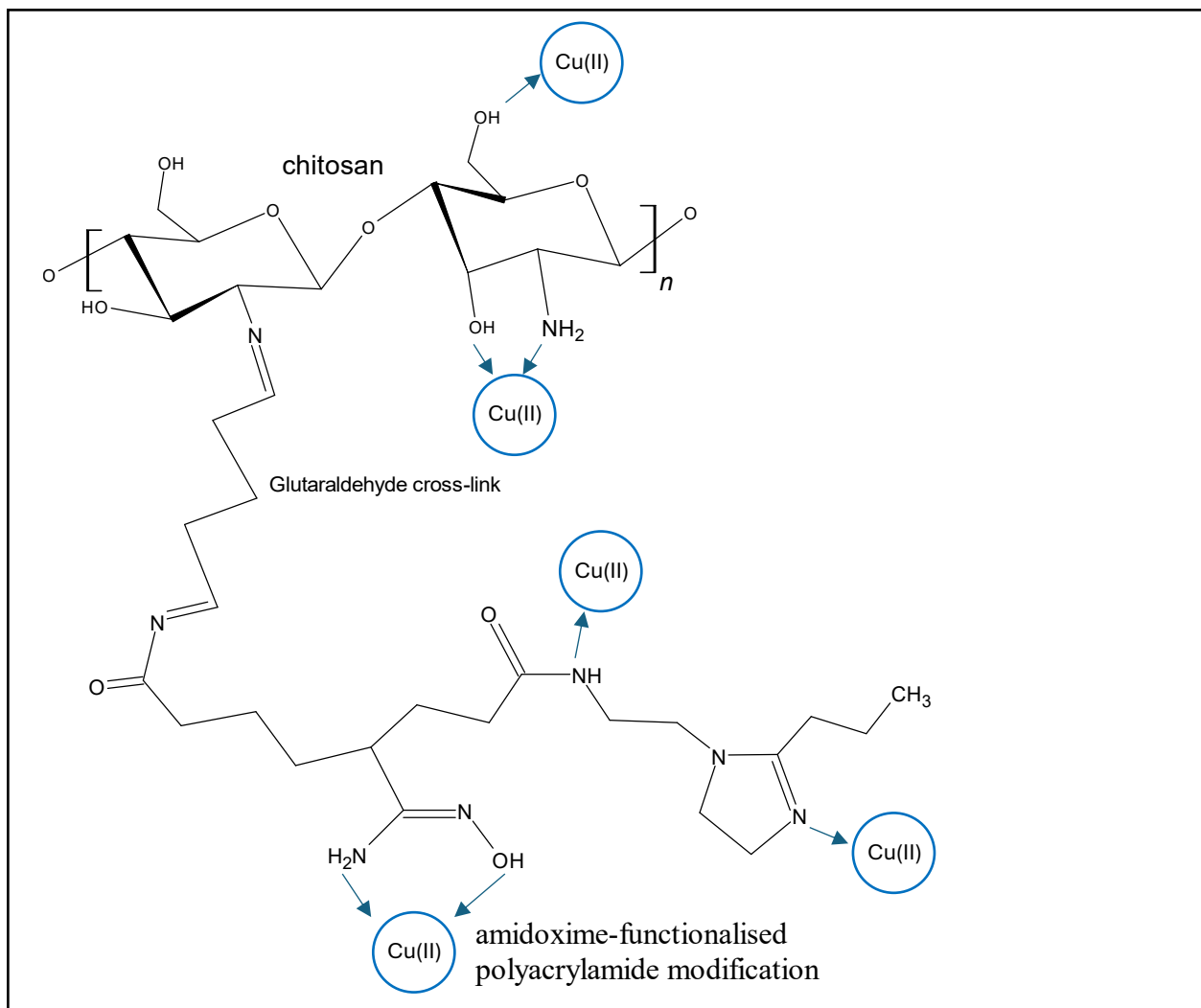
**Adsorption of Pb(II):** El Kaim Billah *et al.* (2024) utilised chitosan crosslinked with glutaraldehyde and acid-activated bentonite clay (CsG@AAB). The success of this adsorbent was largely attributed to mono and bidentate ligand interaction causing complexation by chitosan functional groups – NH<sub>2</sub> and -OH. Also, electrostatic interaction between HCrO<sub>4</sub><sup>-</sup> and protonated NH<sup>+</sup> and NH<sub>3</sub><sup>+</sup> groups and an ion exchange mechanism known to clay-based adsorbents (El Kaim Billah *et al.*, 2024). The acid activated bentonite clay provided further adsorption sites for ion exchange increasing the mechanisms of adsorption of Pb(II) as shown in figure 12 below.

**\*IMAGE REDACTED FOR COPYRIGHT REASONS\***



**Figure 12 – Representation of CsG@AAB adsorbent where ion exchange and complexation are shown as mechanisms of adsorption of Pb(II).** ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from El Kaim Billah *et al.* (2024)

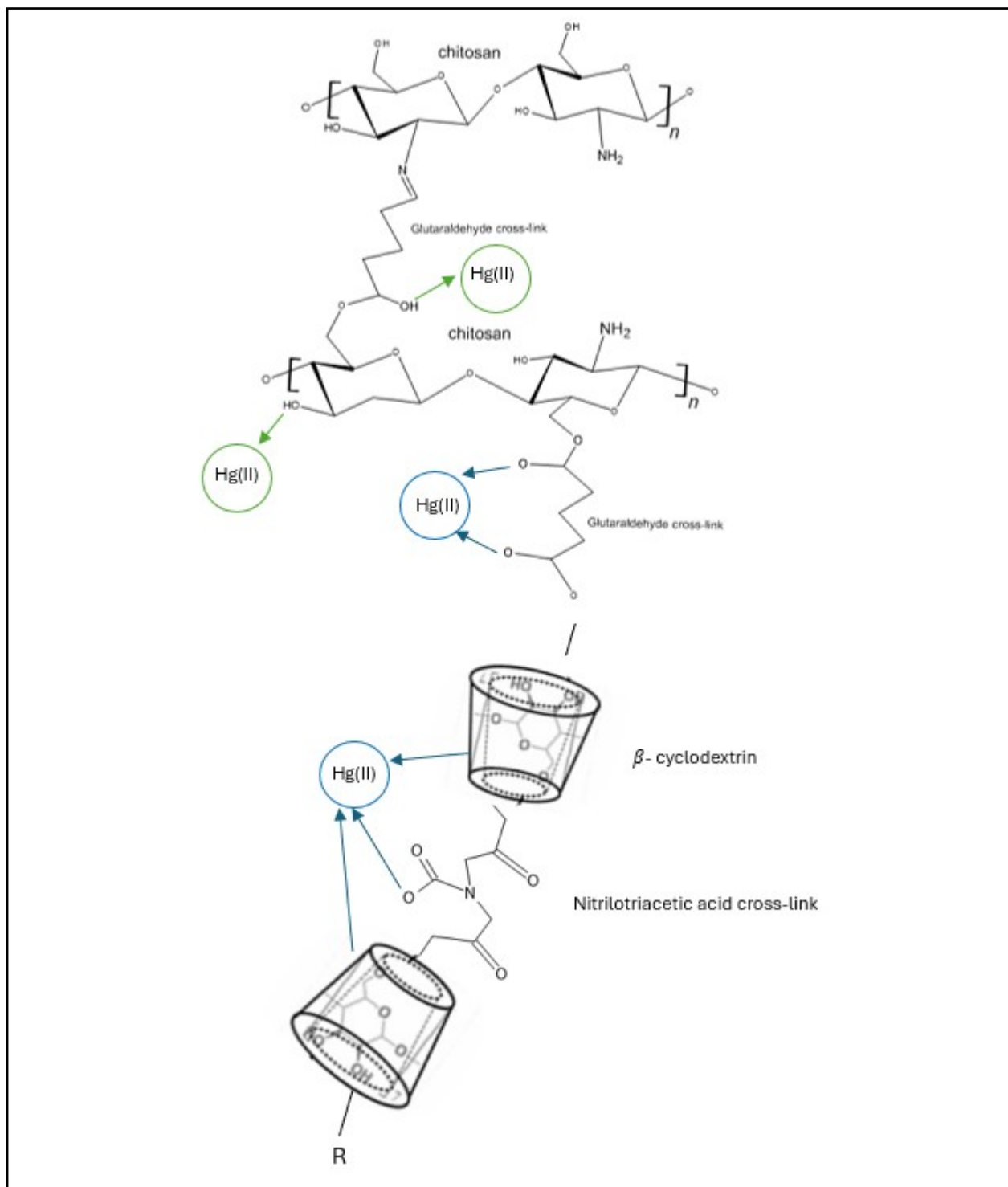
**Adsorption of Cu(II):** Chitosan and amidoxime-functionalised polyacrylamide crosslinked with glutaraldehyde (AM/AO/AEBI-CTS) was tested by He *et al.* (2021) and it was found that chelation by amide, amidoxime, imidazoline ring and hydroxyl groups were key contributions to this success. Some of these groups were provided by chitosan but many of the suggested contributors came from the addition of the amidoxime-functionalised polyacrylamide modification of chitosan as Figure 13 below portrays.



**Figure 13 – Depiction of AM/AO/AEBI-CTS adsorbent and proposed complexation of Cu(II).** ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from He *et al.* (2021)

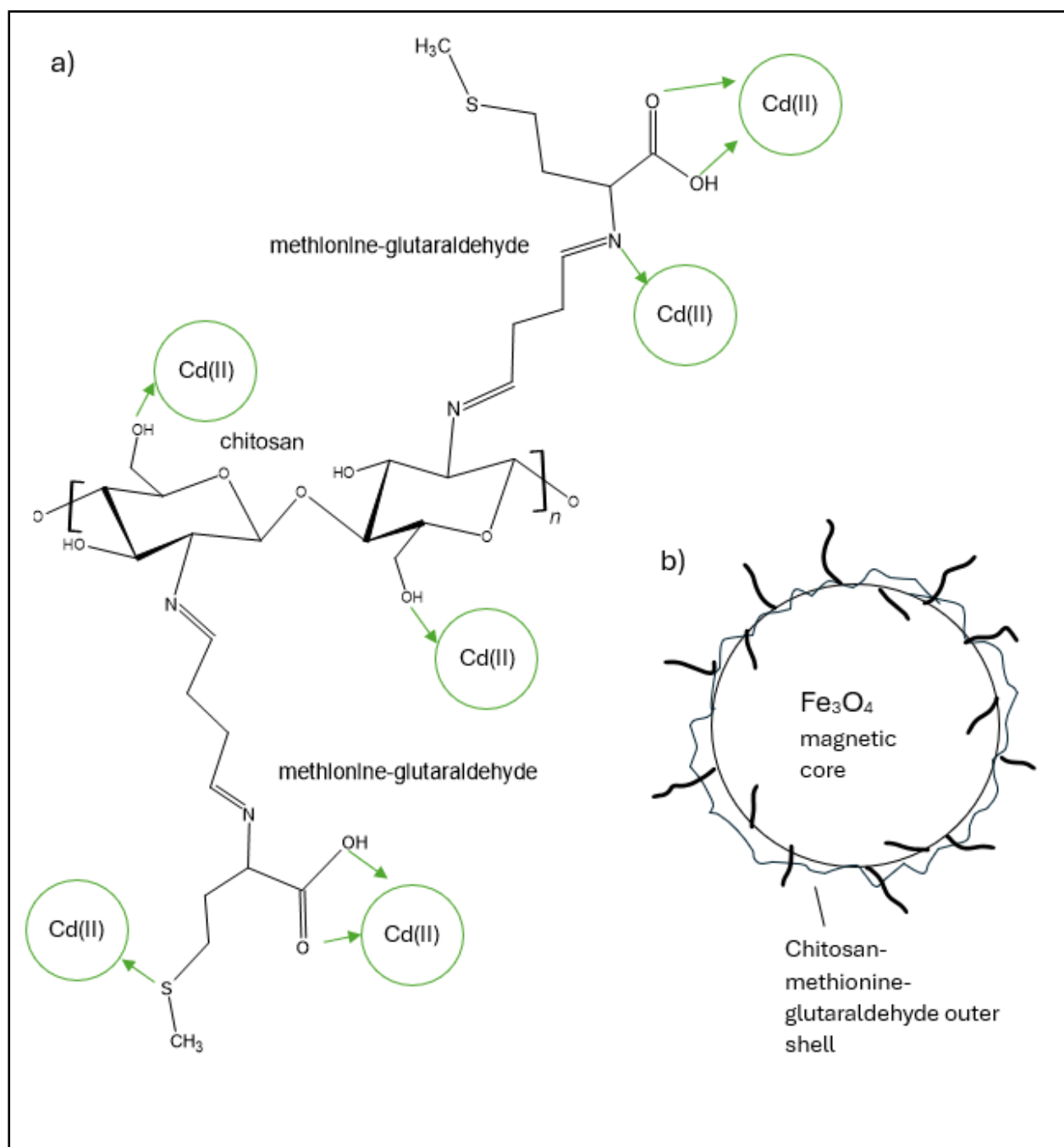
**Adsorption of Hg(II):** creation of Chitosan crosslinked with glutaraldehyde and nitrilotriacetic acid crosslinked  $\beta$ -cyclodextrin (NTA-  $\beta$ -CD-CS) showed success for capture of Hg(II) in its divalent form. Chitosan did not seem to participate in the capture of Hg(II), instead provided more useful for the capture of methyl orange dye (Usman *et al.*, 2021) which is not covered here. Theoretically, the -OH groups of chitosan and glutaraldehyde could chelate Hg(II). Figure 14 below overviews the possible adsorption sites.. These are largely provided by the crosslinkers glutaraldehyde and nitrilotriacetic acid.





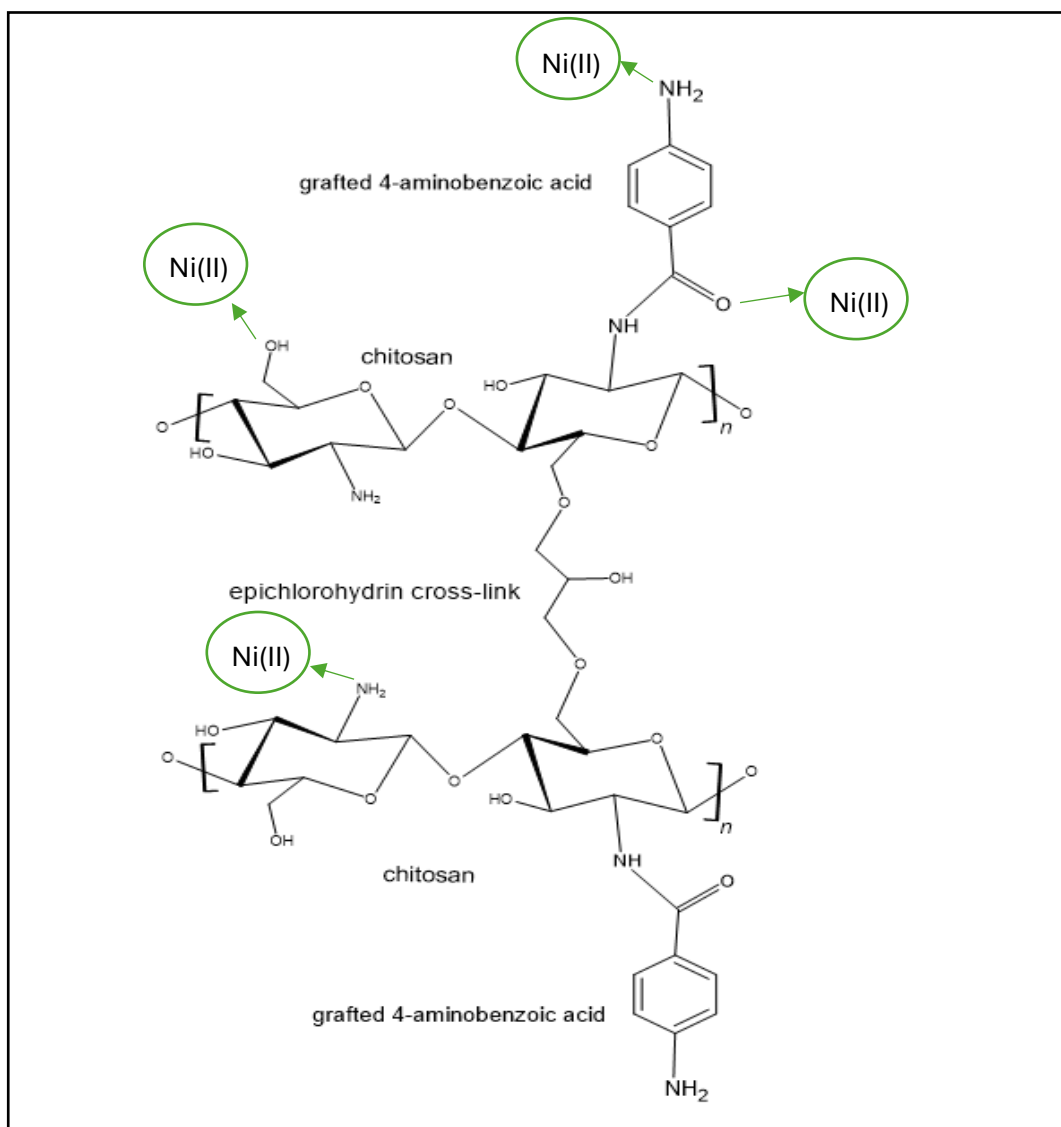
**Figure 14 – Schematic of NTA- β-CD-CS adsorbent and proposed mechanisms for capture of Hg(II).** ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from Usman *et al.* (2021)

**Adsorption of Cd(II):** Chitosan crosslinked with methionine-glutaraldehyde and magnetic iron oxide (MG-Chi/Fe<sub>3</sub>O<sub>4</sub>) created by Salehi *et al.* (2022) possesses key functional groups like -COO<sup>-</sup>, -CN and -S- (Salehi *et al.*, 2022). Also present are -OH groups in chitosan that may, when deprotonated, contribute as ligand donors towards Cd(II). These key groups are depicted in figure 15 below and are thought to be the main contributors to adsorption of Cd(II) by chemisorption. It appears successful adsorption of Cd(II) is largely attributed to multiple additional functional groups that can contribute to complexation of the heavy metal.



**Figure 15 – a) chemical structure of the chitosan- methionine glutaraldehyde modification. b) overview of the adsorbent bead structure showing magnetic core and adsorbent outer shell of MG-Chi/Fe<sub>3</sub>O<sub>4</sub>.** ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from Salehi *et al.* (2022)

**Adsorption of Ni(II):** Chitosan crosslinked with epichlorohydrin, grafted with 4-aminobenzoic acid (G/ECH-CS) was proposed by Igberase *et al.* (2019). Success is likely due to complexation by abundant amine, hydroxyl and carboxyl groups contributing to a tetrahedral metal complex. Figure 16 below shows an overview of the possible ligand donors that may form such a complex.

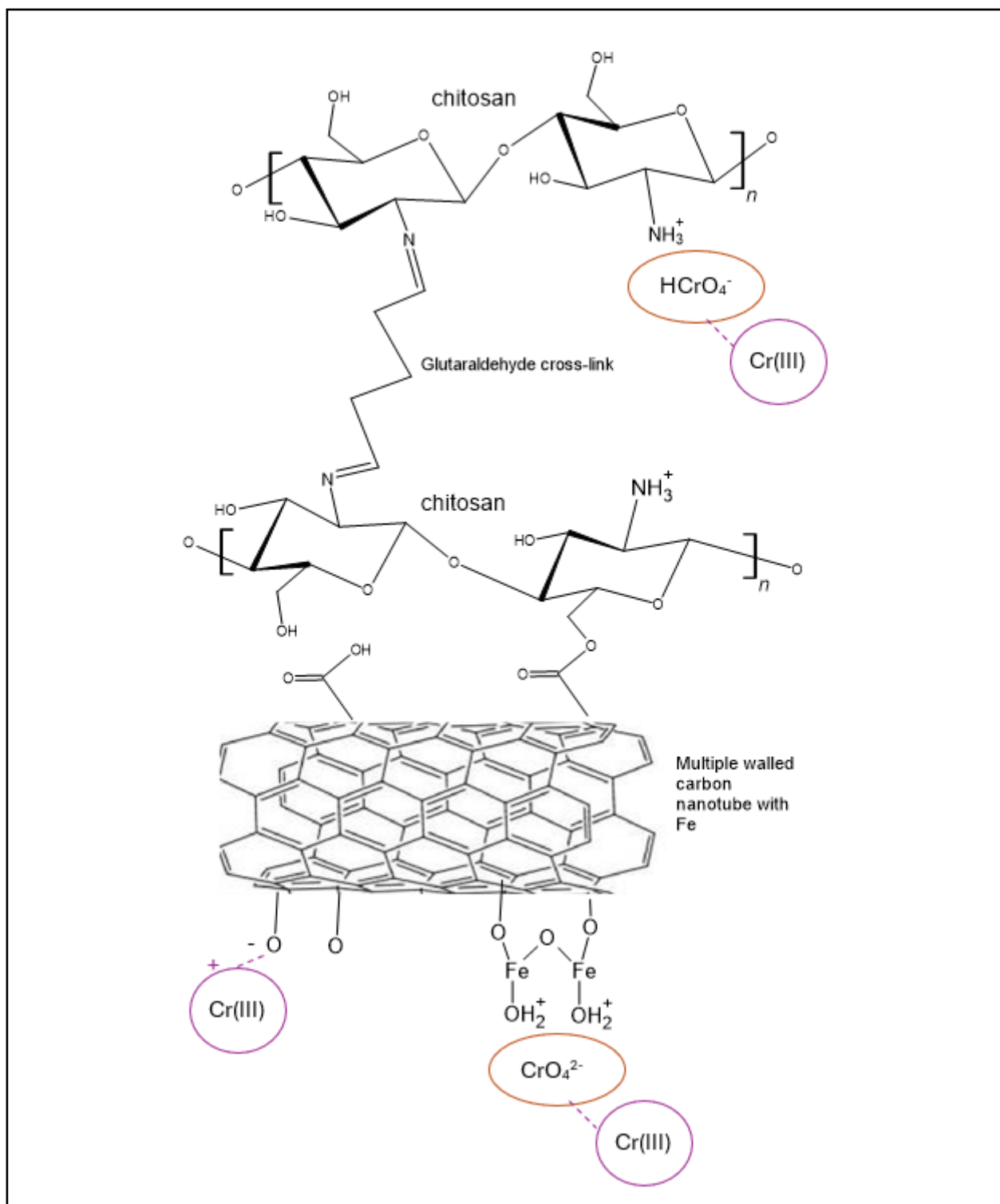


**Figure 16 – Structure of G/ECH-CS adsorbent and proposed complexation of Ni(II).**

ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from Igberase *et al.* (2019)

**Adsorption of Cr(III):** CLCh/MWCNT/Fe adsorbent used for Cr(VI) was also successful for adsorption of Cr(III) (Neto *et al.*, 2019). The successful adsorption of Cr(III) was attributed to the protonated  $-NH_2$  groups of chitosan and protonated  $-OH$  groups in the MWCN/Fe. These groups required the presence of Cr(VI) which facilitated co-adsorption as Figure 17 below shows. Also acting as an adsorption site was  $-O$  from the multiple walled

carbon nanotube after acid treatment. This additional electrostatic interaction further increased the adsorption of Cr(III) by the modified chitosan adsorbent.

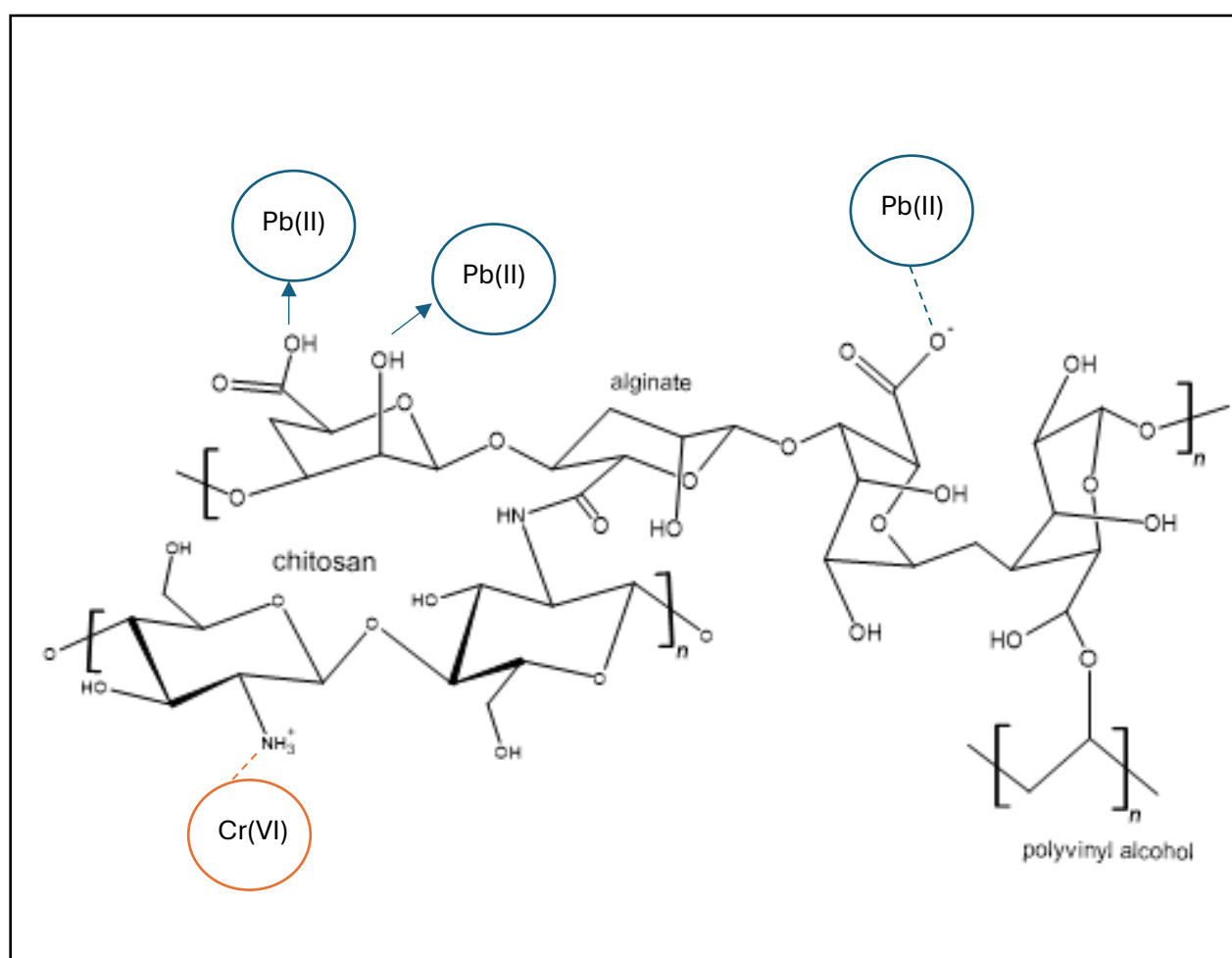


**Figure 17 – Capture of Cr(VI) and Cr(III) species by CLCh/MWCNT/Fe adsorbent.**

ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from Neto *et al.* (2019)

#### 4.2.2 - Selectivity

**Selective adsorption of Cr(VI):** Zhang *et al.* (2022) employed chitosan with crosslinked blended polyvinyl alcohol and alginate (PVA/ALG/CS). The study found that increasing the ratio of chitosan increased adsorption of Cr(VI) and decreased adsorption of Pb(II). Increasing chitosan content increases available  $\text{-NH}_3^+$  sites for adsorption of Cr(VI) by electrostatic attraction as shown in Figure 18 below. It also decreases the relative amount of  $\text{-COOH}$  groups from alginate that can form a complex with Pb(II) thus making the adsorbent more selective to Cr(VI).

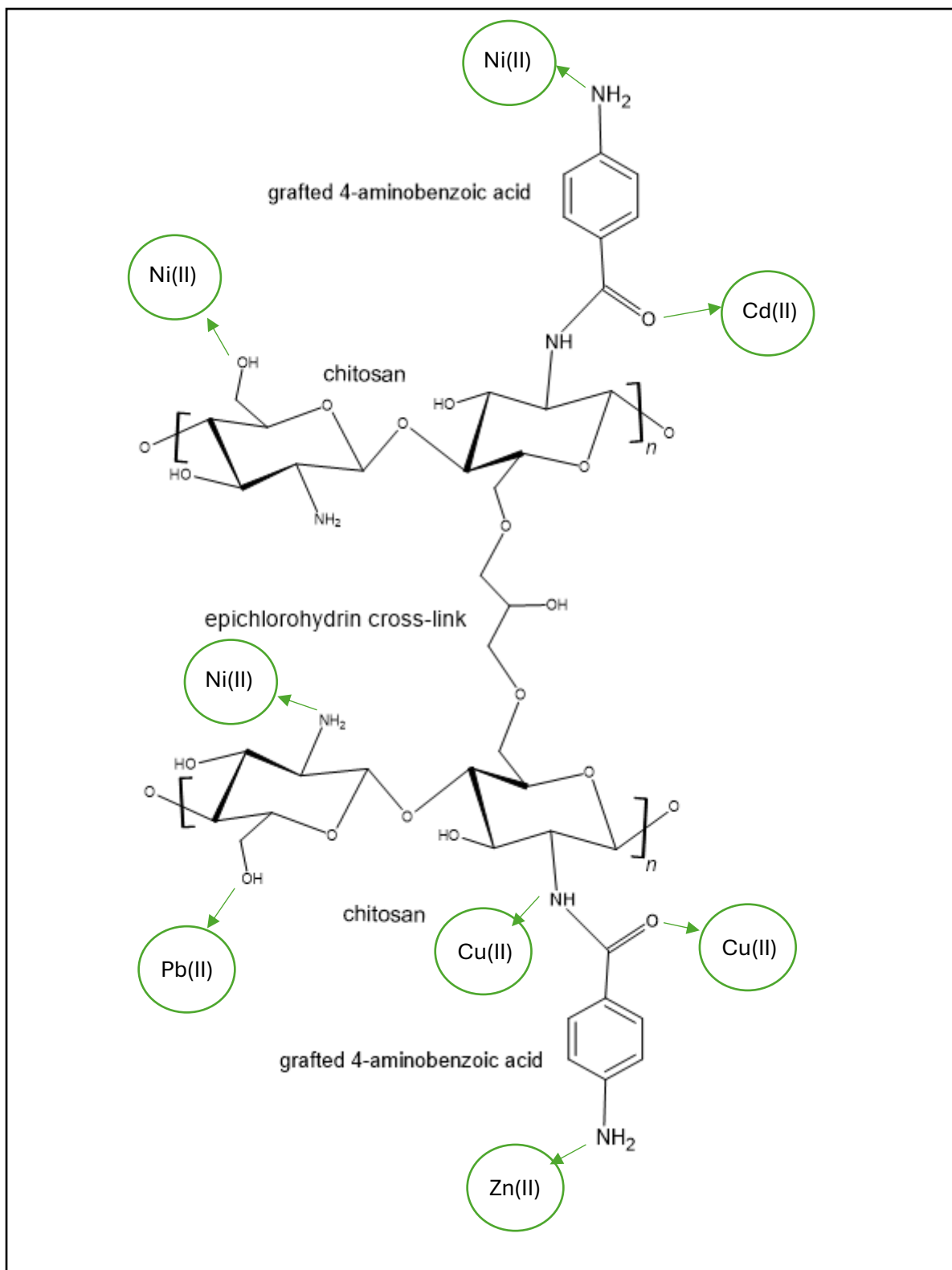


**Figure 18 – Plausible structure of PVA/ALG/CS adsorbent showing complexation and electrostatic interaction of Pb(II) and Cr(VI).** ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from Zhang *et al.* (2022)

### 4.3.3 - Broad range

**Effective adsorption of Pb(II), Cu(II), Zn(II), Ni(II) and Cd(II):** Igberase *et al.* (2019) utilised G/ECH-CS adsorbent, most effective for Ni(II). This is likely due to complexation by amine and hydroxyl groups forming a tetrahedral complex. It is probable that the mechanism of adsorption is similar for Cu(II) and Zn(II) due to their similar d shell electron chemistry as discussed in chapter 2. Evidently this may create competition for sites where the adsorption of Ni(II) is more favourable overall. The modification includes a wide range of functional groups that could adsorb by other methods such as electrostatic attraction of Cu(II) anions and  $\text{-NH}_3^+$  groups (Li *et al.*, 2024) shown in figure 19 below.





**Figure 19 – Proposed donors for complexation of a range of different heavy metals by G/ECH-CS adsorbent.** ACD/ChemSketch 1.2 (ACD/Labs, 2020). Microsoft Word (2024). Adapted from Igberase *et al.* (2019) and El Kaim Billah *et al.* (2024).

## Chapter 5 – Conclusions and Further work

### 5.1 – Conclusions

In conclusion, chitosan modifications were extremely varied and work by complicated simultaneous methods of adsorption, including chemical and physical interactions of the adsorbent and heavy metal adsorbate. Chitosan was improved by the process of chemical crosslinking, increasing its strength and stabilising it in acid. This was particularly important as many results found that acidic conditions provide key protonated sites for adsorption via electrostatic interactions. At  $\text{pH} > 6$  generally metals precipitate as hydroxides and so the pH range focused on is 2 – 6. The heavy metal ion species at this pH range was integral when considering the adsorbate functional groups contribution to mechanisms including chelation, complexation, electrostatic interaction, and ion exchange.

Addition of further materials was successfully shown to increase adsorption sites and consequently improved adsorption of heavy metal ions. Among the most successful modifications were addition of 3-indoleacetic acid, multiple walled carbon nanotubes, acid activated bentonite clay, amidoxime functionalised polyacrylamide,  $\beta$ -cyclodextrin, 4-aminobenzoic acid, methionine-glutaraldehyde with iron and polyvinyl alcohol and alginate.

### 5.2 – Further work

Within the scope of this review, it is apparent that there are multiple directions of future research to consider including refinement of selective adsorbents focusing on a particular heavy metal; improvement of adsorption capacity of a wide range of heavy metals by one adsorbent; progressing successful adsorbents to wider study such as cost, feasibility, real water testing and pooling results from studies to inform new modifications.

One suggestion would be the importance of continued refinement in the work of selective adsorbents in the interest of acquiring the highest possible adsorption rates due to heavy metal toxicity. For example, continuing the work of Zhang *et al.* (2022) to investigate selectivity towards Cr(VI).

## References

- Aghababi Beni, A., Esmaceli, A., Behjat, Y., (2021) 'Invent of a simultaneous adsorption and separation process based on dynamic membrane for treatment Zn(II), Ni(II) and, Co(II) industrial wastewater', *Arabian Journal of Chemistry*, 14(7). Available at: <https://doi.org/10.1016/j.arabjc.2021.103231> (Accessed: 27/06/24)
- Aranaz I., Alcántara A.R., Civera M.C., Arias C., Elorza B., Heras Caballero A., Acosta N., (2021) 'Chitosan: An Overview of Its Properties and Applications' *Polymers*, 19. Available at: doi: [10.3390/polym13193256](https://doi.org/10.3390/polym13193256) (Accessed: 01/03/24)
- Atangana, E., and Oberholster, P.J., (2020) 'Modified Biopolymer (Chitin–Chitosan Derivatives) for the Removal of Heavy Metals in Poultry Wastewater', *Journal of Polymers and the Environment*, 28(2), pp. 388-398. Available at: <https://doi-org.libezproxy.open.ac.uk/10.1007/s10924-019-01616-7> (Accessed: 27/06/24)
- Cheung, R.C., Ng, T.B., Wong, J.H., Chan, W.Y., (2015) 'Chitosan: An Update on Potential Biomedical and Pharmaceutical Applications.' *Mar. Drugs*, 13, 5156-5186. Available at: <https://doi.org/10.3390/md13085156> (Accessed: 26/02/24)
- Chopra, H., and Ruhi, G., (2016) 'Eco friendly chitosan: An efficient material for water purification' *The Pharma Innovation Journal*, 5, pp. 92-95. Available at: <https://api.semanticscholar.org/CorpusID:55229516> (Accessed: 25/04/24 )
- Contreras-Cortés, A., Almendariz-Tapia, F., Gómez-álvarez, A., Burgos-Hernández, A., Luque-Alcaraz, A., Rodríguez-Félix, F., Quevedo-López, M., Plascencia-Jatomea, M., (2019) 'Toxicological Assessment of Cross-Linked Beads of Chitosan-Alginate and *Aspergillus australensis* Biomass, with Efficiency as Biosorbent for Copper Removal', *Polymers*, 11(2). Available at DOI: [10.3390/polym11020222](https://doi.org/10.3390/polym11020222) (Accessed: 27/06/24)
- El Kaim Billah, R., Islam, Md. A., Nazal, M.K. Bahsis, L., Soufiane, A., Abdellaoui, Y., Achak, M., (2024) 'A novel glutaraldehyde cross-linked chitosan@acid-activated bentonite composite for effective Pb (II) and Cr (VI) adsorption: Experimental and theoretical studies', *Separation and Purification Technology*, 334, 126094. Available at: <https://doi.org/10.1016/j.seppur.2023.126094>. (Accessed: 27/06/24)
- Fan, S., Chen, J., Fan, C., Chen, G., Liu, S., Zhou, H., Liu, R., Zhang, Y., Hu, H., Huang, Z., Qin, Y., Liang, J., (2021) 'Fabrication of a CO<sub>2</sub>-responsive chitosan aerogel as an effective adsorbent for the adsorption and desorption of heavy metal ions', *Journal of Hazardous Materials*, 416, 126225. Available at: <https://doi.org/10.1016/j.jhazmat.2021.126225>. (Accessed: 27/06/24)
- He, Y., Gou, S., Zhou, L., Tang, L., Liu, T., Liu, L., Duan, M., (2021) 'Amidoxime-functionalized polyacrylamide-modified chitosan containing imidazoline groups for effective removal of Cu<sup>2+</sup> and Ni<sup>2+</sup>', *Carbohydrate Polymers*, 252, 117160. Available at: <https://doi.org/10.1016/j.carbpol.2020.117160>. (Accessed: 27/06/24)
- Huang, T., Shao, Y., Zhang, Q., Deng, Y., Liang, Z., Guo, F., Li, P., Wang, Y., (2019) 'Chitosan-Cross-Linked Graphene Oxide/Carboxymethyl Cellulose Aerogel Globules with

High Structure Stability in Liquid and Extremely High Adsorption Ability' *ACS Sustainable Chemistry & Engineering*, 7(9), pp. 8775-8788. Available at: <https://doi.org/10.1021/acssuschemeng.9b00691> (Accessed: 27/06/24)

Igberase, E., Ofomaja, A., Osifo, P.O., (2019) 'Enhanced heavy metal ions adsorption by 4-aminobenzoic acid grafted on chitosan/epichlorohydrin composite: Kinetics, isotherms, thermodynamics and desorption studies', *International Journal of Biological Macromolecules*, 123, pp. 664-676. Available at: <https://doi.org/10.1016/j.ijbiomac.2018.11.082>. (Accessed: 23/04/24)

Igberase, E., and Osifo, P.O., (2019) 'Application of diethylenetriamine grafted on glyoxal cross-linked chitosan composite for the effective removal of metal ions in batch system', *International Journal of Biological Macromolecules*, 134, pp. 1145-1155. Available at: <https://doi.org/10.1016/j.ijbiomac.2019.05.179>. (Accessed: 29/06/24)

Issahaku, I., Tetteh, I.K., Tetteh, A.Y. (2023) 'Chitosan and chitosan derivatives: Recent advancements in production and applications in environmental remediation', *Environmental Advances*, 11, 100351. Available at: <https://doi.org/10.1016/j.envadv.2023.100351> (Accessed: 25/04/24)

Kaveh, R., and Bagherzadeh, M., (2022) 'Simultaneous removal of mercury ions and cationic and anionic dyes from aqueous solution using epichlorohydrin cross-linked chitosan @ magnetic Fe<sub>3</sub>O<sub>4</sub>/activated carbon nanocomposite as an adsorbent', *Diamond and Related Materials*, 124, 108923. Available at: <https://doi.org/10.1016/j.diamond.2022.108923> (Accessed: 27/06/24)

Khan, N., Khan, I., Zada, N., Sadiq, M., Saeed, K., (2022) 'Utilization of cross-linked chitosan for cobalt adsorption and its reutilization as a photocatalyst for the photodegradation of methyl violet dye in aqueous medium', *Applied Water Science*, 12, 107. Available at: <http://dx.doi.org.libezproxy.open.ac.uk/10.1007/s13201-022-01633-3> (Accessed: 27/06/24)

Li, H., Dong, X., de Silva, E., de Oliveira, L., Chen, Y., Ma, L.Q., (2017) 'Mechanisms of metal sorption by biochars: Biochar characteristics and modifications', *Chemosphere*, 178, pp. 466-478. Available at: <https://doi.org/10.1016/j.chemosphere.2017.03.072> (Accessed: 21/08/24)

Li, J., Wang, L., Jiang, G., Wan, Y., Wang, J., Li, Y., Pi, F., (2024) 'Luminescent carbon dots-rooted polysaccharide crosslinked hydrogel adsorbent for sensitive determination and efficient removal of Cu<sup>2+</sup>' *Food Chemistry*, 447, 138977. Available at: <https://doi.org/10.1016/j.foodchem.2024.138977> (Accessed: 27/06/24)

Liu, J., Wang, S., Fu, J., Ding, X., Zhao, J., (2020) 'Zn<sup>2+</sup> adsorption from wastewater using a chitosan/ $\beta$ -cyclodextrin-based composite membrane', *Journal of Food Biochemistry*, 44(12), pp. 1-10. Available at DOI: 10.1111/jfbc.13483. (Accessed: 27/06/24)

Midya, L., Das, R., Bhaumik, M., Sarkar, T., Maity, A., Pal, S., (2019) 'Removal of toxic pollutants from aqueous media using poly (vinyl imidazole) crosslinked chitosan synthesised

- through microwave assisted technique', *Journal of Colloid and Interface Science*, 542, pp. 187-197. Available at: <https://doi.org/10.1016/j.jcis.2019.01.121>. (Accessed: 27/06/24)
- Negm N.A., Hefni, H.H., Abd-Elaal, A.A., Badr, E.A., Abou Kana, M., (2020) 'Advancement on modification of chitosan biopolymer and its potential applications', *International Journal of Biological Macromolecules*, 152, pp. 681-702. Available at: <https://doi.org/10.1016/j.ijbiomac.2020.02.196> (Accessed: 25/05/24 )
- Neto, J., Bellato, C., Silva, D., (2019) 'Iron oxide/carbon nanotubes/chitosan magnetic composite film for chromium species removal', *Chemosphere*, 218, pp. 391-401. Available at: <https://doi.org/10.1016/j.chemosphere.2018.11.080> (Accessed: 27/06/24)
- Pal, P., Pal, A., Nakashima, K., Yadav, B.K., (2021) 'Applications of chitosan in environmental remediation: A review', *Chemosphere*, 266. Available at: <https://doi.org/10.1016/j.chemosphere.2020.128934> (Accessed: 21/02/24)
- Panahandeh, A., Parvareh, A., Moraveji, M.K., (2021) ' Synthesis and characterization of  $\gamma$ -MnO<sub>2</sub>/chitosan/Fe<sub>3</sub>O<sub>4</sub> cross-linked with EDTA and the study of its efficiency for the elimination of zinc(II) and lead(II) from wastewater', *Environmental Science and Pollution Research*, 28(8). Available at DOI: 10.1007/s11356-020-11359-x (Accessed: 27/06/24)
- Pavithra, S., Thandapani, G., Sugashini, S., Sudha, P.N., Alkhamis, H.H., Alrefaei, A.F., Almutairi, M.H., (2021) 'Batch adsorption studies on surface tailored chitosan/orange peel hydrogel composite for the removal of Cr(VI) and Cu(II) ions from synthetic wastewater', *Chemosphere*, 271, 129425. Available at: <https://doi.org/10.1016/j.chemosphere.2020.129415> (Accessed: 27/06/24)
- Refaat, A., Elhaes, H., Ammar, N.S., Ibrahim, H.S., Ibrahim, M., (2020) 'Green route for the removal of pb from aquatic environment', *Combinatorial Chemistry and High Throughput Screening*, 23(7), pp. 587-598. Available at DOI: 10.2174/1386207323666200127123349. (Accessed: 27/06/24)
- Salehi, N., Moghimi, A., Shahbazi, H., (2022) 'Preparation of cross-linked magnetic chitosan with methionine-glutaraldehyde for removal of heavy metals from aqueous solutions', *International Journal of Environmental Analytical Chemistry*, 102(10), pp. 305–2321. <https://doi-org.libezproxy.open.ac.uk/10.1080/03067319.2020.1753718> (Accessed: 27/06/24)
- The Open University (2024) '6.5 square planar complexes'. *S315: Chemistry Further Concepts and Applications*. Available at: <https://learn2.open.ac.uk/mod/oucontent/view.php?id=1916707&section=6.5> (Accessed 12/08/24)
- Wang, Y., Ai, Y., Liu, X., Chen, B., Zhang, Y., (2022) 'Indole-functionalized cross-linked chitosan for effective uptake of uranium(vi) from aqueous solution' *Polymer Chemistry*, 13(12), pp. 1751-1762. Available at: <https://doi.org/10.1039/d1py01725j> (Accessed: 27/06/24)
- Watwe, V., and Kulkarni, P., (2021) 'Evaluation of Cr(VI) adsorption on glutaraldehyde crosslinked chitosan beads using cyclic voltammetry employing gold electrode', *Journal of*

*Analytical Science and Technology*, 12(1), pp. 1-10. Available at DOI: 10.1186/s40543-021-00291-5. (Accessed: 27/06/24)

Zhang, P., Zou, K., Yuan, L., Liu, J., Liu, B., Qing, T., Feng, B., (2022) 'A biomass resource strategy for alginate-polyvinyl alcohol double network hydrogels and their adsorption to heavy metals', *Separation and Purification Technology*, 301, 122050. Available at: <https://doi.org/10.1016/j.seppur.2022.122050> (Accessed: 27/06/24)

Zubair, M., Zahara, I., Roopesh, M.S., Ullah, A., (2023) 'Chemically cross-linked keratin and nanochitosan based sorbents for heavy metals remediation', *International Journal of Biological Macromolecules*, 241, 124446. Available at: <https://doi.org/10.1016/j.ijbiomac.2023.124446>. (Accessed: 27/06/24)

Upadhyay, U., Sreedhar, I., Singh, S.A., Patel, C.M., Anitha K.L., (2021)'Recent advances in heavy metal removal by chitosan based adsorbents', *Carbohydrate Polymers*, 251, 117000. Available at: <https://doi.org/10.1016/j.carbpol.2020.117000> (Accessed: 25/04/24)

Usman, M., Ahmed, A., Yu, B., Wang, S., Shen, Y., Cong, H., (2021) 'Simultaneous adsorption of heavy metals and organic dyes by  $\beta$ -Cyclodextrin-Chitosan based cross-linked adsorbent', *Carbohydrate Polymers*, 255, 117486. Available at: <https://doi.org/10.1016/j.carbpol.2020.117486>. (Accessed: 25/04/24)

