Use of complex-formation method in a selective metal separation

Lappeenranta-Lahti University of technology LUT

Bachelor's Thesis in Chemical Engineering

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ABSTRACT

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The goal of this bachelor thesis is to study bio-based complexing agents and their selectivity towards metals. Feasibility of combination of metal-complexation with other separation methods is studied. A comparison with currently used complexing agents like EDTA is also provided. Selectivity, stability, cost-effectiveness, sustainability and availability of different complexing agents is discussed.

As a rule, metal-containing streams, such as ore leachates or a spent battery waste leachates are multicomponent. Variety of industrial effluents are usually mixtures of variety of metal ions that may cause severe environmental and human health risks. In addition, fast development in technology causes an ever-increasing demand for variety of critical metals. However, this surge in demand is leading to supply challenges due to their limited availability. Therefore, there is a need for a selective, sustainable and cost-effective separation of mixture into single metal streams.

For example, poor selectivity is a significant drawback of current separation methods. The complex-formation of biomolecules with metals is widely known in biochemistry: iron is forming complex with protein in a hemoglobin structure, enzymatic reactions inside cells require the presence of co-factors (metals), vitamin B12 consists of cobalt-containing complex. This thesis suggests that, in theory, these molecules have potential as an alternative for separation methods and complexing agents in industrial use today. More research is needed to examine their selectivity and scalability to real industrial applications in order to unlock their full potential.

TIIVISTELMÄ

Lappeenranta–Lahden teknillinen yliopisto LUT

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Kemianteknikka

Veera Ihalainen

Kompleksinmuodostuksen hyödyntäminen selektiivisessä metallien erotuksessa

Kemiantekniikan kandidaatintyö

2024

50 sivua, 16 kuvaa, 6 taulukkoa ja 1 liite

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Tämän kandidaatintyön tavoitteena on tutkia biopohjaisia kompleksinmuodostajia ja niiden selektiivisyyttä metalleja kohtaan. Työssä tarkastellaan myös kompleksinmuodostuksen ja muiden erotusmenetelmien yhdistämisen mahdollisuutta. Työssä tehdään myös vertailu nykyisin käytettyihin kompleksinmuodostajiin, kuten EDTA:han. Lisäksi eri kompleksinmuodostajien selektiivisyyttä, stabiiliuutta, kustannustehokkuutta, kestävyyttä ja saatavuutta käsitellään.

Metalleja sisältävät sivu- ja jätevirrat ovat yleensä monikomponenttisia. Erilaiset teollisuuden jätevedet ovat yleensä sekoituksia monista metalli-ioneista, jotka voivat aiheuttaa vakavia ympäristö- ja terveysriskejä. Lisäksi teknologian nopea kehitys aiheuttaa jatkuvasti kasvavaa kysyntää monille kriittisille metalleille. Tämä kysynnän kasvu johtaa kuitenkin saatavuushaasteisiin niiden rajallisen saatavuuden vuoksi. Siksi tarvitaankin selektiivisiä, kestäviä ja kustannustehokkaita menetelmiä seosten erottamiseksi yksittäisiksi metalleiksi.

Esimerkiksi huono selektiivisyys on merkittävä haittapuoli nykyisissä erotusmenetelmissä. Biomolekyylien kompleksinmuodostus metallien kanssa on laajalti tunnettu biokemiassa: rauta muodostaa kompleksin proteiinin kanssa hemoglobiinirakenteessa, solujen sisäiset entsymaattiset reaktiot vaativat kofaktoreiden (metallien) läsnäoloa, ja B12-vitamiini koostuu kobolttia sisältävästä kompleksista. Tämä työ esittääkin, että teoriassa näillä molekyyleillä on potentiaalia myös teollisuudessa nykyisten erotusmenetelmien ja kompleksinmuodostajien vaihtoehtoina. Tarvitaan kuitenkin lisää tutkimusta niiden toimivuudesta todellisissa teollisissa sovelluksissa, jotta niiden täysi potentiaali saadaan käyttöön.

Table of Contents

1 Introduction

1.1 Background

Variety of industrial effluents, for instance from mining, metal, electronics or battery industry are usually mixtures of variety of metal ions that may cause severe environmental and human health risks (Huang & Feng, 2019; Llanos et al., 2010). For example, the presence of heavy metals in seawater has become a significant concern due to its harmful effects on marine life and human health. Human activities along coastal areas are major contributors to the accumulation of heavy metals in marine ecosystems. These metal ions, found in trace amounts in seawater, are often toxic and long-lasting, posing risks to both marine organisms and humans. (Kane et al., 2016.)

In addition, continuous advancements in technology, new developments and the functionality of electronic equipment result in a skyrocketing demand for variety of metals, particularly critical metals, such as cobalt and lithium. These elements play pivotal roles in the manufacture of clean energy technologies (Solano & Mišković, 2024). However, this surge in demand is leading to a supply crisis due to their limited availability in the Earth's crust and geopolitical constraints, which could potentially result even in political challenges (Zhang et al., 2017). Limited availability of critical metals in local mines, soaring production expenses, environmental hazards linked with extraction, and geopolitical trade concerns have rendered their supply chains fragile (Solano & Mišković, 2024).

As a result, it is highly important to find as selective, sustainable and cost-effective methods as possible to separate these mixtures into single metal streams (Llanos et al., 2010). In addition, current methods of metal separation are discussed and reviewed in this thesis.

1.2 Research objectives

In heavy metal separation different membrane filtration techniques are of interest because of their simplicity and high efficiency (Sadeghi et al., 2018; Xiang et al., 2022). However, the biggest drawbacks of membrane filtration are low selectivity and risk of contamination (Hedberg et al., 2011; Sadeghi et al., 2018).

Complex formation is another effective method for metal separation. There are several synthetic complexing molecules currently used, but they are not always the most sustainable, selective or cost-effective options either. (Molnar, 2013.) This thesis looks at a few well-known biomolecules, such as vitamin B12, and tannins, and their ability to form complexes as a possible solution to this problem. Availability, costs and sustainability of the molecules are also discussed. Ethylenediaminetetraacetic acid, EDTA, currently the most common synthetic molecule in metal separation today (Molnar, 2013), is used as a reference of comparison. Another aim of this thesis is to find out if complex formation and biobased complexing agents could be combined with other separation methods, resulting in a more efficient separation process. This thesis is carried out as a literature review. Materials and methods are described in appendix 1.

2 Biomolecules able to form complexes

This chapter provides a brief description of principles of complex formation. Selected biomolecules are considered as an alternative for synthetic chelating agents. Different approaches such as sustainability, selectivity, stability, availability and cost-effectiveness are taken into account.

2.1 Introduction to chelating agents and complex formation

Chelating agents, also known as chelants, are organic compounds designed to bind to metal ions in solutions, effectively trapping them and reducing their interactions with the surrounding environment by forming complexes called chelates. These compounds exhibit varying degrees of stability depending on the specific metal ion involved, with stability constants differing significantly across different metal ions. Chelants have a highly versatile properties and they find applications in diverse fields such as paper and pulp processing, water softening in detergents, removal of toxic metals from the human body, and supplementation for agricultural crops. (Gentry et al., 2021.)

However, there's increasing worry about the buildup of current chelating agents in ecosystems because they are highly stable and soluble in water. This accumulation leads to higher concentrations of chelants at various points in the water cycle. The accumulation of chelating agents can adversely affect the availability of metal ions in ecosystems, highlighting the need for sustainability improvements in this area. Despite this recognition, progress in identifying viable alternatives to existing chelants has been slow. The entrenched use of current chelating agents in global economies coupled with the time-consuming and expensive nature of experimental testing has hindered the development of alternatives. (Gentry et al., 2021).

Ethylenediaminetetraacetic acid, EDTA, is one of the most common synthetic complexing agent with variety of industrial applications (Molnar, 2013). However, the environmental challenges and low selectivity of EDTA have created a need for more sustainable, selective and cost-effective methods for metal separation (Jez & Lestan, 2016; Molnar, 2013). The following provides a closer review of both EDTA and some biobased molecules able to form complexes with critical metal ions. The potential of these biomolecules as an alternative for EDTA is discussed.

2.2 Ethylenediaminetetraacetic acid (EDTA)

Ethylenediaminetetraacetic acid, EDTA, is a widely used, low toxic and cost-effective synthetic aminopolycarboxylic acid with six coordination sites superior for metal removal (Jez & Lestan, 2016, 204; Yu et al., 2022). EDTA is utilized in wide range of different industries, and the global consumption is constantly increasing (Molnar, 2013). It creates a binding pocket formed by two nitrogen atoms and four COO^- -groups (Foreman et al., 2023). The structure of EDTA is presented in Figure 1.

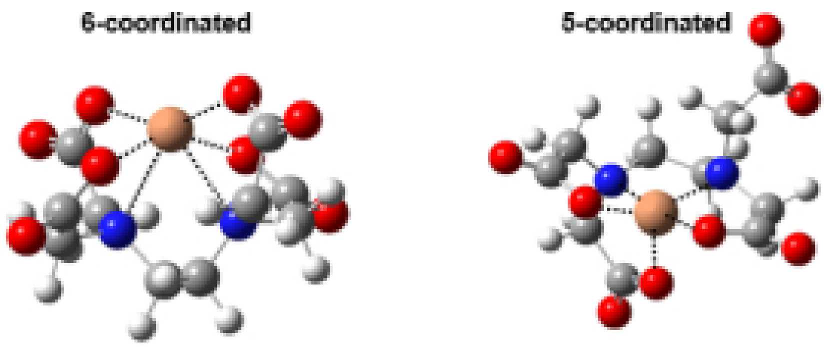

Fig. 1. Structure of an EDTA-molecule (Foreman et al., 2023).

To sum up, compared to other commonly used extraction or chelating agents, EDTA and its homologs stand out for their strong chelating ability, low cost, vast amount of possible applications and recyclability (Chen et al., 2022). The metal removal efficiency of EDTA is compared with a few bio-based chelating agents in Table 1.

Table 1. The metal removal efficiency of common chelating agents (Chen et al., 2022).

Chelating agents	**Soil texture**	**Concentration**	**Removal efficiency**
Ethylenediaminetetraacetic acid	Sand 78,20 %	0,50 M	Cu 70,30 %
(EDTA)	Silt 13,20 %		Zn 60,40 %
	Clay 8,60 %		Cd 56,70 %
			Pb 50,50 %
			Ni 62,50 %
Citric acid (CA)	Red loam	1,00 M	Cu 66,59 %
			Zn 43,10 %
			Cd 77,48 %
			Pb 37,95 %
Glutamic acid (GLDA)		0,02 M	Cu 61,00 %
			Pb 78,00 %
Ethylenediamine disuccinic acid	Sand 67,12 %	0,05 M	Zn 25,40 %
(EDDS)	Silt 19,75 %		Cd 24,10 %
	Clay 13,13 %		Pb 36,50 %

Even though the efficiency of EDTA for separating toxic metals, for example, from soil and process waters has been shown by many scientists, the metals or other chelates EDTA forms complexes with may be toxic and risky for human health and environment as the complexes easily remain and spread in the soil. (Jez & Lestan, 2016.) The biggest challenge with EDTA as a multidentate chelant is the non-selectiveness in nature. This usually leads to extra amount of chelant added to ensure the sufficient separation of the target metal, leading to increasing environmental stress. (Molnar, 2013.) These negative effects, in addition to the increasingly stringent environmental regulations, have gained more and more attention among scientists (Jez & Lestan, 2016; Molnar, 2013).

EDTA is released to the environment predominantly via wastewaters and considered non-biodegradable. Depending on concentration, pH and other co-existing complexing agents, once released into aquatic environments, EDTA may enable metal ions to remobilize from soil into the water phase extending the residence time of the metals. Long-time negative environmental effects, such as eutrophication and desorption, are probable due to the poor rate of photo-, chemo-, and biodegradability of EDTA. (Molnar, 2013.)

One way to approach these environmental issues is to pay attention to pre-release management and degradation treatment of EDTA-containing effluent waters. For example, electrochemical reduction treatment followed by membrane separation, precipitation treatment, addition of suitable reagents or application of molecular recognition technology have been suggested to recover and reuse EDTA and metals. However, some operational challenges, such as fouling, membrane degradation and high costs, are usually associated with these technologies. On the other hand, scientists have found that EDTA can potentially be oxidized by specially enriched bacterial cultures. (Molnar, 2013.)

2.3 Biomolecules able to form complexes

This chapter presents different bio-based molecules like vitamin B12, tannins and amino acids as possible alternatives for EDTA. Their properties and basic characteristics are provided.

2.3.1 Vitamin B12

Vitamin B12, cyanocobalamin, is the largest vitamin of all. It is a water-soluble and essential nutrient in mammals produced by certain bacteria and archaea. Consequently, vitamin B12 has an extremely low bioavailability and for example mammals can gain it only through diet. Deficiency of vitamin B12 can cause, for example, weakness, fatigue, constipation, anemia and neurological problems. (Pettenuzzo et al., 2017.)

Cobalamin, or more precisely its derivates adenosylcobalamin and methylcobalamin, are cofactors with a significant role in various important biological processes, such as DNA synthesis and regulation, nervous system function and red blood cell formation (Giedyk et al., 2015). Due to naturality, nontoxicity and environmental friendliness, vitamin B12 and its derivates have gained interest as catalysts for different organic reactions. For example, in terms of enzymatic reactions or metal binding, the most interesting features of the vitamin B12-molecule structure are the cobalt center and the Co-C bond. (Giedyk et al., 2015.) These structures are discussed further in chapter 3.1.

With the increasing adoption of vegan diets, vitamin B12 deficiency is on the rise. While complete synthesis of B12 is possible, it is not economically feasible for mass production. The strains that naturally produce B12 are not suitable for the large-scale industrial fermentations, unlike *E. coli* or yeast, making B12 the most expensive vitamin on the market. Challenges in commercial production include the addition of cobalt to growth media and the need for careful disposal due to health and environmental concerns. Improvements in safer production methods may have driven the increase in B12 prices. Sustainable and cost-effective large-scale manufacturing is a topic of further research. (Osman et al., 2021.)

2.3.2 Tannins

Tannins are natural polyphenolic compounds derived from plants, known for their adaptable molecular structure and desirable characteristics suitable for a diverse array of industrial uses. They can be grouped as condensed tannins, CT, and hydrolysable tannins, HT. CTs, for example, exist in the bark of conifers, eucalypts, leguminous hardwoods and other timber species, and they have bigger molecular weight than HTs. Tannins are able to form stable complexes with several different metal ions, such as Al^{3+}, Fe^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+}. (Zhang et al., 2023.) This chapter looks at these complexes and their implications in human health, the environment and industries. The structures of CTs and HTs are shown in Figure 4.

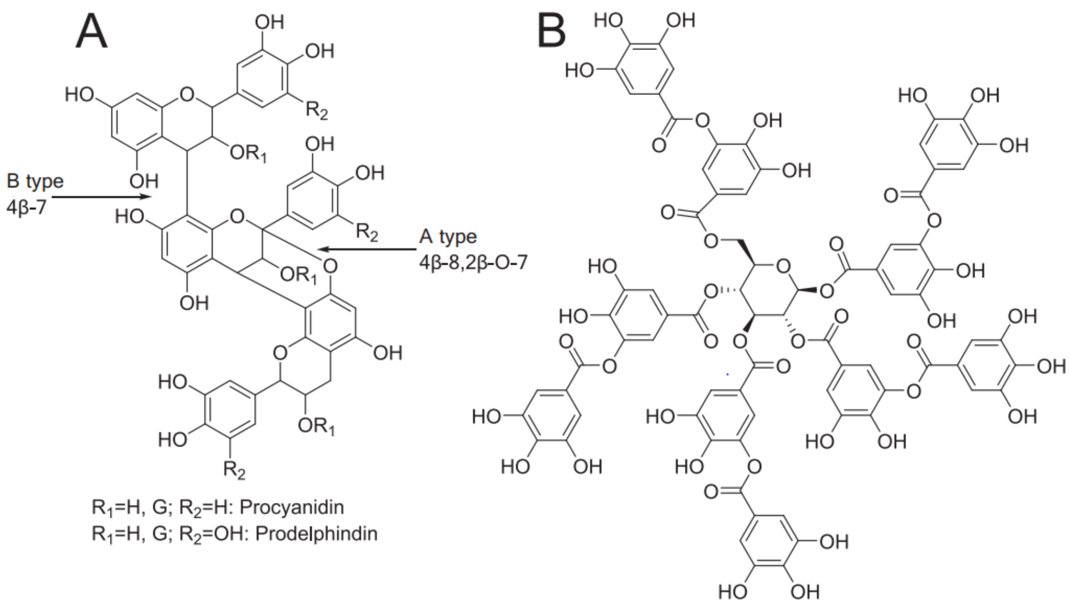

Fig. 2. The structure of A: condensed tannins, and B: hydrolysable tannins (Zhang et al., 2023).

Complexation of iron by tannins is has also well-established and representative consequences in biology and human health. For example, drinks with high concentrations of PPs, such as wine or tea, together with iron digested from food form complexes resulting in impeded iron absorption from the gut barrier. However, this effect depends on the other nutrients present and can be limited with a versatile diet. Besides iron, researchers have also investigated the effects of other metals like copper and zinc in this context, yielding mixed findings. Intriguingly, moderate wine consumption has been linked to a decreased risk of senile dementia, likely attributed to PPs in wine forming complexes with aluminum present in drinking water. Since largely metabolized, PPs lose their functionality after absorption, which is why their role in metal ion complexation is mainly limited to the gut. However, iron chelation by PPs has been shown to have antioxidant effects in the human body, resulting e.g. in cytoprotective effects. Additionally, PPs can also protect DNA from damage by forming complexes with Fe^{2+}. On the other hand, there is a need for additional investigation into the relationship between the findings from cellular studies and the efficacy of preventing diseases related to oxidative stress in clinical trials involving animals or humans. (Zhang et al., 2023.)

In addition to human health, tannin's interactions with metals may have a significant role for example in plant defense and soil treatment as well. Plants produce various organic metal binding compounds, including tannins. Tannins can be found in high concentrations in protective layers of plants, such as bark of fruit periderms, where they are able to bind iron, limit the penetration of microorganisms and protect the plant from damage efficiently. Additionally, after released to the environment for example through root exudation or leaf litter decomposition, some studies suggest that tannins and other PPs can bind with environmentally hazardous metals, such as Ni^{2+}, Pb^{2+}, Cd^{2+} or Cr^{3+} and mitigate the detrimental effects of Al^{3+} for example on plant roots. (Zhang et al., 2023.) An illustration of a tannin complexing with Al^{3+} is shown in Figure 3. However, the interactions between PPs and metals are intricate, influenced by various factors in the surrounding environment, making them challenging to predict reliably. Additionally, the concentration of tannins tends to be specific to each species and correlates with factors like soil fertility, pH levels, light exposure, plant maturity, temperature and the concentration of CO_2 in the atmosphere. (Zhang et al., 2023.)

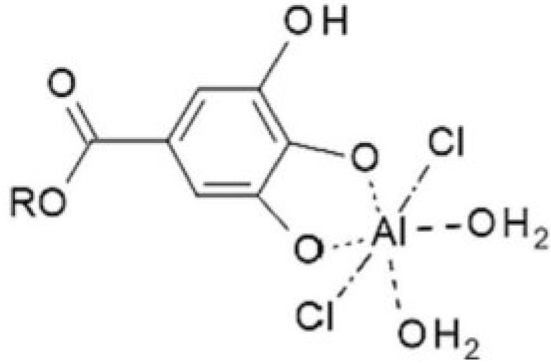

Fig. 3. Tannins forming a complex with Al^{3+} (Zhang et al., 2023).

The industrial significance of interactions between metals and polyphenols is extensive and widely utilized due to their cost-effectiveness and high efficacy in removing heavy metal ions and dyes from industrial wastewater. Tannins find application in various industries such as wood adhesives, concrete additives for reducing water content, viscosity reducers in oil drilling fluids, as well as in pharmaceuticals, mineral processing, water treatment, gas desulfurization, anticorrosion coatings, printing and dyeing processes, liquor clarification, oil antioxidants, and the formulation of daily chemical products. In corrosion protection, tannins have shown superior effectiveness compared to synthetic phenols. Vegetal tannins are particularly appealing due to their cost-effectiveness, eco-friendliness, non-toxicity, and biodegradability. Nonetheless, further research is necessary to explore the full potential of vegetal tannins across a wider range of metals and mixtures. (Zhang et al., 2023.)

One of the main factors contributing to the effectiveness of tannins as binders of metal ions is their high degree of ionization and the elevated cationic charge of metal species, which facilitate the reactions between them. However, further research is required to gain a deeper understanding of how metals influence the biological activities of natural PPs. In addition, the effect of pH level and metal concentration on affinity and stability of tannin-metal complexes are yet to be studied. (Zhang et al., 2023.)

2.3.3 Amino acids

Amino acids are fundamental organic compounds crucial for constructing proteins and polypeptides within living organisms. Structurally, they comprise both amino and acid groups. Typically categorized as essential, non-essential, and functional amino acids, they play vital roles in biological processes. Essential are not produced by the body and must be acquired from the diet, while non-essential amino acids are synthesized adequately within the body. Amino acids are vital for numerous physiological functions, including nutrient absorption and metabolism, cellular signaling, hormone production and release, regulation of blood flow, immune system function, and overall body homeostasis. (Wu, 2009.)

Moreover, some studies have analyzed the potential roles of amino acids in metal complexation and detoxification processes. It has been observed that e.g. certain plants are able to absorb, accumulate, and tolerate especially high concentrations of heavy metals or metalloids in their aerial tissues without experiencing toxic effects by utilizing a process called hyperaccumulation. It is a specialized mechanisms to mobilize metal ions from the soil, transport them within the plant, and sequester them in specific tissues, organelles or leaf cells. Metals are then bonded to ligands forming stable complexes. These metal complexes help to detoxify the plant by decreasing the concentration of free toxic metal ions in the cytoplasm and preventing metal-induced damage to cellular structures. Overall, hyperaccumulation enhances the plant's ability to cope with high metal concentrations by effectively managing metal complexation and storage. (Callahan et al., 2007.)

For example, hyperaccumulation in *Thlaspi* species, involves the circulation of nicotianamine and nicotianamine-nickel chelates from roots to shoots, contributing to the sequestration and storage of nickel in above-ground tissues. The presence of nicotianamine in these hyperaccumulator plants is associated with the complexation of nickel, zinc, and iron, highlighting the role of these compounds in metal binding and detoxification processes. Some studies have shown a strong correlation especially between nickel and nicotianamine, which might imply to some level of selectivity. However, as seen in Table 2, association constants of nicotianamine towards different metal ions seem slightly lower than those of EDTA. (Callahan et al., 2007)

Table 2. The logarithmic values representing the strength of the bonding between metal ions and specific ligands. Co = cobalt, Cu = copper, Fe = iron, NA = nicotinamine, Ni = nickel, Zn = zinc. (Callahan et al., 2007).

Ligand	**Ni^{2+}**	**Zn^{2+}**	**Fe^{3+}**	**Fe^{2+}**	**Cu^{2+}**	**Co^{2+}**
NA	16,1	14,7-15,4	20,6	12,1-12,8	18,6	14,8
EDTA	18,7	16,2	25,8	14,2	18,9	16,3
Citric acid	5,4	5,0	11,5	4,4	5,9	4,1

Even though hyperaccumulation is considered relatively selective and efficient process for nickel separation, an inverse relationship between nickel and iron concentrations in the leaves may result in a competitive interaction between nickel and iron for complexation to nicotianamine. Furthermore, further research to study the significance of other amino acids, for example histidine and glycine, in relation to nickel exposure and hyperaccumulation processes is also needed. (Callahan et al., 2007)

2.3.4 Environmental aspects

Environmental aspects of separating critical metals from industrial effluents is a crucial and topical issue. Sustainable methods for metal extraction are needed to minimize environmental impact, reduce waste generation, promote resource efficiency, save energy and increase cost-effectiveness. By focusing on green chemistry approaches, closed-loop processes, and biotechnological methods, researchers aim to enhance the efficiency of metal extraction while minimizing environmental pollution and waste generation. Chelation technology is often considered one of the most promising, cost-effective, energy-efficient and applicable methods. However, traditional non-biodegradable chelating agents can potentially harm the ecosystem. (Prajapati & Singhai, 2020.)

With that being said, biodegradable chelating agents are particularly significant in promoting sustainable metal separation practices. They offer a more environmentally friendly approach to extracting metals from industrial waste streams, serving as alternatives to non-biodegradable agents that may pose risks to ecosystems. For instance, in the fertilizer industry, biodegradable chelating agents have proven successful in extracting metals like Fe, Mn, Ni, Mo, Cu, Pb, Cd, Zn, Rh, and Ru from spent catalysts. Various biodegradable chelating agents, such as ethylenediamine disuccinic acid, EDDS, possess specific molecular structures that enable them to form stable complexes with metal ions. (Prajapati & Singhai, 2020.)

The structure of e.g. EDDS is characterized by the presence of multiple functional groups that can coordinate with metal ions. The molecule includes two carboxylic acid groups and two amino groups, which provide multiple sites for metal ion binding. The biodegradable properties are of these molecules are often linked to the existence of functional groups that can be readily broken down through biological mechanisms. This breakdown process results in the degradation of the chelating agent into harmless byproducts. This makes biodegradable chelating agents more environmentally friendly compared to non-biodegradable counterparts. (Prajapati & Singhai, 2020.) The structure of EEDS is shown in figure 7. Another biodegradable chelating agent, glutamic acid, GLDA, complexed with sodium by a ligand substitution (Prajapati & Singhai, 2020) is also shown in Figure 4.

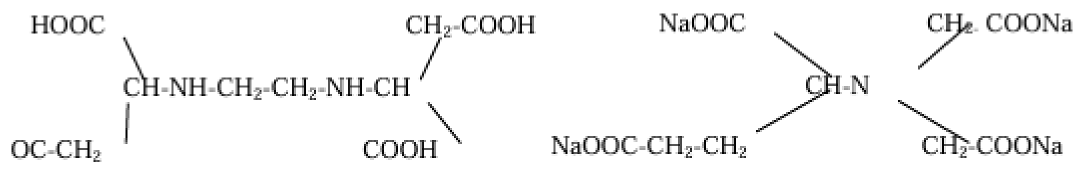

Fig. 4. Molecular structure of EEDS and L-GLDA-Na_4 (Prajapati and Singhai, 2020).

Comparison between several different biodegradable chelating agents is made in Table 3. These agents can be compared based on various factors such as their biodegradability, metal binding capacity, stability, pH range, environmental impact, and application suitability. For example, GLDA mentioned above is considered environmentally friendly, which can be explained by its biobased carbon source and high natural material content. EEDS, however, has shown high affinity for heavy metals, but lower levels of biodegradability. (Prajapati & Singhai, 2020.)

Table 3. Common biodegradable chelating agents and their properties. (Prajapati & Singhai, 2020.)

	Chelating agent				
Properties	IDS	EDDS	GLDA	MGDA	DS
Molecular weight, g/mol	337,1	358,1	351,1	271	
pH	10,3-11,4	9,2	13,5	11,0	9,5-10,5
Density, g/mL	1,32-1,35	1,26	1,38	1,31	1,30
Solubility in water	In any ratio	In any ratio	In any ratio	In any ratio	In any ratio
Biodegradability	> 80 %	> 60 %	> 83 %	> 68 %	> 60 %

IDS = iminodisuccinic acid, EDDS = ethylenediamine disuccinic acid, GLDA = glutamic acid, MGDA = methyl glycine diacetic acid, DS = polyaspartic acid.

While traditional chelating agents are effective chelating agents with strong metal binding capacities, their resistance to biodegradation and potential environmental risks have resulted in development and adoption of biodegradable chelating agents that offer similar metal binding capabilities in a manner that is more ecologically sustainable and considerate of the environment. EDTA, for example, is recognized for its enduring presence in the environment owing to its limited ability to degrade naturally, which raises concerns about its long-term impact on ecosystems. In contrast, biodegradable chelating agents are designed to be readily biodegradable, with high rates of degradation into non-toxic byproducts, making them greener alternatives and offering comparable metal binding capabilities while addressing concerns related to biodegradability and environmental impact. (Prajapati & Singhai, 2020.)

3 Mechanism(s) of complex formation/stability of complexes

The effective utilization of chelation technology in metal extraction exemplifies a sophisticated ligand substitution mechanism. However, its industrial implementation is hindered by insufficient comprehension of competing reactions that could influence metal-ligand complexation. Further experimental investigations are essential to deepen our understanding of the ligand substitution mechanism and to uncover the broad applications of chelation technology prioritizing sustainability, economics, and environmental considerations to address the increasing industrial requirements. (Prajapati & Singhai, 2020.)

This chapter looks at both complexing mechanisms of metals with both EDTA and selected bio-based ligands and stability of these complexes. Finally, the effect of pH level on complex stability is also discussed.

3.1 Mechanisms of complex formation of EDTA, vitamin B12 and tannins

There are various mechanisms through which metal-ligand complexes can form. For example, metal ions, having empty orbits, accept electrons, while ligands, possessing free electron pairs, donate electrons, leading to the formation of coordination covalent bonds. Additionally, electrostatic forces come into play, particularly between cationic polymers and positively charged metal ions. (Huang & Feng, 2019.) In the following, EDTA, vitamin B12, tannins and their mechanism to form complexes are covered more thoroughly.

3.1.1 EDTA and complex formation

Basically, EDTA can form complexes with all the metals in the periodic table (Molnar, 2013). In total, it has six coordination sites able to capture metal ions and form chelates. It has four carboxyl groups and two amino nitrogens, all applicable to take part in chelation. (Yu et al., 2022.) As an example, EDTA forming a complex with copper is presented in Figure 5. In case of copper, one one of the carboxyl groups in the ligand does not participate in coordination (Yu et al., 2022).

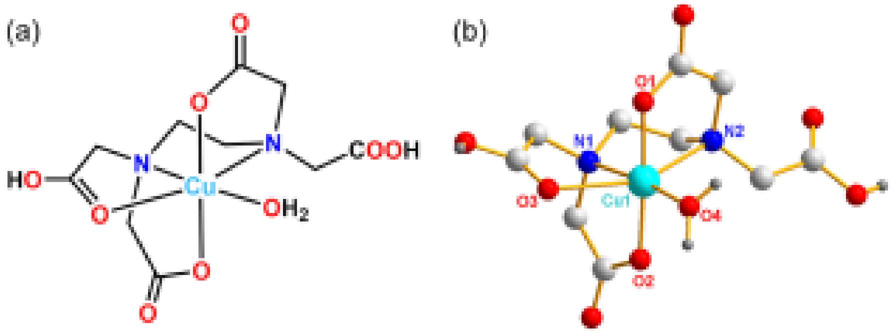

Fig. 5. (a) Molecular and (b) crystal structure of EDTA forming a complex with copper (Yu et al., 2022).

3.1.2 Vitamin B12 and complex formation

Vitamin B12 is a complex organic compound containing a cobalt center, a corrin ring, and surrounding substituents. Different forms of cobalamin, such as methylcobalamin, vary based on the type of axial ligand attached, like a methyl group. In nature, vitamin B12 serves as a co-factor for enzymes involved in various biological processes. The corrin ring in vitamin B12 coordinates to the central cobalt, acting as a monoanionic ligand. Under reductive conditions, the central cobalt takes a low-valent state, becoming highly nucleophilic and reactive. This reactivity has attracted attention among researchers. Thus, the Co-C bond in vitamin B12 acts as a coordination site for metal ions. The cobalt center in vitamin B12 can coordinate with various metal ions, forming stable complexes through coordination bonds. The metal ion interacts with the Co-C bond, resulting in the coordination of the metal ion to the cobalt center of vitamin B12. (Koide et al., 2022.) Chemical structures of cobalamin and its derivates are given in Figure 6.

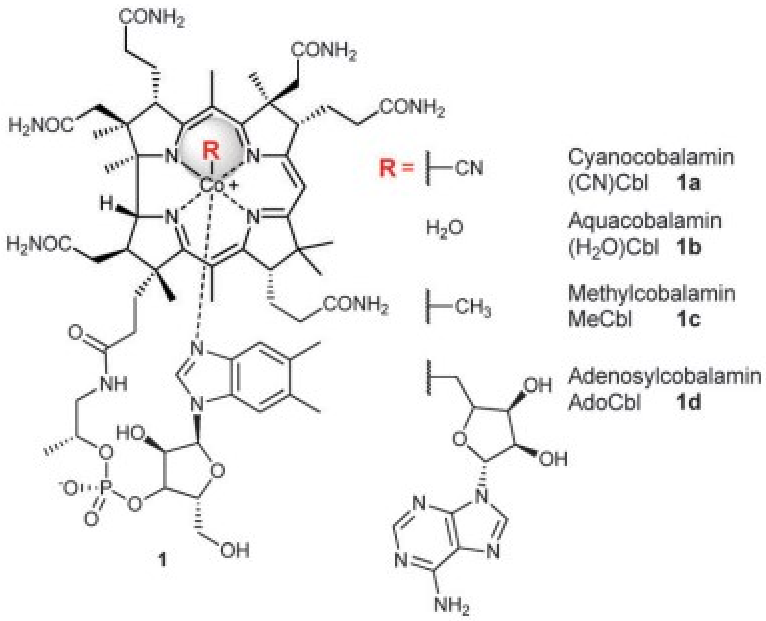

Fig. 6. Cobalamin and its derivatives cyanocobalamin, aquacobalamin, methylcobalamin and adenosylcobalamin. (Giedyk et al., 2015.)

3.1.3 Tannins and complex formation

CTs are believed to interact with metals with their O-dihydroxyphenyl groups of the B-ring. However, the ability to chelate metals depends on the hydroxylation pattern of the B-ring and the level of polymerization. Tannins can form percipitates with their O-dihydroxyphenyl functional groups. In terms of successful complexation, optimal ratio of tannin and metal concentrations as well as pH control are key factors. (Zhang et al., 2023.)

Currently, the reaction between Fe^{3+} and PPs is gaining increasing interest among researchers due to the ability of PPs, especially tannins containing the O-dihydroxyphenyl group, to mobilize iron for example in acid soils forming extremely stable complexes. The reaction is shown in Figure 7. According to some studies, at lower pH-level, the semiquinone ligand oxidized during the process is protonated as neutral ligand, stabilizing Fe^{3+} over Fe^{2+}. At neutral or even higher pH, appear to be significantly slower. (Zhang et al., 2023.)

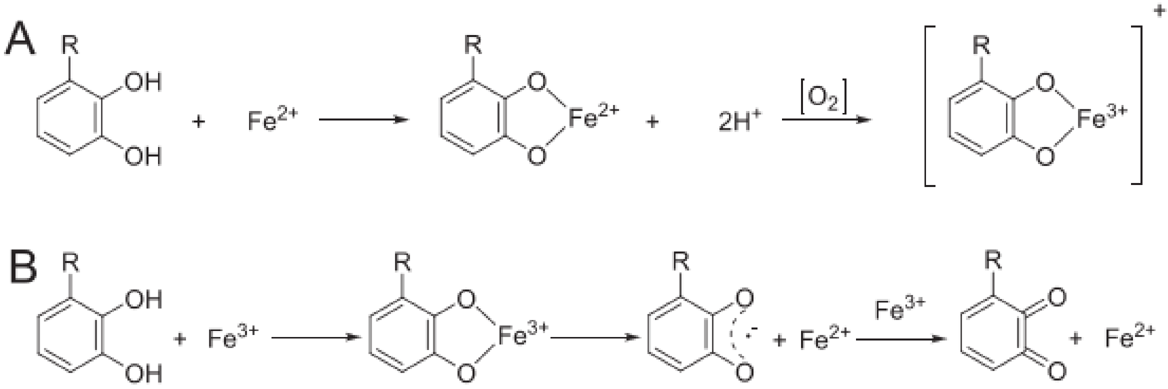

Fig. 7. A: Polyphenols coordinate with Fe^{2+} ions, leading to electron transfer reactions, especially in the presence of oxygen. This process results in the formation of the Fe3+-polyphenol complex. B: Coordination of Fe^{3+} by polyphenols, subsequent iron reduction and semiquinone formation, and reduction of Fe^{3+} to form a quinone species and Fe^{2+}. (Zhang et al., 2023.)

The reduction of iron that occurs during the reaction is typically due to the antioxidant and prooxidant properties of these compounds. PPs stand out as one of the select ligands with chelating abilities comparable to substances like EDTA. They possess specialized characteristics that allow them to effectively inhibit iron-mediated prooxidant activity. (Zhang et al., 2023.)

Tannins can form complexes with metal ions through various functional groups present in their structures. They can create complexes using e.g. ortho-dihydroxyl groups, phenolic hydroxyl groups, catechol or pyrogallol residues or pi-cation binding sites. These functional groups in tannins play a crucial role in their ability to bind and form complexes with metal ions, influencing various environmental, health, and industrial processes. (Zhang et al., 2023.) According to studies with apple and banana condensed tannins interacting with Fe, Cu and Zn, complexation and especially ion exchange seem to be the primary types of interactions between tannins and metals (Zeng et al., 2019a, 2019b).

3.2 Stability of complexes

The stability of a metal complex generally refers to its ability to remain intact without undergoing decomposition under favorable conditions, thus having a substantial shelf life. This stability can be understood through two main aspects: thermodynamic stability and kinetic stability. (Srivastva, 2020.)

Thermodynamic stability of a complex relates to its ability to persist under equilibrium conditions. Essentially, it measures how likely a metal ion is to form a specific metal complex, which directly correlates with the energies of the metal-ligand bonds. This stability is quantified by a formation constant, also known as a stability constant, which represents the equilibrium constant for the formation of the metal complex. Determining the stability constant involves various methods such as spectroscopic and potentiometric techniques. Understanding these constants is crucial for comprehending the role and behavior of ligands in stabilizing metal complexes, with applications spanning across biology, environmental studies, metallurgy, food chemistry, and numerous industrial processes. Apart from stability constants, factors like ligand concentration, chelating effect, and steric effects play significant roles in complex formation as well. (Srivastva, 2020.)

The principles of coordination chemistry between metals and ligands involve understanding the stability and specificity of metal-ligand complexes, which are influenced by both the metal ion and the chelating agent. For example, the preferences of donor atoms in metal-ligand interactions can be explained by the Hard and Soft Acids and Bases Principle categorizing acids and bases based on their polarizability. (Haas and Franz, 2009). This classification is presented in Figure 8. The principle suggests that hard acids prefer hard bases, soft acids prefer soft bases, and borderline acids prefer borderline bases (Haas and Franz, 2009). Characteristics and differences of both hard and soft acids and bases are shown in Figure 9.

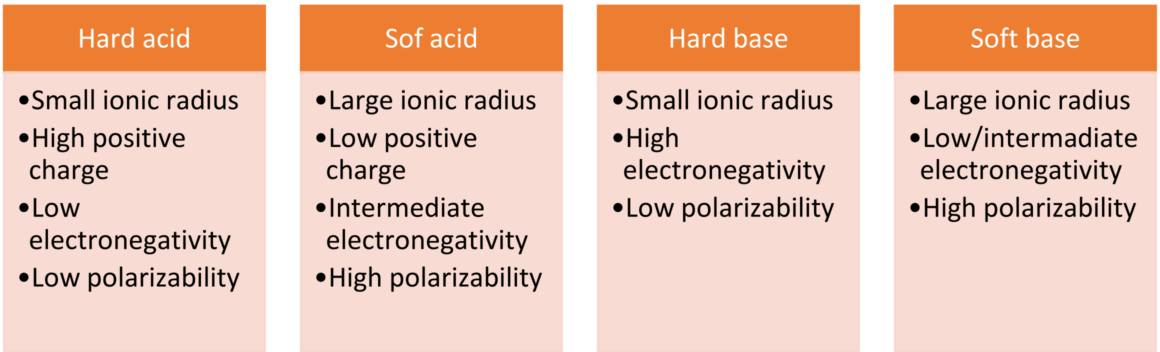

Fig. 8. Characteristics and differences of both hard and soft acids and bases (Marakatti, 2015).

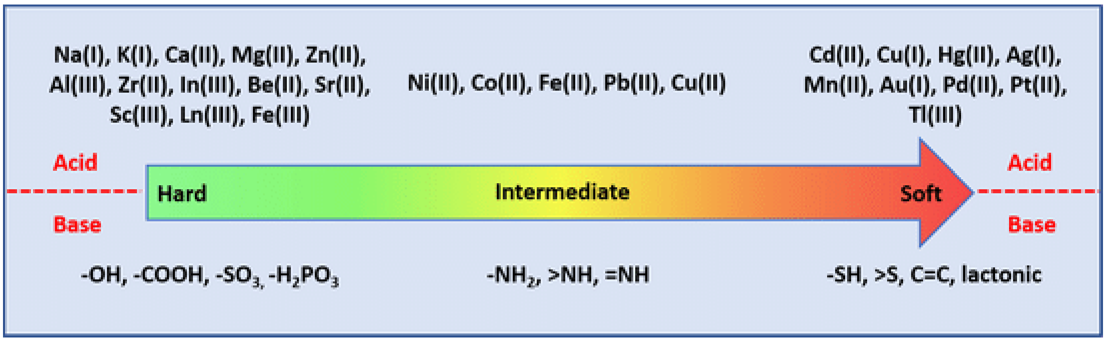

Fig. 9. Calssification of selected metal ions and donor atoms following the Hard and Soft Acids and Bases principle (Han et al., 2022).

In line with the description of metal-ligand coordination as Lewis acid-base interactions, it might seem logical that boosting the Lewis basicity of the donor would strengthen the bond between the metal and the ligand. However, while this concept can indeed be utilized to adjust the affinity between metal and ligand, it's crucial to consider other factors as well. (Haas and Franz, 2009.) The acid dissociation constant, pKa, is a measure of the strength of an acid in solution quantifying the equilibrium between the dissociated and non-dissociated forms of an acid. It is described as the negative logarithm of the equilibrium constant for the dissociation of an acid. Temperature, ionic strength, and solvent composition all affect the pKa level and the equilibrium between the acid and its ions. It's noted that pKa values are essential for understanding the behavior of chemical substances, particularly in relation to pH. (Reijenga et al., 2013.) In this case, for instance, elevating the basicity of a phenolate group also raises its pKa value. This is significant because in an aqueous solution, metal ions compete with protons to bind to the ligand. Therefore, such an adjustment could potentially reduce the effectiveness of metal binding at a specific pH level. (Haas and Franz, 2009.)

3.3 Stability of vitamin B12

Stability of Vitamin B12 is an important aspect to consider due to its susceptibility to degradation under certain conditions such as exposure to light, heat, and acidic pH. It is known that Vitamin B12 can be sensitive to light, oxygen, and high temperatures, which can lead to its degradation over time. (Randaccio et al., 2010). However, the stability of vitamin B12 can be improved e.g. by adjustment of pH to a range of 4-7, as well as proper storage away from heat, light, oxidants, and reductants (Temova Rakuša et al., 2023).

3.4 Stability of tannins

When it comes to tannins, researchers are especially interested in complexes between iron and PPs. This is due to several reasons, including their antioxidant activity, biological effects and high stability. Stability constants of complexes between iron and PPs have been investigated in various studies. (Zhang et al., 2023). However, as shown in Table 4, when complexed with gallic acid, iron appears to have one of the lowest stability constants compared to other transition metals (Rahim et al., 2017).

Table 4. Stability constants *logβ* for gallic acid and its complexes with different transition metals (Rahim et al., 2017).

Metal ion	**Logβ**
Cu(II)	18,9169
Zn(II)	15,3119
Co(II)	14,7033
Ni(II)	13,7793
Cd(II)	13,7625
Fe(III)	10,979

3.5 Stability of amino acids

The interaction between amino acids and metal cations is a fundamental process in bioinorganic chemistry, particularly in metalloenzymes where amino acids coordinate to metal cations. Various experimental methods are currently employed to determine the binding affinities of amino acids to metals and scientists have calculated some potential coordination modes. Even with simple molecules like glycine or alanine, there are three atoms within the molecule that can donate electrons to coordinate with a metal cation. (Jover et al., 2008.) These potential coordination modes are illustrated in Figure 10.

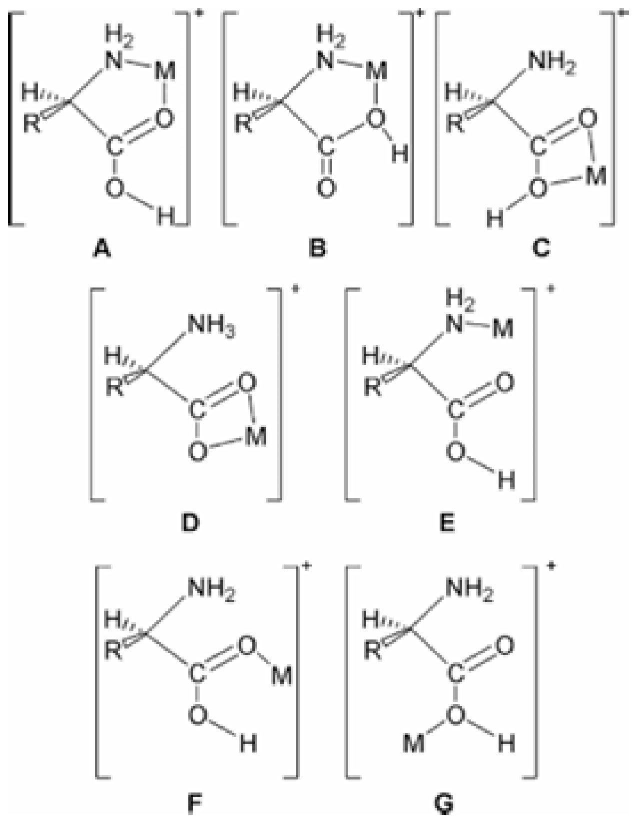

Fig. 10. Various coordination modes can exist between the metal *M* and the amino acids. (Jover et al., 2008).

In type A structures, the carbonyl oxygen and the nitrogen atom are coordinated to the metal. Type B involves coordination between the metal and the nitrogen atom along with the hydroxyl oxygen. Type C sees interaction with both oxygen atoms, with the amino acid remaining in a neutral form. Lastly, in type D, the ligand takes a zwitterionic form. Alternatively, the cation can coordinate with just one heteroatom as shown in structures E, F and G. However, monodentate forms are typically higher in energy due to chelation-induced stabilization. With a small size and charge of the cation type A coordination is considered favorable. And as the structure of amino acid gets more complex and the number of donor atoms increase, the number of coordination modes increases as well (Jover et al., 2008).

In a study examining stability constants of sulfur and selenium amino acids with Cu and Fe, the stability constants of Cu with methionine, selenomethionine, methylcysteine, and methylselenocysteine fall into the range of 8.0–8.2 for the $[CuL]^+$ species and 14.5–14.7 for the CuL_2 species, where L represents the respective amino acid. Stability constants were determined by potentiometric titration. (Murphy et al., 2019). More detailed examples of the stability constants between Cu or Fe and selected amino acids are given in Table 5.

Table 5. Stability constants for complexes between Cu or Fe and different amino acids determined by potentiometric titration (Murphy et al., 2019).

	logβ	
Amino acid	**Cu(II)**	**Fe(II)**
Gly	8,11	4,13
Met	7,85	3,24
MeCys	7,65	3,49
SeMet	7,77	3,51
MeSeCys	8,2	3,84
hCys	11,92	6,69
Pen	16,5	7,58

Interestingly, the stability constants of Fe with sulfur and selenium amino acids are consistently lower than the stability constants of Cu with the same amino acids. The Fe stability constants for all tested sulfur and selenium amino acids are in the range of 3–4 for the $[FeL]^+$ species, indicating weaker binding compared to Cu complexes. This suggests that the sulfur and selenium atoms do not interact strongly with Fe as they do with Cu. Thiol-containing amino acids like penicillamine exhibit stronger binding to Fe compared to other sulfur and selenium amino acids, but still lower than Cu complexes. (Murphy et al., 2019.)

3.6 Effect of pH on stability constants on biodegradable chelating agents

Biodegradable chelating agents, such as EDDS and GLDA, contain specific functional groups that are involved in complex formation with metal ions. These groups include carboxylic acid groups, amine groups, and sometimes hydroxyl groups. The synergy of these functional groups in biodegradable chelating agents enables efficient complex formation with metal ions. This property facilitates the removal of heavy metals from various sources in an environmentally friendly manner. (Prajapati & Singhai, 2020.)

By potentiometric titration, researchers have investigated the complex formation equilibria of Fe and Cr ions with the chelants GLDA and 3-hydroxy-2,2-iminodisuccinic acid, HIDS, and determined the formation constants of various metal-chelant species under different pH conditions. The results were then compared with EDTA and other biodegradable chelants, such as EDTA and nitrilotriacetic acid, NTA. (Begum et al., 2013). The outcome of the study is illustrated in Figure 11.

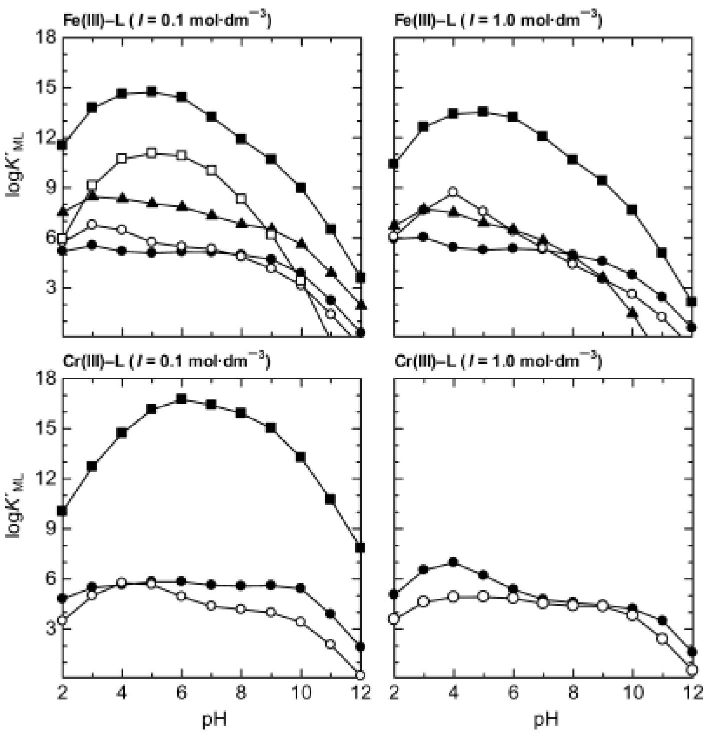

Fig. 11. The stability constants for the Fe-chelant and Cr-chelant complexes in an aqueous medium at two different ionic strengths *I* at 25°C as a function of pH. ● M(III)−GLDA ○ M(III)−HIDS ▲ M(III)−NTA □ M(III)−EDDS ■ M(III)−EDTA (Begum et al., 2013).

4 Separation of metals

The aim of this chapter is to discuss and compare a few current techniques for metal separation. Various techniques for separating heavy metals involve converting metal ions into solid precipitates, which are then separated from the liquid phase. In addition, in methods like ion exchange the metal ions are concentrated from a liquid phase to a solid surface and then released to the concentrate media. Limiting factors with these techniques are, however, high costs, low removal efficiency and secondary pollution. On the contrary, membrane separation technologies exhibit several advantageous qualities typically sought after in methods for removing metals. These include outstanding rejection of heavy metals, high efficiency, straightforward operation, and minimal space requirements. Thus, these methods are currently receiving increasing interest. (Xiang et al., 2022.) This chapter provides a comparison of the methods discussed above. The aim is to discuss the opportunities and the challenges of each method or technique for heavy metal removal.

4.1 Precipitation

Chemical precipitation involves the elimination of heavy metals from a liquid solution through the introduction of specific chemical substances prompting the heavy metals to form compounds that are insoluble in the solution. As a result, these compounds precipitate out of the liquid, settling as solid particles. Afterwards, the formed solid precipitates can be separated from the liquid phase. This process effectively separates heavy metals from the solution, rendering it cleaner and safer. The insoluble compounds are less likely to dissolve in water, reducing the mobility of the metals and their potential to leach into surrounding water sources. (Marchioretto et al., 2005.)

Lithium-ion batteries, LIBs, are widely used in electronic devices due to their high energy density, light weight, long lifespan, and lack of memory effect. However, the extensive production of LIBs to meet the constantly increasing demand leads to environmental problems and poor recycle rate of the valuable metals if not properly treated. Lithium carbonate, Li_2CO_3, is an important compound used in various applications, and its recovery through precipitation is common after the leaching process. For example, researchers have derived a lithium-rich solution from industrial battery waste and treated to mimic the impurity ratios found in such waste. Lithium was successfully recovered as Li_2CO_3 using a semi-batch precipitation process, resulting in uniform particles. High-purity Li_2CO_3 was obtained and using saturated Na_2CO_3 solution as a washing liquid further improved purity. This research highlights the potential of combining leaching and precipitation for efficient lithium recovery from industrial waste, and the methods used provide a foundation for further studies. (Han et al., 2018.)

Commonly used reagents in chemical precipitation for removing heavy metals are typically either alkalis or sulfides. Alkalis, such as lime, magnesia, sodium hydroxide, sodium bicarbonate, and sodium carbonate, are used to adjust the pH of the solution to promote the precipitation of heavy metals as hydroxides. Different sulfides like sodium sulfide, hydrogen sulfide, sodium hydrosulfide or iron sulfide can be employed to precipitate heavy metals as insoluble sulfide compounds. These compounds are suggested to have even lower solubility than hydroxides. In the end, the choice of reagent depends on factors like the specific heavy metals present, the desired pH range for precipitation, and cost considerations. (Marchioretto et al., 2005.)

Studies have shown that different compounds can be recovered at different pH levels, affecting the leaching and precipitation efficiency, as well as the formation of low-solubility metal compounds that can be separated from the liquid phase (Han et al., 2018; Marchioretto et al., 2005). For example, heavy metals like Cr, Cu, Pb, and Zn do form solid precipitates if the pH of the solution is below 7. (Marchioretto et al., 2005.) Ni and Co can also be recovered using precipitation methods under appropriate pH conditions (Han et al., 2018). In addition, by adjusting the pH of the sludge through chemical precipitation, the solubility of heavy metals is decreased. Lower solubility limits the ability of metals to dissolve in water and migrate into groundwater or surface water bodies. (Marchioretto et al., 2005.)

One of the challenges regarding chemical precipitation is the vast amount of chemicals needed, which can contribute to the overall cost of the treatment. In addition, the precipitation process results in the generation of precipitates, which need to be properly managed and disposed of, adding to the overall waste produced during treatment. The costs and labor associated with chemicals, separation processes, waste disposal, and equipment for the precipitation can be substantial, impacting the overall economic feasibility of heavy metal removal.

Additional research is required to optimize the process, reduce costs, and enhance the efficiency of heavy metal removal on a larger scale. (Marchioretto et al., 2005.)

4.2 Solvent extraction (SX)

Solvent extraction, SX, is a separation process used to extract and separate metals or other compounds from a liquid phase by using an organic solvent (Arslan et al., 2023.). It is a widely used technique in hydrometallurgy for the purification and concentration of various elements crucial for energy production, spanning from transition metals like copper, nickel, cobalt, molybdenum, zinc, and manganese to platinum group metals, lithium, and rare earth elements (Arslan et al., 2023; Solano & Mišković, 2024).

In SX, the target metal ions are transferred from an aqueous phase into an organic phase, where they form complexes with specific extractant molecules present in the solvent. To retrieve the metal species from the organic phase and to reuse the reagent, a process called stripping is employed. This involves using strong acids like sulfuric acid or hydrochloric acid, HCl. During extraction, metal ions in the aqueous phase replace hydrogen ions on the organic reagent. However, during stripping, the metal ions on the organic reagent are replaced by hydrogen ions from the stripping agent. As a result, the organic reagent returns to its acidic form, ready to be reused for extraction, while the metal species can be recovered for subsequent processing. (Arslan et al., 2023.) A typical SX circuit is shown in Figure 12.

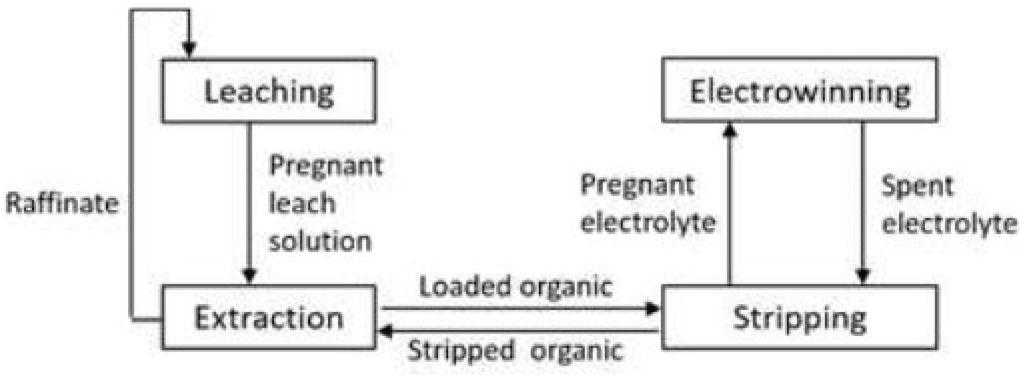

Fig. 12. Solvent extraction circuit (Arslan et al., 2023).

However, there are a few key challenges worth paying attention to within SX. Firstly, continuous test campaigns are crucial for monitoring and measuring the various physicochemical factors essential for evaluating and optimizing SX performance. Secondly, inadequate design of equipment capacity and inefficient development of SX circuits can lead to higher capital and operational costs. When it comes to test durations and overall cost, managing reagent consumption remains is also another significant challenge. Achieving efficient mass transfer and reducing the number of stages in the SX process requires intensive research and optimization efforts. Some studies have suggested miniaturized solvent extraction plants to be a potential solution to increase efficiency, cost-effectiveness, and accuracy in SX processes. (Solano & Mišković, 2024.)

4.3 Membrane filtration

Membrane filtration is a method in separation science where a special type of filter called a semi-permeable membrane is used to sort out various substances from a mixture. This sorting is based on characteristics like the size of the molecules, the size of tiny holes in the membrane (known as pores), the concentration of the solution being filtered, and the pressure applied to the system. Essentially, it's like using a molecular sieve to sift through different components, allowing some to pass while trapping others based on specific criteria. (Xiang et al., 2022.) Today, conventional pressure-driven liquid filtration methods, such as nanofiltration, ultrafiltration, reverse osmosis, microfiltration and electrodialysis, are essential technologies in wastewater treatment. (Huang & Feng, 2019). Ultrafiltration, nanofiltration and reverse osmosis have gained highest attention in heavy metal separation (Xiang et al., 2022). Hence, the following chapter will focus on these four methods.

Compared to many other separation technologies, membrane filtration or membrane separation systems are extremely energy efficient, simple to operate, reliable, easily scalable and suitable for both small- and large-scale industrial separations (Sadeghi et al., 2018). Despite their promising properties and feasibility even to large scale applications, membrane filtration methods have also a few drawbacks, such as risk for contamination (Hedberg et al., 2011) and poor selectivity (Sadeghi et al., 2018), that will also be discussed in the following chapters.

To achieve successful filtration process, the right membrane pore size chosen according to the size and the type of the molecule to be separated is of high importance. However, separation of even the smallest molecules can be facilitated by using complexing agents, which is utilized for example in polymer-enhanced ultrafiltration discussed later. (Xiang et al., 2022.) Rejection capabilities of MF, UF, NF and RO are presented in Figure 13.

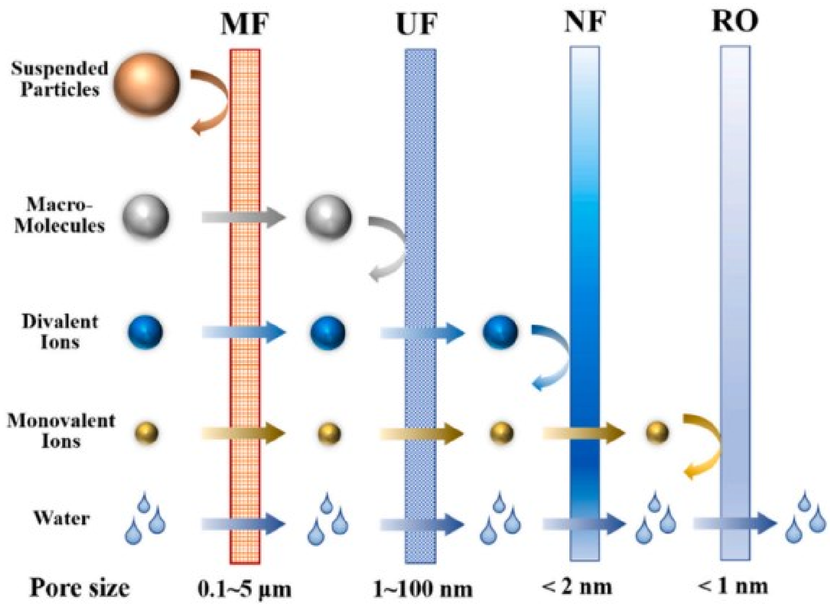

Fig. 13. The effect of molecule size and type on rejection capasities of membranes with four different pore sizes in MF, UF, NF and RO. (Xiang et al., 2022.)

Probably the biggest limitation for wider use of membrane systems is the lack of membranes selectively separating exactly the desired component from the filtrated stream. Now, membranes usually separate all the solutes instead of a specific one or specific ones of interest, especially if they are relatively similar in size. All in all, creating membranes with higher selectivity and feasibility for large-scale applications is a game changing but challenging task. The biggest challenge is the so-called permeability-selectivity trade-off. As the selectivity of the membrane increases, permeance or permeability usually decreases leading to lower energy efficiency. (Sadeghi et al., 2018.) To sum up, the more selective the separation desired, the less efficient the typically effective conventional filtration techniques become (Ritchie & Bhattacharyya, 2002). Osmotic pressure may sometimes bring limitations to applicability of filtration techniques (Haerens et al., 2010). Developing numerical tools to predict the performance of separations, particularly for ionic mixtures, is essential. Mass transfer through membranes has been widely studied, but the partial rejection of solutes causes their accumulation near the membrane, known as concentration polarization, which affects membrane selectivity. A predictive tool for filtration membrane processes requires accurate mass transfer modeling. (Déon et al., 2013.)

4.3.1 Ultrafiltration (UF)

Ultrafiltration, UF, is a filtration method utilizing a membrane pore size from 5 nm to 20 nm. Dissolved metal ions to be separated are usually smaller. This creates a need to modify the UF process to filtrate heavy metals from aqueous solution. The modifications are called polymer-enhanced ultrafiltration and micellar-enhanced ultrafiltration. These methods combine macromolecular complexation with UF enabling selective separation of small solute molecules, including metal ions. (Xiang et al., 2022.)

Polymer-enhanced ultrafiltration (PEUF)

Polymer-enhanced ultrafiltration, PEUF, is an interesting and relatively new technique for removal of environmentally hazardous contaminants for example from wastewaters. Even though PEUF is relatively similar to the conventional technologies mentioned earlier, it is able to separate species with lower molecular weight, including metal ions, better than conventional ultrafiltration due to high removal efficiency and high formation of macromolecules. (Huang & Feng, 2019, 53; Xiang et al., 2022.)

The basic principle of PEUF is very similar to conventional ultrafiltration. However, in PEUF, water-soluble polymers introduced into the feed solution. The interaction between the small contaminants and the polymers enables capturing the metal before undergoing ultrafiltration. The polymers used in PEUF are typically macromolecular ligands able to capture the metal ions to form complexes. (Huang & Feng, 2019.) They attach metal ions and form large complexes that are eventually retained by the membrane (Xiang et al., 2022).

The effectiveness of the PEUF process depends greatly on the strength of interactions between the metal and the ligand polymer. Moreover, operating conditions, membrane properties, type and amount of polymer used, pH levels, and metal concentration in the feed solution all influence the process outcome. (Huang & Feng, 2019.)

There are several different polymer types investigated for PEUF-process, including biopolymers, synthesized polymers and commercial polymers (Xiang et al., 2022). Many different biopolymers or natural polymers, such as amylose, polyglutamic acid, sericin and acacia gum, have shown promising results in capturing several different metals, such as Ni^{2+}, Cu^{2+}, Fe^{3+} and Cr^{3+}, from water, as well as unique properties in terms of biocompatibility and biodegradability. Even so, to achieve the best possible separation in the PEUF-process, variant structures and impurities present in these natural polymers have to be considered. (Huang & Feng, 2019.) Some studies indicate that natural and synthesized polymers, for example EDTA, nitrilotriacetic acid, citric acid, polyacrylate sodium and PEI, produce excellent results in lab-scale applications, but on a large scale, their applications seem limited. In addition, polymers have a complex structure, and especially natural polymers typically exhibit limited solubility in water., which makes specific and selective separation more difficult. (Xiang et al., 2022.)

4.3.2 Reverse osmosis (RO) and nanofiltration (NF)

Reverse osmosis, RO, is a water purification method that employs a semi-permeable membrane to eliminate contaminants from water. During the RO process, water is pushed through the membrane, allowing water molecules to pass while obstructing contaminants like heavy metal ions. (Fu & Wang, 2011).

Nanofiltration, NF, stands as a middle ground between UF and RO, characterized by its relatively low energy demand and remarkable efficiency in removing heavy metals. It is easy to operate and demands lower pressure than RO, offering an easily operated, reliable, less energy consuming, and highly efficient alternative. (Fu and Wang, 2011; Xiang et al., 2022.) NF is recognized as a promising technology for the rejection of e.g. nickel, chromium, copper, and arsenic from wastewaters (Fu & Wang, 2011). The NF membranes typically carry either a positive or negative charge, which improves separation by facilitating electrostatic interactions between the membrane and metal ions. The electrostatic interaction may sometimes enhance the hydrophilicity of the membrane as well, resulting in better anti-fouling properties. However, some studies with copper suggest better results with smaller concentrations in feed stream. (Xiang et al., 2022.)

Due to its high water flux and precise separation capabilities, NF is effective for example for lithium recovery, particularly in distinguishing lithium from magnesium. However, traditional polyamide-based NF membranes are not suitable for this purpose due to their poor

Li^+/Mg^{2+} selectivity and the earlier mentioned trade-off between water permeability and selectivity—high permeability often results in low selectivity. Therefore, researchers developed a novel nonpolyamide NF membrane using a metal-coordinated structure that enhances both water permeability and Li^+/Mg^{2+} selectivity simultaneously. The optimized copper-m-phenylenediamine, Cu-MPD, membrane achieved a high water permeance and Li^+/Mg^{2+} selectivity, effectively overcoming the traditional permeability-selectivity trade-off. Additionally, the presence of copper in the Cu-MPD membrane improved its resistance to biofouling and provided pH-responsive properties. (Wang et al., 2021.)

Some studies also suggest that the combination of RO and NF can offer enhanced treatment capabilities for removing metals from wastewater. Successful applications of RO and NF in treating various heavy metal effluents have been reported, demonstrating the potential benefits of combining these two membrane processes for more efficient and effective removal of contaminants. (Fu & Wang, 2011.)

4.3.3 Electrodialysis (ED) and ion exchange (IE)

Electrodialysis, ED, is a process utilizing membranes and electricity to transfer ions. In ED, both anionic and cationic membranes are positioned between two electrodes, allowing only anions to pass through the anionic exchange membrane and vice versa. Numerous studies have demonstrated the effectiveness of ED in removing heavy metals without the need for chemicals, while its ability to achieve high water recovery rates stands out as one of its major advantages. (Xiang et al., 2022, p. 7) When it comes to sustainability, some studies indicated relatively low energy demand for ED due to moderate salt discharge, wastewater production and chemical oxygen demand (Greiter et al., 2004). Schematic diagram of ED process for metal separation from wastewater is shown in Figure 14. The cationic exchange membrane, CEM, and the anionic exchange membrane, AEM, are placed between two electrodes. With the help of electricity, CEM allows cationic and AEM allows anionic metal ions from the wastewater flow to pass through. Finally, the removed metal ions form salts or other substances with the electrode materials. (Xiang et al., 2022.)

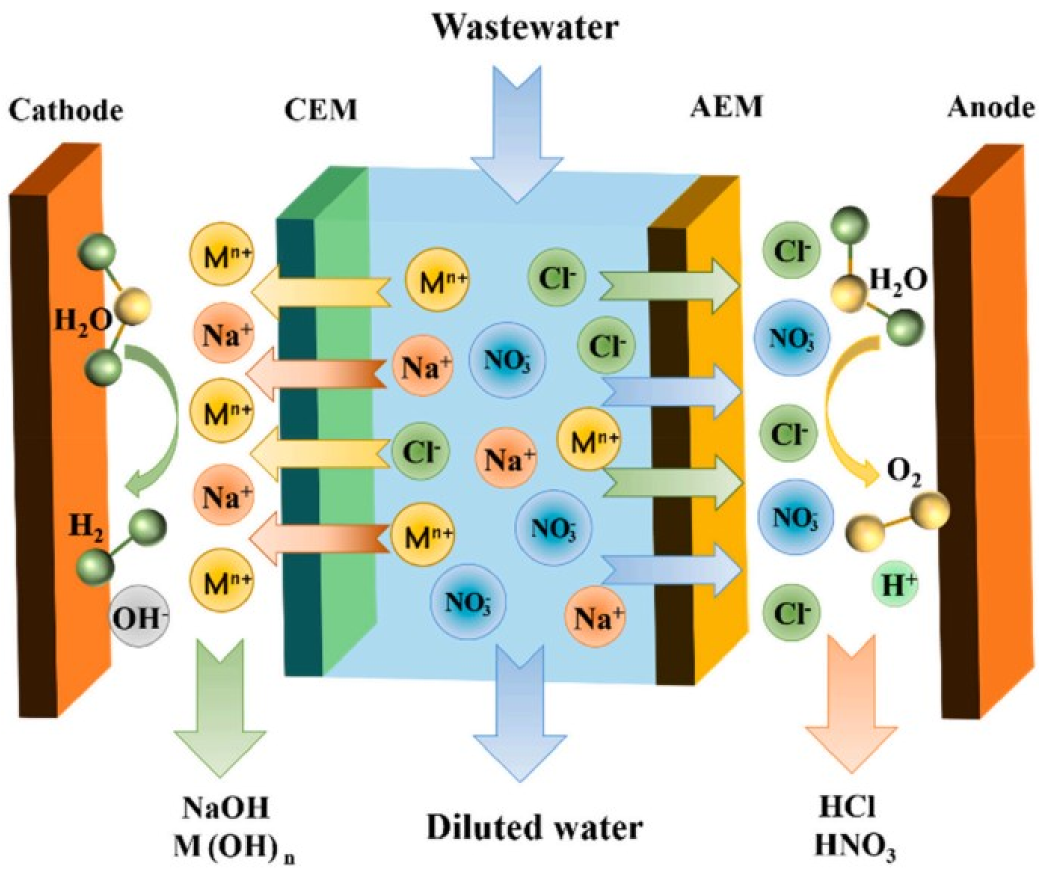

Fig. 14. ED process for heavy metal removal from wastewater (Xiang et al., 2022).

4.3.4 Evaluation and comparison of membrane filtration techniques

Even though membrane filtration has many feasible properties when it comes to heavy metal separation, few risks must be addressed as well. A study conducted for zinc, copper, and nickel examines the levels of contamination introduced through membrane filtration of various aqueous solutions. The goal is to assess the potential risks associated with using membrane filtration, particularly when isolating trace metals. In this study, researchers address the lack of clear information and consensus on different definitions, procedures, protocols and pre-planning treatments to avoid contamination. When it comes to for solid-liquid separation, they preferred centrifugation to membrane filtration. (Hedberg et al., 2011).

This trace metal analysis stated that, depending on the metal ion and the membrane material, metals in solution of interest can sometimes both interact with and adsorb within the membrane, which can be a significant risk for contamination (Hedberg et al., 2011). In addition, other studies have stated that NF membranes require higher operational pressures and, consequently, stricter process conditions. Therefore, the risk of membrane fouling is more significant in NF than in UF. (Xiang et al., 2022.)

To sum up, various membrane methods are chosen for specific applications based on their unique characteristics. All in all, as the drawbacks are addressed and performance is enhanced, membrane technology shows significant promise to emerge as the most efficient method for removing heavy metals. (Xiang et al., 2022, p. 11) As a wrap-up, performance comparison of UF, NF and ED for heavy metal separation from wastewater is summarized in Figure 15.

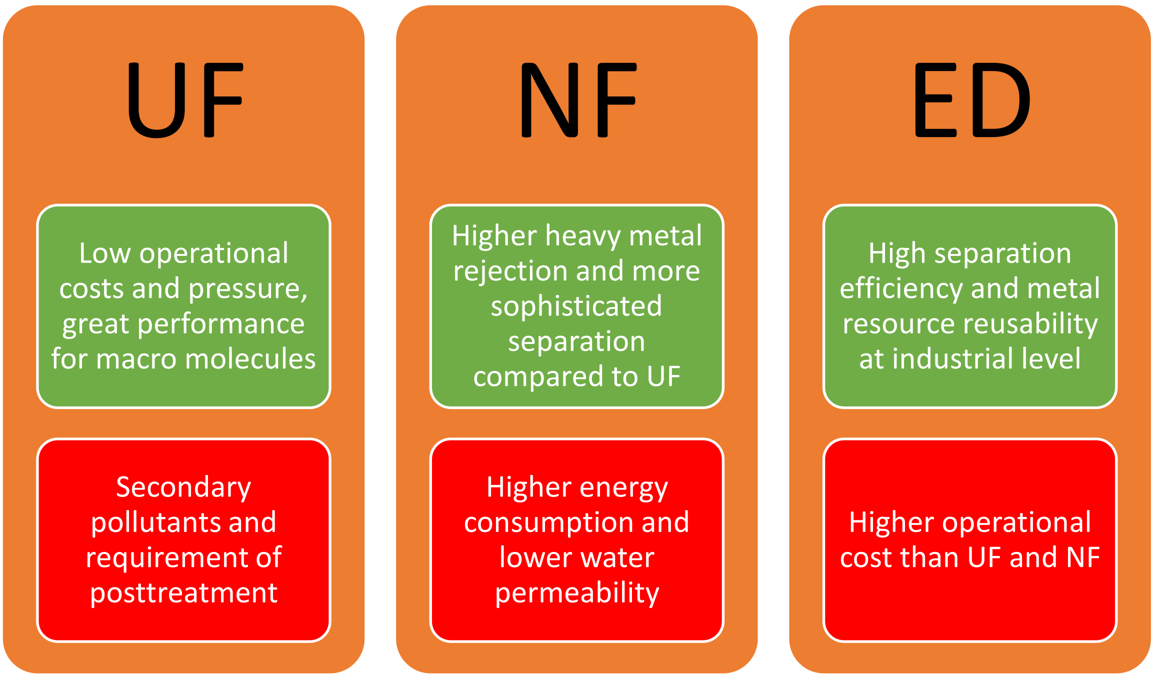

Fig. 15. Advantages and disadvantages of UF, NF and ED (Xiang et al., 2022, p. 11).

5 Integration of complex formation with other methods

This chapter looks at integration of complex formation with other metals separation methods and how they can enhance each other. Examples of complex formation combined with other metal separation methods are provided.

5.1 EDTA and electrodialysis

One classic example of this kind of integration is to separate cobalt and nickel by employing ED and IE together with EDTA. Separating cobalt and nickel from each other is challenging due to their similar properties. However, nickel ions can be effectively separated from cobalt sulfate solution with the assistance of EDTA, acting as a complexing agent, within a three-compartment ED cell. The study also clarifies the behavior of EDTA within the cell, demonstrating that it migrates to the anolyte as a metal complex and undergoes degradation on the anode, releasing hydrated nickel ions. However, these ions are incapable of passing through the anion exchange membrane to go back to either the feed or catholyte compartments. In the catholyte chamber, most cobalt ions remain in solution, but cobalt metal can be deposited onto the cathode by adjusting the pH to 4 or 4.5. Replicate experiments indicate good reproducibility, with a standard deviation of 1 %. However, complete removal of nickel from cobalt and successful electrodialysis process require optimal conditions, including the right EDTA:Ni mole ratio, current density and sulfuric acid concentration in the feed chamber. (Chaudhary et al., 2000.) Table 6 presents Co and Ni levels in the catholyte chamber after 8 hours of ED time in different conditions. According to the results, addition of EDTA to the ED process significantly increases the ratio of nickel in the catholyte chamber.

Table 6. Effects of EDTA concentration, pH and Co:Ni ratio on the Co and Ni levels in the catholyte chamber using two compartment cell and 8h ED time (Chaudhary et al., 2000).

Co:Ni 500: 500 mg/L	**Con-trol, no EDTA**	**EDTA 0,05 mol/L**	**EDTA 0,01 mol/L**	**EDTA 0,025 mol/L**	**Co:Ni 500:300 mg/L + EDTA 0,06 mol/L**	**Co:Ni 500:100 mg/L + EDTA 0,002 mol/L**	**Co:Ni 500:50 mg/L + EDTA 0,001 mol/L**
Co transfer	279 mg/L	264 mg/L	226 mg/L	131 mg/L	258 mg/L	287 mg/L	319 mg/L
Ni transfer	289 mg/L	180 mg/L	96 mg/L	22 mg/L	60 mg/L	24 mg/L	16 mg/L
Co:Ni	0,97:1	1,5:1	2,3:1	5,9:1	4,3:1	12:1	20:1

Current methods primarily focus on efficiently removing cobalt from nickel rather than vice versa, often leveraging disparities in the solubilities or the kinetic and thermodynamic stabilities of their chemical compounds. This method remains unoptimized for nickel removal from cobalt solutions. Additionally, ED with EDTA has enabled separations such as Ca from Cd, Ag from Zn and Cu, and Na from Ca. (Chaudhary et al., 2000.)

5.2 Bio-based chelating agents and membrane separation

In selective zinc recovery from electroplating waste waters, ED enhanced by complex formation has shown promising results. However, the type of complexing agent and membranes used influence the selectivity of the process. (Babilas & Dydo, 2018.) This is shown in Figure 16

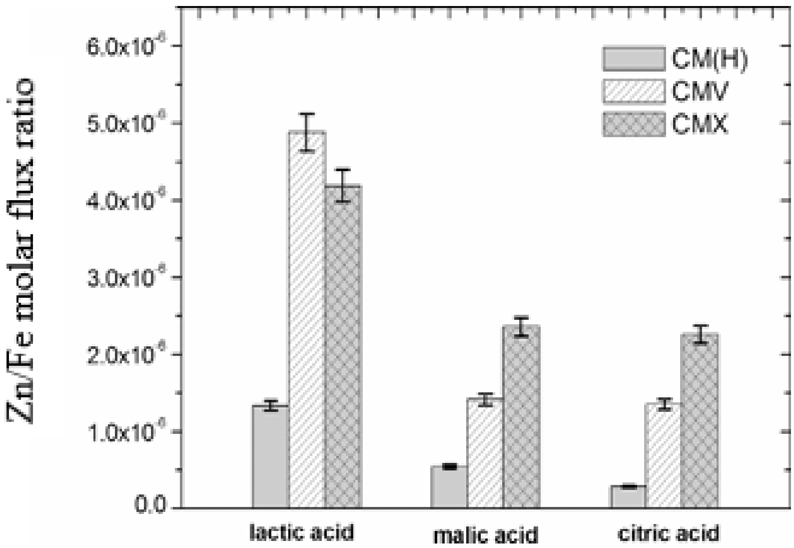

Figure 16. The effect of chelating agent and membrane type on zinc to iron molar flux ratio. Citric acid as chelating agent and CM(H) as membrane type separate zinc most effectively. (Babilas & Dydo, 2018.)

Researchers wanted to find the best possible complexing agent and commercially available membrane type for the process. Lactic, malic, and citric acid were investigated as possible chelators. All these agents are known to form more stable complexes with ferric ions than with zinc. The study suggested that the rates of iron transport in the system are primarily dictated by complex stability. The more stable the ferric complex, the lower the iron flux, as metal ions combined in complexes are transported across the membrane at a slower rate than non-complexed ions. For effective electrodialytic separation of zinc from ferric cations, it's crucial to operate at a minimum iron flux, as observed with citric acid solutions. (Babilas & Dydo, 2018.)

The influence of membrane types on iron transport rates were examined. As for CEMs, iron molar fluxes were statistically larger through homogeneous CMX and CMV membranes compared to heterogeneous CM(H) membranes. This difference can be attributed to variations in membrane thickness, with CM(H) being relatively thicker than CMV and CMX. Thicker membranes tend to hinder the transport of iron species. Additionally, heterogeneous membranes have a higher proportion of non-conducting zones, further affecting iron transport rates. In addition, iron was also transported across anion-exchange membranes in either neutral or anionic form through diffusion, migration, or a combination of both mechanisms. The observed iron fluxes across AEMs were approximately one order of magnitude lower than those across CEMs, indicating that the cation exchange membrane adversely affects the process. Therefore, careful selection of the membrane type, along with the complexing agent, is crucial for optimizing the process. Finally, CM(H)-AM(H) membrane pair was suggested as the most promising alternative for the process. (Babilas & Dydo, 2018.)

Selectivity coefficients were also calculated to quantify the reduction in iron content relative to the amount of zinc recovered, providing insight into the system's selectivity. Together with the most effective membrane pair, AM(H)-CM(H), the selectivity constant was approximately three times higher with citric acid as a complexing agent compared to lactic acid. (Babilas & Dydo, 2018.)

Citric acid together with CM(H)-AM(H) membrane pair gave the most promising results compared to lactic or malic acid. Additionally, a high ferric retention coefficient of 92.36% was recorded. Although the addition of complexing agents contributes to operating costs, the difference in concentrations between zinc and iron ions in the initial diluate solution is notable. This approach offers advantages such as reduced reagent consumption, minimized waste volume, and decreased need for different purification steps. (Babilas & Dydo, 2018.)

As mentioned earlier, one of the biggest limitations of for example membrane separation technologies is their lack of selectivity and incapability to separate organic or nonaqueous solvents (Sadeghi et al., 2018). Combining other separation methods with complex formation can be a potential method for increasing selectivity and efficiency of the process (Babilas and Dydo, 2018).

6 Discussion

One primary advantage of utilizing complex formation is its potential for selective metal separation. Biomolecules such as EDTA, vitamin B12, tannins, and amino acids have demonstrated the ability to form stable complexes with specific metal ions, enabling the targeted extraction of desired metals from complex mixtures. This selectivity is crucial in environmental remediation efforts, where the removal of toxic heavy metals such as zinc, copper, and nickel from contaminated water sources is of vital importance. Furthermore, the sustainability aspect of complex formation methods cannot be overlooked. By exploring naturally occurring biomolecules as complexing agents, researchers can potentially reduce the reliance on synthetic chelating agents that may have adverse environmental impacts. The investigation into the availability, costs, and sustainability of biomolecules for metal separation is a critical step towards developing more eco-friendly and cost-effective separation processes. (Kane et al., 2016; Sadeghi et al., 2018; Xiang et al., 2022.)

In addition to selectivity and sustainability, the efficiency of complex formation in metal separation processes is a key consideration. The stability of complexes formed between biomolecules and metal ions is an essential factor in determining the effectiveness of the separation process. Understanding the mechanisms of complex formation and the factors influencing the stability of these complexes is essential for optimizing separation efficiency and reducing costs and reagent consumption. (Solano and Mišković, 2024).

Moreover, the integration of complex formation with other separation methods, such as membrane filtration techniques, presents an opportunity to enhance the overall efficiency of metal separation processes. By combining complex formation with techniques UF, RO, ED and NF, researchers can potentially improve the selectivity and throughput of metal separation processes while mitigating the risks associated with membrane filtration, such as low selectivity and contamination. (Babilas & Dydo, 2018; Biver et al., 2014; Chaudhary et al., 2000).

Overall, the exploration of complex-formation methods in selective metal separation represents a promising approach towards addressing the challenges posed by heavy metal contamination in various environmental matrices. By leveraging the unique properties of biomolecules to form stable complexes with metal ions, researchers can develop more sustainable, selective, and cost-effective metal separation processes that are crucial for environmental protection and human health. (Kane et al., 2016; Llanos et al., 2010).

In summary, complex formation is a promising technique within metal separation. The potential efficacy of biomolecules in selective metal extraction and the necessity for continued exploration and refinement of this approach is stressed in this thesis. Further research and optimization endeavors are crucial to fully harness the capabilities of biomolecules in enhancing metal separation processes. These findings pave the way for advancements in sustainable and efficient metal separation methodologies, with potential far-reaching implications across various industrial and environmental sectors.

7 Conclusions

The exploration of complex-formation methods in selective metal separation has provided understanding regarding the possible uses of biomolecules in addressing the challenges associated with heavy metal contamination in environmental systems. This thesis has highlighted the significance of biomolecules such as vitamin B12, tannins, and amino acids in forming stable complexes with metal ions, enabling the selective extraction of target metals from complex mixtures. The ability of these biomolecules to exhibit varying degrees of stability with different metal ions underscores their potential for tailored metal separation processes, offering a sustainable and environmentally friendly alternative to synthetic chelating agents.

Moreover, the investigation into the mechanisms of complex formation and the factors influencing the stability of metal-biomolecule complexes has shed light on the importance of understanding the underlying chemistry of these interactions. By elucidating the key parameters that govern complex stability, researchers can optimize metal separation processes, enhance efficiency, and reduce reagent consumption, contributing to more sustainable and cost-effective separation strategies. In addition, by combining complex formation with membrane technologies like ultrafiltration, reverse osmosis, ion exchange and nanofiltration, researchers can improve selectivity, throughput, and contaminant removal, addressing the limitations associated with traditional separation methods and advancing the field of metal separation.

In conclusion, this thesis underscores the potential of complex-formation methods as a valuable tool in selective metal separation processes. By harnessing the unique properties of biomolecules and integrating them with existing separation technologies, researchers can advance the field of metal separation, contribute to environmental protection, and promote sustainable practices in metal extraction. Continued research and collaboration in this area are essential to unlocking the full potential of complex formation and ensuring a cleaner and healthier environment for future generations.

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APPENDIX

Appendix 1. Materials and methods

In this literature review, the aim was to utilize a wide range of databases and scientific publications. The databases utilized included Google Scholar, Scopus and LUT Primo. In the exploration of the databases, the following keywords and phrases were used, among others:

B12 AND metal AND complex

Percipitation AND metal AND separation

“Membrane filters” AND selectivity

‘’Electrodialysis versus ion exchange’’

‘’Precipitation and separation''

EDTA AND ‘’critical metals’’

EDTA AND structure

Precipitation AND ‘’metal removal’’

‘’Solvent extraction’’ AND ‘’metal separation’’

"Solvent AND extraction" AND "critical AND metals"

Adsorption AND "critical metals''

"Vitamin b12" AND "metals" AND "membrane"

‘’Vitamin b12" AND "metals" AND "reactions"

Tannins AND metals AND binding

"Complex formation AND "metal separation methods"

EDDS AND "stability constant"

"Vitamin B12" AND metal AND stability

Metal AND complex AND stability

Lithium AND precipitation

"Concentration polarization phenomenon"

"Osmotic pressure" AND metal AND filtration