CZECH UNIVERSITY OF LIFE SCIENCES – PRAGUE

Faculty of Environmental Sciences

# BACHELOR THESIS

Author: Oleg Artem Ferran

**CZECH UNIVERSITY OF LIFE SCIENCES, PRAGUE**

**Faculty of Environmental Sciences**

Bachelor
Environmental Engineering

# BACHELOR THESIS

# Heavy metal removal from wetland plants by four ionic liquids

Supervisor: Doc. Zhongbing Chen,
Ph.D. Author: Oleg Artem Ferran

## CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

Faculty of Environmental Sciences

# BACHELOR THESIS ASSIGNMENT

Oleg Ferran

Environmental Engineering

Thesis title

**Heavy metal removal from wetland plants by four ionic liquids**

---

### Objectives of thesis

This work will use different ionic liquids to remove heavy metals from the biomass of wetland plants and investigated the influences of pH values as well as structures of ILs on the removal efficiency of different ionic liquids.

### Methodology

The harvested roots and leaves of G. maxima will be separately washed carefully and dried in an oven at 80□ for 72 hours. To perform the leaching experiments and measure the content of heavy metal elements in the harvested plants, the cutting mill PULVERISETTE 15 will be used to pulverize and homogenize the dried roots and leaves, respectively.

This work will investigate three factors for leaching cadmium (Cd) from wetland plants, including four imidazolium-based ionic liquids with various anions, stirring time and five pH values (from 3 to 11). The nitric acid and sodium hydroxide solution will be used to adjust the pH values for distilled water. 0.5g milled roots, 0.1g ionic liquids and 10mL distilled water (with various pH values) 5:1:20 (m/m/m) will be employed and put in a 15 mL centrifuge tube for each leaching experiment. Then the samples mixed with ground roots, ionic liquids and distilled water will be continuously rotated for 24/48 hours through a multi RS-60 programmable rotator. Three replicates will be conducted for each treatment.

**The proposed extent of the thesis**
40

**Keywords**
heavy metals; plants; ionic liquids

---

**Recommended information sources**

Fuerhacker M, Haile T M, Kogelnig D, et al. Application of ionic liquids for the removal of heavy metals from wastewater and activated sludge[J]. Water Science and Technology, 2012, 65(10): 1765-1773
Phillips D P, Human L R D, Adams J B. Wetland plants as indicators of heavy metal contamination[J]. Marine pollution bulletin, 2015, 92(1-2): 227-232
Platzer S, Kar M, Leyma R, et al. Task-specific thioglycolate ionic liquids for heavy metal extraction: synthesis, extraction efficacies and recycling properties[J]. Journal of hazardous materials, 2017, 324: 241-249
Rai P K. Heavy metal pollution in aquatic ecosystems and its phytoremediation using wetland plants: an ecosustainable approach[J]. International journal of phytoremediation, 2008, 10(2): 133-160
Stojanovic A, Keppler B K. Ionic liquids as extracting agents for heavy metals[J]. Separation Science and Technology, 2012, 47(2): 189-203
Vergara M A V, Lijanova I V, Likhanova N V, et al. The removal of heavy metal cations from an aqueous solution using ionic liquids[J]. The Canadian Journal of Chemical Engineering, 2014, 92(11): 1875-1881
Yadav M, Gupta R, Arora G, et al. Current status of heavy metal contaminants and their removal/recovery techniques[M]//Contaminants in Our Water: Identification and Remediation Methods. American Chemical Society, 2020: 41-64
Yudaev P A, Chistyakov E M. Ionic Liquids as Components of Systems for Metal Extraction[J]. ChemEngineering, 2022, 6(1): 6

---

**Expected date of thesis defence**
2023/24 SS – FES

**The Bachelor Thesis Supervisor**
doc. Zhongbing Chen

**Supervising department**
Department of Applied Ecology

Electronic approval: 15. 3. 2024
**prof. Ing. Jan Vymazal, CSc.**
Head of department

Electronic approval: 25. 3. 2024
**prof. RNDr. Michael Komárek, Ph.D.**
Dean

Prague on 28. 03. 2024

## BACHELOR THESIS AUTHOR’S DECLARATION

I hereby declare that I have independently elaborated the bachelor/final thesis with the topic of: Filter Media and its uses in Green Walls for treating Greywater and that I have cited all of the information sources that I used in the thesis as listed at the end of the thesis in the list of used information sources. I am aware that my bachelor/final thesis is subject to Act No. 121/2000 Coll., on copyright, on rights related to copyright and on amendments of certain acts, as amended by later regulations, particularly the provisions of Section 35(3) of the act on the use of the thesis. I am aware that by submitting the bachelor/final thesis I agree with its publication under Act No. 111/1998 Coll., on universities and on the change and amendments of certain acts, as amended, regardless of the result of its defence. With my own signature, I also declare that the electronic version is identical to the printed version and the data stated in the thesis has been processed in relation to the GDPR.

28.03.2024 Oleg Artem Ferran

## ACKNOWLEDGEMENTS

I would like to thank my supervisor Zhongbing Chen for his guidance in writing my bachelor thesis and giving me advice. I also want to thank my family for always supporting me throughout the way in university and always reassuring me. Last, but not least I’d like to thank Xuejing Kang for helping me and guiding me throughout the all the laboratory experiments.

# Abstract

Tato studie zkoumá použití čtyř imidazoliových iontových kapalin jako zdroje extrakce kadmia z mokřadních rostlin. Čtyři iontové kapaliny s různými anionty, 1-butyl-3-methylimidazolium tetrafluoroborát ([Bmim][BF4]), 1-butyl-3-methylimidazolium triflát/trifluormethansulfonát ([Bmim][OTf]), 1-butyl-3-methylimidazolium methylsulfát ([Bmim][MeSO4]) a 1-butyl-3-methylimidazolium chlorid ([Bmim][Cl]), byly vybrány jako louhovací činidla. Studie ukázala různou míru vlivných faktorů iontového kapalného systému, jako jsou hladiny pH a doba míchání, na extrakční rychlost. Iontové kapaliny s vysokými hodnotami pH a prodlouženou dobou míchání se chovaly lépe. Například experiment zjistil, že pro destilovanou vodu při různých pH byly koncentrace kadmia 132,07 µg/L, 127,20 µg/L a 120,01 µg/L při pH 3. Při pH 5,03 byly koncentrace 192,73 µg/L, 279,54 µg/L a 303,67 µg/L. Různé hodnoty byly pozorovány pro iontové kapaliny při různém pH, přičemž ([Bmim][Cl]) měl 245,97, 240,75 a 214,52 ug/L koncentraci kadmia při pH 3, zatímco pro ([Bmim][BF4]) byly množství kadmia 179,73 ug/L, 163,08 ug/L a 191,45 ug/L. Rozdíly výsledků byly pozorovány také při vyšším pH. Například při pH 9,02 byla koncentrace kadmia po použití ([Bmim][MeSO4]) rovna 280,11 ug/L, 351,52 ug/L a 264,16 ug/L, zatímco ([Bmim][BF4]) ukázal koncentrace Cd 206,6ug/L, 2-18,9ug/L a 212,84ug/L. Výsledky se překrývají s předchozími zjištěními, která zdůrazňují užitečnost iontových kapalin při zlepšování praxe fytočištění tím, že usnadňují vznik vodních transportních cest v rostlinách prostřednictvím příjmu a transportu těžkých kovů. Studie žádá o intenzivnější výzkum molekulárních interakcí mezi iontovými kapalinami a ionty těžkých kovů a studie dlouhodobých environmentálních dopadů jejich rozsáhlých čistících opatření, která se používají. Shrnutě tato výzkumná práce přináší jedinečný soubor znalostí o osudu iontových kapalin používaných při závažné kontaminaci kovy v ekologii mokřadů, zdůrazňující, že multidisciplinární spolupráce musí hrát klíčovou roli ve úspěšných projektech fytočištění.

## Key Words

Těžké kovy, účinnost extrakce, louhovací činidlo, iontové kapaliny, strategie remediací, fytočištění, mokřadní rostliny

# Abstract

This study examines the use of four imidazolium-based ionic liquids as the source for extraction of Cadmium from wetland plants. Four ionic liquids with different anions, 1-Butyl-3-methylimidazolium tetrafluoroborate ([Bmim][$BF_4$], 1-Butyl-3-methylimidazolium triflate/trifluoromethanesulfonate ([Bmim][OTf], 1-Butyl-3-methylimidazolium methyl sulfate ([Bmim][$MeSO_4$], and 1-Butyl-3-methylimidazolium chloride ([Bmim][Cl], were selected as leaching agents. The study showed different extents of the influential factors of the ionic liquid system, such as pH levels and stirring time, on extraction rate. Ionic liquids with high pH values and prolonged stirring time performed better. For instance, the experiment found out that for distilled water under different pH, cadmium concentrations were found to be 132.07µg/L, 127.20µg/L, and 120.01 µg/L at pH of 3. At pH 5.03, the concentrations were 192.73 µg/L,279.54 µg/L, and 303.67 µg/L. Different values were observed for the ionic liquids at different pH with ([Bmim][Cl] having 245.97, 240.75, and 214.52 ug/L of cadmium concentration at pH 3 while for ([Bmim][$BF_4$], the amounts of cadmium were 179.73 ug/L, 163.08 ug/L, and 191.45 ug/L. The variation in results was also be observed at higher pH. For instance, at pH 9.02, the cadmium concentration after using ([Bmim][$MeSO_4$]) was equal to 280.11 ug/L, 351.52 ug/L, and 264.16 ug/L while ([Bmim][$BF_4$]) showed Cd concentrations of 206.6ug/L, 2-18.9ug/L, and 212.84ug/L respectively. The outcomes overlap with previous findings, which emphasize the utility of ionic liquids in improving phytoremediation practice by facilitating the formation of water transport pathways in plants through heavy metal uptake and translocation. The study calls for more intensive research of the molecular interactions between ionic liquids and heavy metal ions and the long-term environmental impact studies of their extensive scale remediation, which is being used. In summary, this research delivers a unique pool of knowledge on the destination of ionic liquids employed in severe metal contamination in wetlands ecology, highlighting that multidisciplinary cooperation has to play a critical role in successful phytoremediation projects.

**Key Words**

Heavy metal, extraction efficiency, leaching agent, ionic liquids, remediation strategies, Phytoremediation, wetland plants

**Table of Contents**

# 1. Introduction

## 1.1. Background information on heavy metal pollution

The problem of heavy metal contamination is among the most significant global threats to all aquatic species, causing the inevitable compromise of environmental and human health. These hazardous chemicals comprise the group of Cadmium, lead, mercury, and arsenic, which come primarily from industrial quantities, mining residues, and runoff from farming activities. Once discharged into surface water bodies, heavy metals can stay in wastewater and sediments for long periods and amass in the sediments and aquatic systems, inhibiting the food chain.

Due to the extensive impacts of heavy metal contamination, getting rid of heavy metals from the environment is one of the major global environmental issues that future generations need to be concerned with. The first point disturbs the aquatic ecosystem's natural balance by changing the community pattern and lessening the diversity of the natural living things. Some organisms will be highly susceptible to heavy metal toxicity and probe populations on the decrease and extinction of the species involved (Phillips et al., 2015). The bioaccumulation phenomenon, in which heavy metals accumulate through food webs and reach predatory species, can adversely affect individuals, populations, and whole ecosystems.

More dangerous than the constituents of the aquatic environment itself, the net effect of heavy metal pollution may also be reflected in human health. Ruined water sources may induce the drinking of heavy metals passed through by water or the consumption of shellfish and fish in contaminated water. The occurrence of these toxic substances after long-term exposure has often been related to several health issues, which include the disruption of the nervous system, organ damage, and cancers in different organs (Rai, 2008). Cases with children and pregnant women being in a precarious position owing to the exceeded sensitivity to toxic metals should be taken into account. Addressing heavy metal pollution necessitates a multistep strategy, including settling the regulations, technical improvements, and ecosystem-oriented solutions. The reduction of industrial emissions and better management of wastewater that has deteriorated without pollution of water bodies are significant. Moreover, Phytoremediation, which utilizes plants to remove and detoxifyants as a sustainable substitute, is becoming the next remediation strategy for polluted waters.

### 1.2. Importance of wetland plants in Phytoremediation

Wetland grasses and plants carry out necessary work in Phytoremediation, a clean technology operated by the natural ability of plants to excrete, degrade, or immobilize hazardous substances from soil, water, or air. In addition to this environmentally friendly alternative, this way of remediation offers several benefits over traditional clean-up procedures. This makes it the preferred solution for removing heavy metals from aquatic environments. Phytoremediation provides the unique ability to absorb and localize high amounts of heavy metals in an area where living is dangerous (Rai, 2008). These plants absorb cleansers through their root systems. Phytoextraction, the transfer of the cleansers into the plant biomass, transfers them to their respective site of accumulation, from which they can be collected and disposed of safely. *Eichhornia Hyacinthoides*, *Lemna*, and *Typha* have high biomass production and robust root systems that are important for filtration and uptaking.

Notwithstanding that, wetland plants are also in the business of immobilizing metals through the hemofiltration of phytostabilization from the soil or the sediment matrix. The rhizosphere adsorbs pollutants onto its surface or the root surface, or even within the rhizosphere, as the first step towards immobilization before movement and ultimate availability near the surroundings according to the process (Salt et al., 1995). Unlike phytoextraction, phytostabilization is when heavy metals are taken up and held within the plant through two routes: first, a complex is formed between root exudates and heavy metals, and second, plant tissues tightly bind and store metallic ions.

Apart from beans possessing the role of immobilizing and absorbing pollutants, wetland plants also work towards improving water and soil quality through different mechanisms. They play a crucial role in providing respiration to soils and stimulation of microbial appearance in the profile of the rhizosphere, as a result of which pollutants' degradation into harmless forms is possible. Besides, highly developed root systems of wetland vegetation are beneficial for soil stabilization and sediment control as they curb situations where pollutants are mobilized into waterways (Dietz & Schnoor, 2001). In addition to the power of wetland plants to clean the environment through Phytoremediation, their capacity to boost ecosystem sustainability and biodiversity is another significant feature. Through their efforts to sustain the existence of neglected wetlands, the remediation projects bring back the allure of the native green environment and ecological functions of the region. Wetlands are essential in being the natural reservoir for a broad spectrum of plants and animals. Hence, they are of crucial environmental importance as they balance ecosystems and ensure the sustainability of aquatic environments.

Furthermore, some wetland plants take charge of nutrient cycling and water purification, leading to better water quality and ecosystem health. They strive to eliminate excess nutrients, mainly nitrogen and phosphorus, which consequently help reduce eutrophication and algal bloom hazards. Wetland’s vegetation performs the function of a natural filter by repulsing water-related pollutants, improving clarity, transparency, and water quality. Seemingly insignificant wetland plants go to lengths and play vital roles in water ecology as the ones that combat heavy metals in aquatic systems (Lebrun, 2001). Unique to them is the possession of the reflection and the role of an organic ecosystem agency responsible for the issue of environmental pollution, providing a sustainable and environmentally friendly option. Taking advantage of the satisfying capabilities of mother nature, we can put our efforts towards improving the health and character of our water resources while ensuring the sustainability of our future generations.

### 1.3. Role of ionic liquids in heavy metal removal

Solvent ionic liquids (ILs) have become an up-and-coming alternative in terms of technologies to recover heavy metals from contaminated ecosystems thanks to their physical properties and variety of applications. The compounds, such as the ions with a complete composition undemand in case of volatility, thermal stability, and other physicochemical properties, are potential substances that can be utilized to treat pollutants (Stojanovic & Keppler, 2012). In the realm of the role of ILs (ionic liquids is the water, which is associated with several worthy features, including extraction, separation, immobilization, and recovery of metal ions in solutions and solid matrices.

The mentioned ILs determine their usage as the main ones since these substances mainly assist in identifying and separating heavy metals from liquid solutions. Although some ILs can form electrostatic solid bonds with the metal ions, such as coordination or complexation reactions, they still give way to complex metal ion-IL that are easier to separate from the aqueous phase. This is commonly known as A liquid-liquid extraction technique, where various kinds of complexes are used to remove particles or contaminants of heavy metals at high-efficiency levels and selectivity (Stojanovic & Keppler, 2012). Moreover, the capability of ILs to change the components produces systems of extraction for metals, especially under various environmental conditions; thus, the efficiency of extraction and side reactions are enhanced.

Alongside liquid-liquid extraction, solids extraction is suitable for dealing with solid matrices, e.g., soils, sediments, and industrial wastes. Developing nanoporous solid adsorbents or matrices, including nanoparticles, polymers, or porous materials, is another critical pathway to be considered. This is because ILs can be incorporated into such matrices, thus significantly enhancing their sorption capacity and selectivity orientation towards specific metal ions (Vergara et al., 2014). IL-implemented sorbents use some features of conventional sorbents, except for higher uptake capacity, fast kinetics, and even better recycling techniques. Water treatment using a solid-phase extraction process developed in ILs removes heavy metals from aqueous solutions and recovers the adsorbents. These techniques reduce the disposal of waste and help curb environmental impact.

On the other hand, ILs are the only solvents employed in electrochemical processes for dedication and reclamation of heavy metals from aqueous solutions. Electocoformation, bimetal diffusion, and electroplating are volte-facing techniques to separate metallic ions that depend on redox reactions or deposition. ILs have two main functions in these techniques: serving an electrolyte function or modifying electrodes, turning the cells more efficient, productive, and stable. Furthermore, through the ionic liquid (IL) medium, the electrolytes deposit metal ions with high purity and precision on electrode surfaces, which is a big help in the reusing and recycling ratio (Platzer et al., 2017). Due to the electrochemical impacts, there is a high chance that industrial effluents and wastewater streams with high concentrations of heavy metals can be treated this way.

The other things that contribute to ILs in the presentation of advanced oxidation reactions (AOPs) are oxidation, reduction, detoxification, and removal of organic pollutants and metal ions. AOPs, such as photocatalysis, ozonation, and Fenton chemistry, produce ROS corpus (highly reactive oxygen species) under relatively mild reaction conditions, thus governing the oxidation of target contaminants (target contaminants are degraded by oxidation). ILs can play the roles of solvents, catalysts, or co-catalysts in these reactions, and therefore, they avail all desirable properties, which involve improved solubility, stability, and reactivity. Generally, the ILs can fortify redox species' formation and persistence, such as hydroxyl radicals, singlet oxygen, or ozone, thus increasing pollutant degradation rates and reducing treatment time (Yudaev & Chistyakov, 2022). IL-based advanced oxidation processes, rather than counteract oxidation methods, make the contaminated environments cleaner the same way with heavy metals and other pollutants.

Although their various benefits are the big pluses for applying ionic liquids to extract heavy metals, they are also not free of challenges. The big problem is the uncertainty for some ILs about their toxicity, with the shared attribute being the possibly toxic cations or anions. Even though researchers are currently involved in the high-throughput screening of biocompatible and environmentally friendly ionic liquids, the health factor still provides obstacles to their application.

Moreover, the cost of synthesis and purification may be prohibitive; thus, their large-scale implementation through industrial electricity may become a seeking expectation. To solve the problem of increasing production costs, further studies should be conducted on designing cost-effective synthesis processes and effective methods for recycling and recovering ILs. These actions will expand the economic feasibility of IL-based technologies. Ionic solvents are of great significance in ejecting heavy metals from water solutions in an assorted and ecological way (Fuerhacker et al., 2012). The unique characteristics of the hydrotreating process, including tunable selectivity, inertness to volatility, and recoverability, offer promising alternatives for metal extraction and separation, which makes them an attractive choice to replace the current processes. Though some issues, including toxicity and cost, are outstanding, the research into alternative IL-based heavy metal removal technologies is progressively underway. Thus, similar advancements might be made to resolve the pollution challenge.

Finally, the task of ILs in the metal removal spectrum covers processes like extraction, separation, stabilization, recovery, and disintegration of metal ions in aqueous environments and solid matrices. Such compounds are beneficial and famous because they have many benefits for remediation methods, as they are very effective, specific, and environmentally friendly. Utilizing peculiar ILs is not an option here. Still, it is the primary tool scientists and engineers apply to eliminate heavy metal pollutants and preserve the environment's safety and health.

### 1.4. Purpose of the study

The goal of the current research is the development of an ionic liquid (IL) process for the decontamination of metal ions, particularly Cd, from the matrices of wetland plants. The goal is to harness the ability of different imidazolium-based ionic liquids with supplementary anions, which comprise the research material. Whether or not these substances can act as efficient leaching agents for purifying heavy metals will be determined. Furthermore, the potential role of the pH levels of the quaternary ammonium compounds on their leaching efficiency will also be studied. The thesis will be part of the architectural process toward constructing eco-friendly techniques in heavy metal-contaminated wetland ecosystems.

## 1.5. Research objectives and hypotheses

### 1.5.1. Objectives

1. To test the efficacy of the four imidazolium-based cation ionic liquids with various anions in the leaching of heavy metal, Cadmium, from the biomass of wetland plants.
2. This study aims to determine the impact of pH levels on the ionic liquid leaching efficiency for heavy metal extraction.
3. To examine the connections between ionic liquid structures and the leaching efficiency of heavy metals from wetland plant tissue.
4. To determine ionic liquid viability as an environmentally friendly and suitable medium for heavy metal removal in wetland areas.

### 1.5.2. Hypotheses

1. The pH level would be the main factor in determining the leaching outcomes by applying ionic liquids at different conditions. Such optimal pH levels will lead to a high leaching rate of Cadmium from wetland plants.
2. Ionic liquids showcase exceptional water-soluble qualities in heavy metal extraction.

# 2. Literature Review

## 2.1. Overview of heavy metal contamination in aquatic ecosystems

Wetland areas become the leading polluted media as they are the winners of contamination from industrial and urban activities. In their article, Phillips et al. (2015) discuss using the macrophytes found close to the water's edge as a means for heavy metal pollution in Swartkops Estuary. The study focuses on three macrophyte species: We shall, for this assignment, employ

*Phragmites australis, Typha capensis,* and *Spartina maritima* plants and explore their accumulative abilities to metals concerning sediment contamination.

One of the most catastrophic outcomes of the Industrial Revolution was the intensive system of heavy metal pollution, thereby endangering the status quo in the water environment. Exceeding the acceptable levels and eventual accrual of the heavy metals differ from that of the organic contaminants because the heavy metals persist in water bodies and ultimately accumulate in sediment, posing long-term threats to ecosystem health and human welfare. Due to the heavy metal pollution caused by the Industrial Revolution, its impact continues to be the main obstacle to ecological equilibrium and good health for humanity. In contrast to the organic contaminants, heavy metals exhibit long-lasting resilience in streams, rivers, and lakes and gradually accumulate in the layers of mud over time. This accumulation has the task of warning since the end, adversely affecting the ecosystem, environment, and human beings (Das et al., 2023). On a worldwide scale, the Industrial Revolution was a pivotal phase in economic adjustment, leading to this transition from an agrarian economy to an industrial one. This transformation did more than increase the rate of economic development; it also greatly improved farming, having a positive effect at the rural level. However, this time of progress is dual-faced because industrialization introduced new possibilities for science and technology. On the one hand, it brought the economy's growth, but on the other, it raised concerns about pollution, which then appeared and became a severe environmental problem.

Constant checking of heavy metal ion contamination in aquatic systems compels the adoption of efficient measures to regulate it and prevent further irreversible deterioration. The measurement of water and sediment involving spatiotemporal variations can be problematic; therefore, the organisms used as bio-indicators offer a more accurate and integrated evaluation of contamination severity. Since plants can stand still and retain some metals, they are good indicators of environmental changes. Accordingly, using plants as monitors is an economical and long-term alternative.

Phillips et al. (2015) suggest that submerged aquatic plants have great promise as a new bioindicator and may even surpass benthic organisms as the best measure of heavy-metal pollution in estuarine ecosystems. The resistance to entangling plant-based biomonitors by linking them to ongoing monitoring programs is a viable way for monitors to trace the degree of pollution and utilize policies to prevent contamination of the ecosystem and the well-being of humans. Measuring heavy metals in water systems involves examining undisputed water, sediments, and biotic species. As the bio-magnification effect is one of the most acute impacts of metal levels in water, metals in water are much lower than sediments and biota. However, they are also profound (Pandiyan et al., 2021). Water-soluble heavy metal uptake is prevalent in aquatic organisms where these metals undergo changes from inactive minerals to active, toxic forms, which, in turn, emphasizes the problem of aquatic pollution and demonstrates the need for an integrated approach. Reducing this risk requires various strategies that ensure human health while preserving aquatic ecosystems. Although this is just preliminary research, the results gained so far must be further substantiated to ascertain whether the ecological indicators are limited to a specific estuary or extend to other environments and in different pollution situations.

Concerning metal distribution within the plants, concentration levels followed the same model in previous studies: the highest in the roots and lower in rhizomes/stems/leaves. For example, the accumulation efficiency of *P. australis* is shown in the following order in root > rhizome > leave > stem for Cd, Cu, Pb, and Zn. The same tendency can also be seen in many other species, including *S. maritima* and *S. capensis*. Precipitation, purging, and structural contamination produce certain metal distributions in sediment and plants (Phillips et al., 2015). Concerning the elements that are not essential, i.e., Cd and Pb, their concentration declined in this ordering: sediments > shoots > rhizomes/stems. Nonetheless, the concentration of crucial microelements like Cu and Zn was higher for roots than for sediments, and that concentration diminished in the progression of roots from the sediments through the stems to the leaves. The study affirmed that the plant species under investigation could be successfully used to indicate contamination by heavy metal ions. In particular, their roots, the most beneficial organ in this process, were found to be an accurate tool for biomonitoring, where Pb and Zn are deeply investigated (Tőzsér et al., 2023). While using one species can provide dynamic monitoring data, using several species with individual distributions across the estuary is recommended for more accurate monitoring.

Rai (2008) provides a detailed presentation of heavy metal pollution in aquatic systems, covering the escalation witnessed during the Industrial Revolution. The author stresses that the primary cause for this rise is mainly the rapid process of urbanization and industrialization that makes the majority of heavy metals enter the environment. The emission of pollutants is caused by different sources such as mining activities, burning fossil fuels, smelting, releasing household wastes, and using industrial processes, which include pesticides and fertilizers. Many energy-consuming industries like thermal power plants and coal mines that pervasively release heavy metals contribute the most to heavy metal contamination, leveraging on those countries that are yet to achieve a developed state like India. Eco-technological innovations are more important now than ever in dealing with this vital environmental problem. Rai added that sustainable practices could help us solve heavy metal pollution in aquatic ecosystems.

Heavy metal contamination can cause aquatic organisms and the ecosystem if the toxic metals are bioaccumulated and biomagnified into the food chains, ultimately resulting in undesirable ecological degradation. Rai remarked that we could only formulate effective remediation plans if we understood the underlying mechanisms of metal uptake, transport, and transformation in aquatic ecosystems. Aquatic ecosystem's water bodies, which are heavily metal-laden, not only cause immediate fish health problems but also persistent ecological impacts. Tightly bunched after a few moments, the heavy metals dissolve in water, eventually accumulating within aquatic animals, especially fish tissues. As a result, these toxic metals express the concept of bioaccumulation, which explains that the fish enters a higher predator in the food chain, like birds, and thus pollutes more as the food chain passes down the hierarchy. The aquatic environment is also forced into a state of physical degradation: its inhabitants, including fish, get exposed to heavy metals, which in turn causes physiological irregularities and a series of health effects like carcinogenic, teratogenic, and mutagenic effects (Jamil Emon et al., 2023). Additionally, the degree of toxicity develops due to the simultaneous factoring in of not only fish species but also metal concentrations and exposure duration, which stresses out the complexity of the ecological matter.

Specifically, heavy metals such as Zn, Ni, Cu, and Cd may enter organisms through direct uptake from water and ingesting contaminated sediment in aquatic ecosystems. The absence of a one-way route via which heavy metals invade aquatic environments strengthens an understanding of pervasive nature and the far-reaching impact of heavy metal pollution on aquatic ecosystems. Metals hazardous to toxicity affect aquatic biota and have connections to the ecosystem and human health problems. Consequently, revealing the hidden facts through which metals get uptake, transported, and transformed is imperative for a strategic decision regarding pollution. Through the comprehensive exploration of these mechanisms, researchers and policymakers can build more purposeful interventions to help attenuate the extreme consequences of metal contamination, like our ecosystem and human well-being in the long run.

Rai's article on aquatic ecosystems covers the founding of the contamination distribution and effects of heavy metals on water-based species fully, including the records of the mid-20th century contamination caused by, for example, atomic tests in the country of Japan. These accidents spur safety awareness, illustrating how the extensive impacts of heavy-metal pollution on naturally degraded environments such as estuaries and freshwater systems may be long-term. One of the main problems mentioned in the study is the contamination of aquatic systems with heavy metals from the industrial sector, urban runoff, agricultural runoff, and atmospheric pollution. Such influences establish a continuous release of pollutants and permanent contamination of rivers, lakes, and seas, leading to significant problems in ecosystem well-being and biological diversity.

A concentrated level of heavy metals such as Cadmium, mercury, and arsenic found in coastal waters and estuaries is also a significant cause of concern because this is where sewage systems, chemical factories, farming, and industrial runoff meet. Rai clarifies that the waters polluted with mercury, lead, chromium, Cadmium, and zinc are the inevitable results of human activity. These pollution symptoms explain the massive influence of humans on the aquatic world. The piece focuses on heavy metal accumulation and resistance in marine environments involving sediment particle absorption, bioaccumulation via organisms, and biomagnification via food chain movement. As a result, these metal-accumulating processes increase the risks to wildlife and human health, chronicling the cases of consuming polluted seafood.

There are various ecological effects on ecosystems due to the pollution of aquatic environments by heavy metals by looking into the distortion of biogeochemical cycles, the modification of habitat structure, and the shift in community dynamics. These impacts might adversely affect the functioning of ecosystems and service provision, leading to deterioration, decline in the stocks, and the overall water quality, fisheries, and recreation. Altogether, heavy metal pollution in aquatic ecosystems is an intricate web of issues surrounding this unhealthiness. Thus, the necessity for a combined effort to implement preventive measures and restore the ecosystem's health is eye-opening. In doing so, scientists and governments can adopt protocols that consider the routes, channels, and ecological consequences of heavy metals' existence and build up ecological systems of the future unharmed.

### 2.2. Phytoremediation using wetland plants

Phytoremediation, which employs plants to attain ecological sustenance, is environmentally friendly and the most effective method for cleaning polluted soil, water, and air. This method uses intrinsic features of the plants, such as the ability to absorb, detoxify, or accumulate pollutants that take part in cleaning up and improving the ecosystem by neutralizing the adverse effects of contamination.

Phytoremediation, which comprises many different processes such as phytoextraction, hemofiltration, phytostabilization, phytodegradation, and phytovolatilization, works on the concept of removing contaminants from the soil or water using plants. Phytoextraction is the purification of metal ions from plants into their tissues or organs. It is a common occurrence in plant cells. In nature, via phytodegradation, one can eliminate organic pollutants by utilizing plants through biochemical processes (Salt et al., 1998). Rhizofiltration uses plant roots to clean up water by absorbing nutrient contaminants. On the other hand, the soil is treated with phytostabilization, which immobilizes the contaminant's profile and reduces mobility. Thus, phytovolatilization chains up the Volatile Organic Compounds (VOCs) through plant uptake and emission back into the atmosphere in the more benign forms.

Hyperaccumulating plant species, ie. *Brassica juncea* and sunflowers extract heavy metals like Cadmium, lead, and arsenic from the contaminated soil. In water bodies, aquatic plants are useful as natural filters of wastewater that will absorb nutrients and pollutants and thus make water pure (Susarla et al., 2002). Phytoremediation use is not limited to brownfields; it is also used in mining site rehabilitation and industrial waste disposal. Among the main advantages of Phytoremediation is its affordability, which is much lower than the expenses of the physicochemical cleaning methods. Besides, landfilling is cheaper since either excavation (time-consuming) or chemical treatments may experience some obstacles that might reverse the results (hence, large-scale clean-up will face difficulties). Phytoremediation is also a non-invasive method that delivers soil structure and fertility, unlike excavation, which can go through ecosystems and destroy them. Also, it can be possible in areas vast distances from the City centers or where the conventional methods are impossible.

However, Phytoremediation as science has its downsides and constraints. The cost can restrict the efforts made, and in most cases, the relief provided can take up to several years. Therefore, the problem might only be resolved after it becomes an emergency. The effectiveness of

Phytoremediation, among other things, depends on factors such as the species of plant to be used, the nature of the soil, and the strength of the contaminants, all of which may differ significantly. In addition, if plant treatment cannot be done correctly, contaminants may be re-released, and plants may be new sources of pollution.

Despite the obstacles, endeavors are being made to seek better ways of Phytoremediation, the technology of which continues to develop. The process is ongoing in the quest of scientists to genetically engineer plants to take up pollution and tolerate adverse conditions. Moreover, Phytoremediation is being complemented by integrated strategies that combine Phytoremediation with other remediation methods, such as bioremediation and nanoremediation, to maximize the efficiency of removing contaminants. Rai (2008) draws our attention to the importance of wetland plants in Phytoremediation, which makes them good at helping the plants absorb pollutants below ground, and in the process of the plants metabolizing these contaminants, they are removed from the environment.

The approach to environmental clean-up, which depicts Phytoremediation as sustainable, uses the plants' natural capacities to take pollutants from the soil and water. The impressiveness of plants that live in water should be considered, particularly for waters and wetlands, where aqua ecology is needed. They not only act as a yardstick for pollution removal, but their capacity to extract pollutants in roots and shoot through systems like phytoextraction, hemofiltration, and phytostabilization shows they effectively cope with contaminants. This feature is of fundamental value since it deals with the problems created in the polluted environment by the metals and macronutrients.

In this case, a critical merit of Phytoremediation is its affordability when compared with alternative remediation methods, e.g., excavation and disposal. After the planting stage, wetlands mainly govern themselves, with the plant uptake naturally required for remediation (Rai, 2008). One of the cost-effective measures is that it is a sustainable approach to resolving environmental contamination and is well clear with ecological restoration and conservation principles. Beyond wetlands' plants' utilitarian benefits, their abundance in varying textures, shapes, colors, and scents decorate landscapes. Wetlands, being such high-quality wetlands with many species living in them and being very productive, become good places for plants that remove pollutants. These species, like reeds, cattails, and rushes, produce a mechanism that eliminates pollutants through direct absorption, engendering the purification reaction by the participation of the root zone in the processes. On the other hand, this aspect makes the project ecologically sound, and environmental restoration and pollution mitigation are possible.

Wetland plants' adaptability to different wetland situations, including natural and constructed wetlands, targeting pollutant removal from industrial, household, and agricultural runoff, such as sewage and stormwater runoff, makes the applications broader. This approach taps the native water filtration intrinsic in wetlands, making it a cost-effective and efficient solution to water quality improvement and pollution control. Different plant species in various environments demonstrate the wide range of applicability of wetlands ecosystems for sustainable growth and environmental issue-handling programs.

Despite its positive effect on remediation, using wetland plants in Phytoremediation presents some difficulties that need to be considered. Therefore, the efficacy of remediation varies depending on several factors, such as plant species to be used, the concentration of contaminants involved, and site-specific conditions, such as in Rai (2008). Furthermore, the number of remediation practices and their effects on surrounding ecosystems requires that these be studied and managed with care. Collaboration of interdisciplinary is essential for phytoremediation integration into comprehensive strategies and if it will be effective long-term and sustainable.

The use of wetland plants for Phytoremediation and vice versa, as well as the plants' talents in thwarting water pollution, offers the best remedy for environmental cleaning. *Water plants* perform the helpful function of sequestering pollutants through various mechanisms, which not only results in the rejuvenation of the negatively impacted environments but also improves water quality. On the one hand, Phytoremediation can reduce costs and improve appearance. However, its success depends on how precisely the projects were designed, seasonal monitoring, and steady management to adjust to the site-dependent problems and provide sustainability. Using eco-friendly characteristics of wetland plants, Phytoremediation is integral to bringing about nature conservation and sustainable development.

### 2.3. Application of ionic liquids in heavy metal removal

Heavy metal pollutants in wastewater potentially impact the environment and health; a suitable cleaning method is necessary. The quest for an effective remediation technique led the researchers to look at the ionic liquid (IL) approach, amongst other options. Fuerhacker et al. (2012) conducted a general study of heavy metal extraction from wastewater and activated sludge using ILs. The primary purposes of this review are to integrate and synthesize the outcomes of their research and define the context in which the topic of heavy metals remediation fits.

Extensive regulations by the EU and Austria regarding the extraction of heavy metals from wastewater stress the consideration of this issue; this process should be severe. Consequently, traditional methods employing chemical precipitation, ion exchange, and adsorption are being looked upon with a sense of limitations, inspiring the generation of alternate ways. Increasing the appearance of the ILs in extraction processes might help us to solve this task. These specific substances that are distinguishable from their spectral properties and wide range of applications take the initiative in removing heavy metals, taking a step forward.

ILs (ionic liquids) efficiently absorb heavy metals in model solutions and natural municipal wastewater. The experimentation results show that the removal ability from solutions varied to some extent. However, industrial effluents can also get the job done if they employ accurate wastewater composition. Additionally, ILs have a robust elimination capability for heavy metals from the activated sludge, and these efficiency values are superior to other approaches. The creation and, especially, the transformation of ILs designed for particular applications, known as "Task-Specific Ionic Liquids (TSILs)," remain a boiling issue at present (Fuerhacker et al., 2012). IL drug formulations that have been widely investigated and searched for examples of such actual extraction of heavy metals from water samples of these formulating quaternary ammonium and phosphonium salts are a case in point (Liu et al., 2010). ILs are characterized by hydrophobic behavior, which allows necessary metal ions to be absorbed from industrial effluents, bringing both monetary benefits and providing environmentally friendly solutions.

More practically, ILs can be one of the economical options for recovering metals from aqueous solutions. Hence, both industry hands and customers can benefit from this cause. One example is the separation of calcium and mercury by ILs from industrial wastewater, which contaminates the environment with heavy metals and creates the possibility of recovering metals for the processes of the industry. The research also emphasizes an opportunity to examine the IL's applicability to sludge treatment, which consists of all the valuable nutrients but has to go through a process of removing heavy metals before safe land application. Chemical and biological methods for this purpose have been considered, entrenching industrial ionic liquid (IL) as an ultimate contender. ILs, which efficiently delineate heavy metallic contaminants from sewage sludge, enable it to become an effective fertilizer further and ensure compliance with environmental rules.

Platzer et al. (2017) figured out the employment of ILs, indicating a significant and practical approach to alleviating heavy metals in wastewater treatment as they give both economic and environmental benefits. Work is needed to fine-tune the operational scheme in the Integrated Life Approach, analyze the environment for the long term, and make it useful in the real world. Modern treatment of heavy metals has been improved by using the features of ionic liquids instead of conventional methods. This shows that more effective, green, and sustainable processing is on the horizon.

Heavy metal pollution is a force as massive as possible; however, it is considered to be a risk to human life and the environment because it is causing the death of millions of people all over the world annually. Heavy metal removal from aquatic environments is done in different ways, comprising chemical precipitation, flotation, absorption, ion exchange, and electrochemical coating. A diverse range of separation methods is available nowadays, which includes liquid-liquid extraction with ionic liquids (ILs) as favorable extractants because of their unique properties. An ionic liquid is a material that has shallow melting points, high thermal stabilities, and negligible vapor pressures. These physical characteristics provide a promiscuous system for targeted applications, including separating heavy metals. Designer solvents can be tailor-made by molding the structure of ILs to make the sols more suitable for specific metallurgy methods. Thioglycolate-based ILs are the most promising cationic ILs and major soft metal ion bonders.

The latter was also shown to contain robust recycling and reusability of the ILs, as there was a successful back-extraction of Cd ions using aqua-nitric acid. The latter procedure made the ultra-efficient removal of Cadmium from IL possible, thus permitting complete cadmium recycling. Likewise, microencapsulation of the immobilized enzyme onto polypropylene fibers was also tried to get the maximum extraction. However, compared to bulk liquid extraction, immobilized ILs demonstrated good extractive capability, leading to their high selectivity for the extraction of Cadmium.

Firstly, the review highlights the problems of heavy metal pollution caused by industrial activities, which could range from metal plating to mining and from batteries to semiconductors. The biodegradation process does not apply to organic pollutants; instead, heavy metals, also non-biodegradable, accumulate inevitably in the environment, causing threats to human health and ecosystems (Platzer et al., 2017). Irrespective, it has become a vital technique for wastewater to eliminate in chief the heavy metals from wastewater streams in the face of the strict regulatory requirements that need to be fulfilled.

Heavy metal removal utilizes different traditional methods, including adsorption, chemical precipitation, ion exchange, and solvent extraction, which are also discussed. Nevertheless, these pseudo metals are management methods that have some things that could be improved, like high costs and maintenance problems, and they are not suitable for low metal concentrations. To remove these contaminants, solvent extraction, which uses organic solvents and extractors, is a method of widespread use, and it causes various environmental concerns due to the volatilization of solvents (Platzer et al., 2017). The review refers to the challenges found and solutions by the authors, who discuss the option of ionic liquids being used as alternative extracting agents for heavy metal removal. Ionic liquids are organic salts that melt below 100° C, with unique properties such as low vapor pressure, high thermal stability, and tuneable solvation behavior. Ownership of these properties gives ILs the right to a broad spectrum of applications, which covers wastewater treatment.

The article centers on liquid-liquid facilitation by applying room-temperature ionic liquids (RTILs). Due to the RTILs based on imidazolium cations being widely studied for their capacity to separate heavy metals from aqueous solutions have been subjected to the most comprehensive research and review. It has been revealed that the efficiency of RTIL extraction is highly affected by the length of the alkyl chain of action and the hydrophobicity of anion. Besides, long-chain quaternary ammonium and phosphonium cations extracted into RTILs have been used for heavy metal removal, which has shown promise in applying this technique to remove heavy metals. The article additionally explains the extraction modes implicated in ILs; understanding them is vital for developing predictive multiplications. Furthermore, certain ILs, especially those with fluorine-containing anions, bear health and environmental risks. Therefore, the safest options should have been taken into account.

### 2.4. Gaps in existing research

The limited coverage in the existing studies is the underdeveloped exploration of pH influence for heavy metal removal, under investigations of the bonded states between ionic liquid's structure and the rate of metal leaching, and not sufficient consideration for the fundamental research on complex formation and property of ionic liquid's physicochemical process. New studies should investigate the chemistry of the components, such as the ability to eliminate the specific ions and stand the dissolved organics. How the structure influences the heavy metals' efficacy in wetland plants' remediation also needs to be evaluated further for a complete theory of their efficiency.

## 3. Methodology

### 3.1. Materials and methods

#### 3.1.1. Experimental materials

Four ionic liquids with different anions, 1-Butyl-3-methylimidazolium tetrafluoroborate ([Bmim][$BF_4$], Density: 1.44g/$cm^3$), 1-Butyl-3-methylimidazolium triflate/trifluoromethanesulfonate ([Bmim][OTf], Density: 1.3013g/$cm^3$), 1-Butyl-3-methylimidazolium methyl sulfate ([Bmim][$MeSO_4$], Density: 1.210g/$cm^3$), 1-Butyl-3-methylimidazolium chloride ([Bmim][Cl], Density: 1.086g/$cm^3$), were selected as leaching agents. The Hoagland's No. 2 Basal Salt Mixture was employed to prepare nutrient solutions for plant growth. All the chemicals were purchased from Sigma-Aldrich Co. LLC.

*Glyceria maxima* (*G. maxima*) is a common wetland plant and was employed in this work. The seedlings of *G. maxima* were collected from a pond at a garden of CULS (Czech University of Life Sciences Prague, Czech Republic). The 75% ethanol and 1% sodium hypochlorite (NaClO) were used for the surface sterilization of G. maxima's roots for 10 and 10 min, respectively. After sterilization, the seedlings with a height of around 15cm were washed with distilled water.

### 3.1.2. Cultivation of wetland plants

*G. maxima* seedlings were grown under outdoor environmental conditions with rain protection at the Czech University of Life Science Prague. They were first cultivated for four weeks using 1/5 strength Hoagland's solutions in a hydroponic system. Consequently, the *G. maxima* plants were exposed to cadmium (Cd) treatment in hydroponic culture (approximately 30 mg/L $Cd(NO_3)_2$) for nine weeks (from August to October). Ultimately, the plants were harvested and divided into roots and leaves.

## 3.2. Description of ionic liquids used in the study

### 3.2.1. 1-Butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF4])

**Density: 1.44g/cm3**

It consists of a 1-butyl-3-methylimidazolium cation coordinated with a tetrafluoroborate anion. It is high-density, a feature believed to calculate the solubility of the medium and make it interact with the cadmium ions and the wetland plants. The tetrafluoroborate [BF4] anion plays this role, assuring the structural stability of the ionic liquid.

### 3.2.2. 1-Butyl-3-methylimidazolium triflate/trifluoromethanesulfonate ([Bmim][OTf])

**Density: 1.3013g/cm3**

It consists of a 1-butyl-3-methylimidazolium quadruple that teams up with a triflate (trifluoromethanesulfonate) anion. The density of [(Bmim)[BF4]] is slightly lower compared to [(Bmim)[PF6]], which may result in different solvation properties and interactions with the cadmium-contaminated wetland plants. Triflates' anions, which are generally weak in charge, assist in controlling the process whereby the component is left behind.

### 3.2.3. 1-Butyl-3-methylimidazolium methyl sulfate ([Bmim][MeSO4]):

**Density: 1.210g/cm3**

This liquid electrolyte comprises the cation 1-butyl-3-methylimidazolium and the anion methyl sulfate. It differs slightly in molar volume and density from [Bmim] [BF4], but it is denser than [Bmim] [Cl], fitting the middle line of solvation properties. The anomenosulfate ion ensures stability, whereas the lower density could influence the ion's performance in penetrating the plant tissues and the extractability of the Cd.

### 3.2.4. 1-Butyl-3-methylimidazolium chloride ([Bmim][Cl])

**Density: 1.086g/cm3**

Such IL consists of IMI cation and chloride ions. Among the highly concentrated ionic liquids, the lowest density is observed in [Bmim][Cl], which suggests it can be involved in entirely different solvation properties and interactions with cadmium and wetland plants compared to others. For instance, chloride anions will dissolve more readily than others, causing a change in leaching. These ionic liquids were selected to develop a high-efficiency process of cadmium extraction from wetland plants. In this regard, target minerals' varying densities and chemical composition allow adjusting the extraction conditions or the processes' mechanism.

## 3.3. Leaching experimental design

a) The harvested roots and leaves of *G. maxima* were carefully washed and dried in an oven at 80°C for 72 hours. To perform the leaching experiments and measure the content of heavy metal elements in the harvested plants, the cutting mill PULVERISETTE 15 was used to pulverize and homogenize the dried roots and leaves, respectively.

b) This work investigated two factors for leaching Cd from wetland plants: four imidazolium-based ionic liquids with various anions and five pH values (3, 5,7,9,11). The nitric acid and sodium hydroxide solution adjusted the pH values for distilled water. 0.5g milled roots, 0.1g ionic liquids, and ten distilled water (with various pH values) 5:1:20 (m/m/m) were employed and put in a 15 mL centrifuge tube for each leaching experiment. Then, the samples mixed with ground roots, ionic liquids, and distilled water were continuously rotated for 24 hours through a multi-RS-60 programmable rotator. Three replicates were conducted for each treatment.

### 3.4. Distribution of Cd in roots and shoots of G. maxima

The concentrations of Cd in plants with two parts of roots and shoots were tested and listed in Table 1. It can be seen that approximately 86.2% of Cr in the plants is distributed in the roots. Therefore, in this study, the roots of *G. maxima* after Cultivation were used as objects for the following removal experiments.

Table 1 The Cd concentration in different parts of plants

| **Plant** | **Concentrations (Cd), mg/g** | **Percentage** |
|---|---|---|
| Roots | 3.761 | 86.2% |
| Shoots | 0.603 | 13.8% |

### 3.5. Experimental setup for leaching experiments

The experimental procedure for leaching experiments involving G. maxima plants and the extraction of Cadmium (Cd) using imidazolium-based ionic liquids can be described as follows:

#### 3.5.1. Preparation of Plant Material:

a) Disinfecting by extensive washing was done before the roots and leaves were harvested.
b) The cleaned leaves and roots were dried in the oven at 80°C for 72 hours for complete dehydration.

#### 3.5.2. Milling and Homogenization:

a) The dried roots and leaves were separately ground and cut to uniform size using the PULVERISETTE 15. This step recognizes the significance of sample composition homogeneity and the ease of extraction.

#### 3.5.3. Leaching Experiment Design

a) The leaching experiments focused on the selection of imidazolium-based ionic liquids with various anions and pH ranges from 3 to 11.

b) Four imidazolium-ionic liquids-based anionic formulations were the main subjects of the experiment.

c) Nitric acid and sodium hydroxide solutions were used to scale pH features, while distilled water was used to dilute them further.

d) Each leaching experiment consisted of 0.5g of milled roots, 0.1g of the selected ionic liquid, and 10 mL of distilled water with varying pH values, mixed in a ratio of 5:1:20 (m/m/m).

e) Other components were added to a 15 mL centrifuge tube in a process that strictly followed the methods of efficient extraction.

### 3.5.4. Experimental Procedure:

a) The samples containing ground roots, distilled water, and ionic liquids were poured into 15 mL centrifuge tubes for the different treatments.

b) After installation, they were attached to one side of the rotator with an RS-60 multi-programmable rotator.

c) Three repetitions of each treatment are established to measure its reproducibility and reliability.

## 3.6. Analysis

a) To test the effect of cadmium leaching from *G. maxima* species in three environmental conditions, the plants were submerged for 48 hours after samples were collected.

b) Exact quantification of the amount of pollutant (Cadmium) releases is obtained via spectrophotometry and inductively coupled plasma mass spectrometry (ICP-MS) by addition.

## 3.7. Variables of the Experiment

### a) Cd-biomass

This parameter is the sum of the Cd concentrations in G. maxima biomass (Gm) plants during the extraction treatment. Cadmium rates are usually expressed as the number of cadmium atoms per weight of the plant material (g/g).

**b) Distilled water (g)**

This is the amount of water purified using the leaching process measured in units of grams.

**c) pH of distilled water**

The pH of the purified water is a significant factor that affects the solubility of cadmium ions in the water and, overall, the success of the leaching method. In the experiment, the pH was altered to get the different pH values and provide different conditions for maximum operation of the ionic liquids.

**d) Cd concentration in leachate**

This value shows the cadmium concentration in the leachate after the leaching process. It manifests in micrograms per liter (μg/L) and is the sign of the cadmium quantity that has passed from the crop's vegetal mass into the solution.

Other variables in the experiment include:

I. **Volume of distilled water**
II. **Rotating time**

### 3.8. Statistical analysis plan

Data on the above variables was collected after setting up the experimental procedures. The Cd biomass in grams was collected, and the weight of distilled water and the pH values of the water after the acidity and alkalinity were altered. A constant volume of 10mL of distilled water was used, and then the rotating time was recorded. Lastly, all these values and the concentration of Cadmium in the leachate were recorded and presented in the table below. The pH against Cd concentration was analyzed, and the values were presented graphically, comparing the four ionic liquids.

# 4. Results and Statistical Analysis

## 4.1. Presentation of data on heavy metal extraction by the different ionic liquids

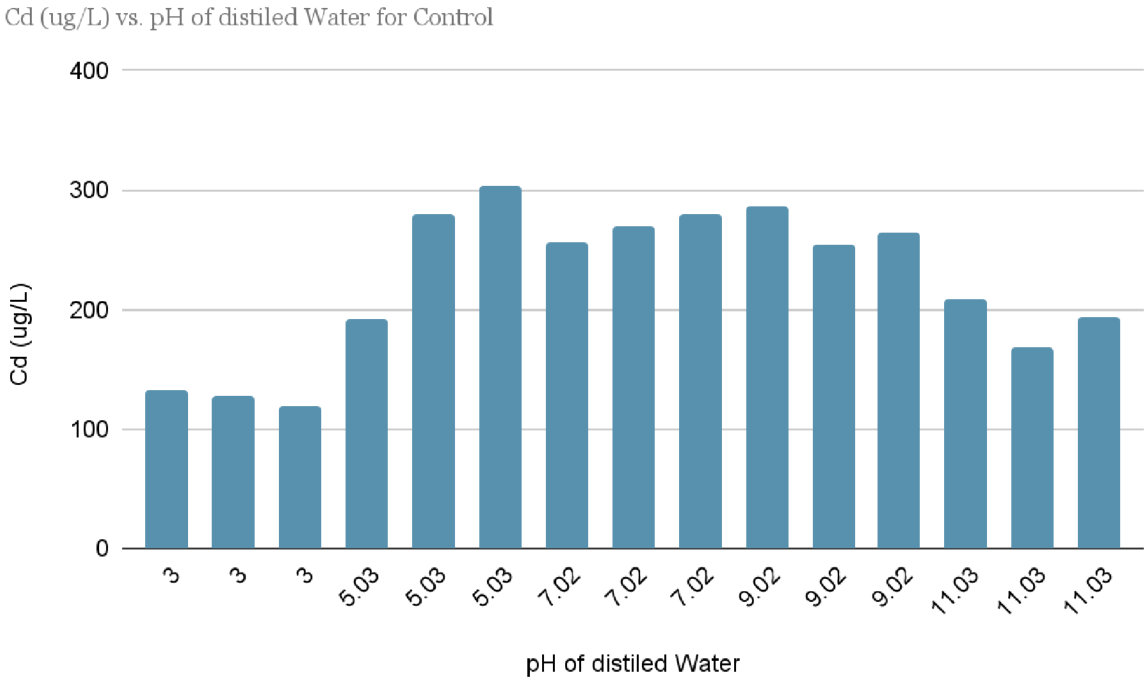


**Figure 3. Extraction of Cd under different pH with distilled water**

The graph above shows the Cd concentration under different pH levels with distilled water. At pH of 3, cadmium concentration was measured, and the presence of 132.07μg/L, 127.20μg/L, and 120.01 μg/L was recorded, respectively. At pH 5.03, the concentrations were 192.73 μg/L,279.54 μg/L, and 303.67 μg/L. At pH 7.02, the concentrations were measured at 256.52 ug/L, 269.17 ug/L, and 279.91 ug/L for Cd. At a pH level of 9.02, the rising values were observed with concentrations as high as 285.95 ug/L, 255.24ug/L, and 264.97ug/L, respectively. Finally, at pH 11.03, the Cd concentrations were detected at 208.69, 168.39, and 193.35 ug/L, respectively.

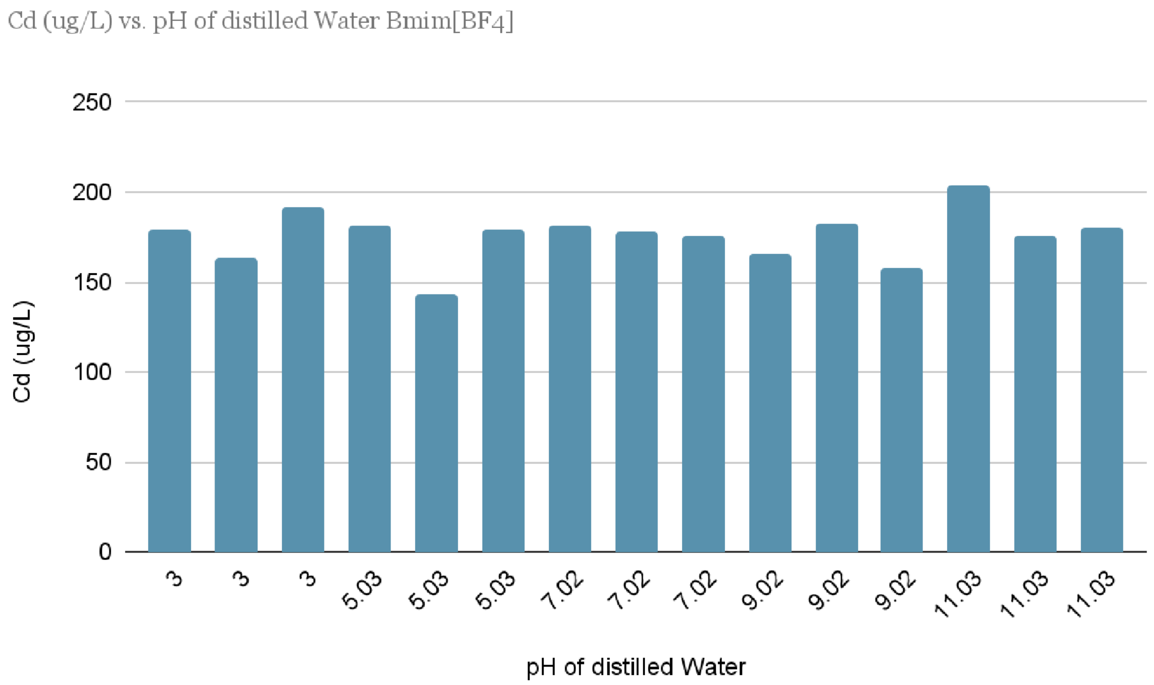


**Figure 4. Extraction of Cd under different pH with Bmim[BF4]**

At pH 3, the amounts of cadmium were 179.73 ug/L, 163.08 ug/L, and 191.45 ug/L. With a pH value 5.03, cadmium concentration was 180.96 ug/L, 143.67ug/L, and 178.7 ug/L. On graphing to pH of 7.02, the recorded cadmium concentrations were 181.72 ug/L, 178.12 ug/Land 175.55 ug/L. At pH 9.02, the cadmium concentration was equal to 165.93 ug/L, 182.12 ug/L, and 158.38 ug/L, respectively. Lastly, the cadmium concentrations at a pH of 11.03 were 204.00 ug/L, 176.31 ug/L, and 180.72 ug/L.

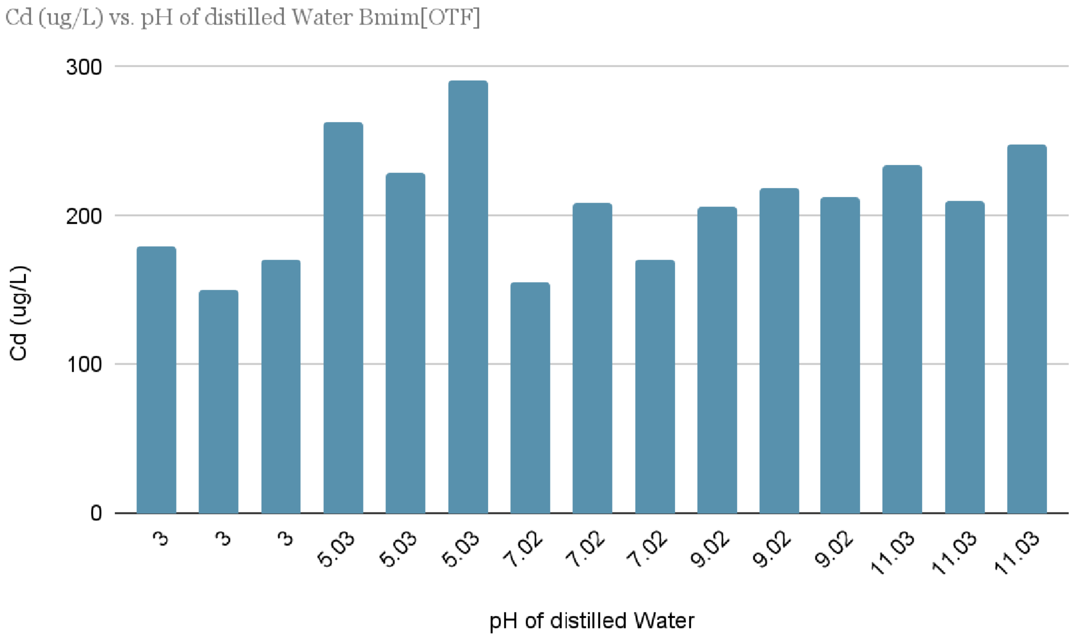


**Figure 5. Extraction of Cd under different pH with Bmim[OTF]**

At pH 3, cadmium concentrations were 179.73 ug/L, 150.11 ug/L, and 170.9 ug/L, respectively. With pH values in the range of 5.03, cadmium levels were 262.78 ug/L, 229.54 ug/L, and 290.77 ug/L. In pH 7.02, the cadmium concentration detected was 155.46 ug/L, 208.71 ug/L, and 171.22 iga/L, respectively. At pH 9.02, the values for cadmium were 206.6ug/L, 2-18.9ug/L, and 212.84ug/L. The last pH of 11.03 showed a cadmium concentration of 233.75 ug/L, 209.8 ug/L, and 248.52 ug/L.

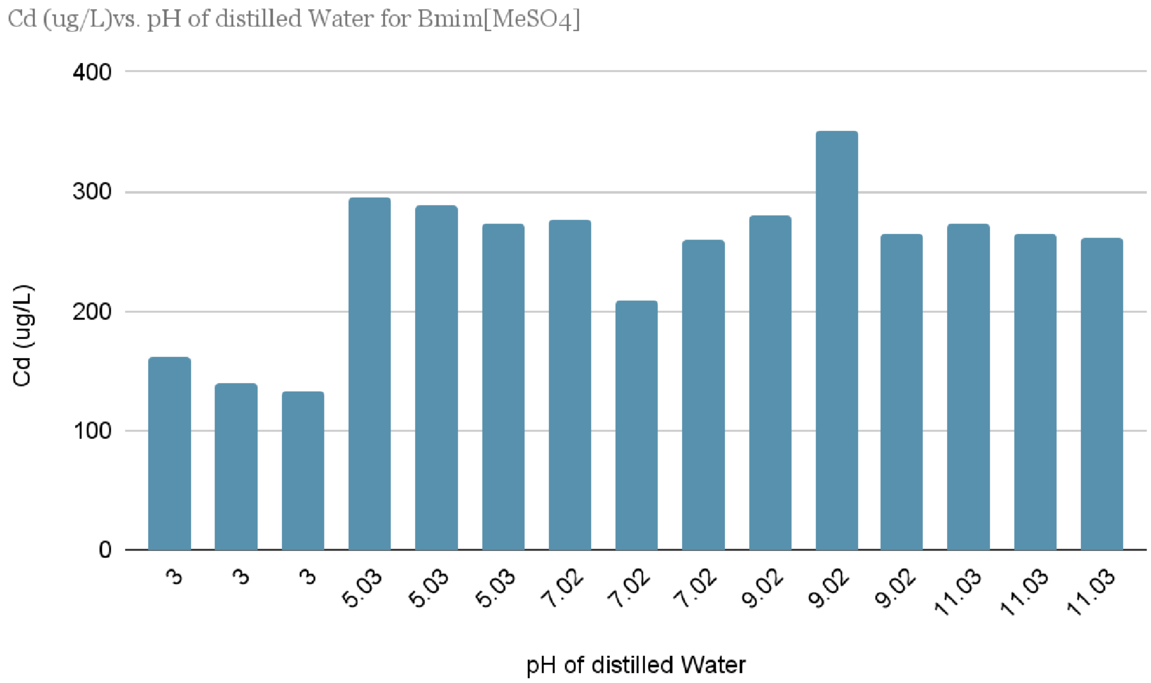


**Figure 6. Extraction of Cd under different pH with Bmim[MeSO4]**

At pH 3, Cd concentrations were 161.2 ug/L, 139.4 ug/L, and 133.38 ug/L. Moving to the pH 5.03, the cadmium concentrations were 295.15 ug/L, 287.75 ug/L, and 273.13 ug/L. At pH 7.02, the observed cadmium levels were 275.81 ug/L, 208.61 ug/L, and 258.97 ug/L. At pH 9.02, cadmium ion concentrations were 280.11 ug/L, 351.52 ug/L, and 264.16 ug/L. The last pH, 11.03, cd concentration, was measured to be 273.35 ug/L, 264.17 ug/L, and 261.6 ug/L.

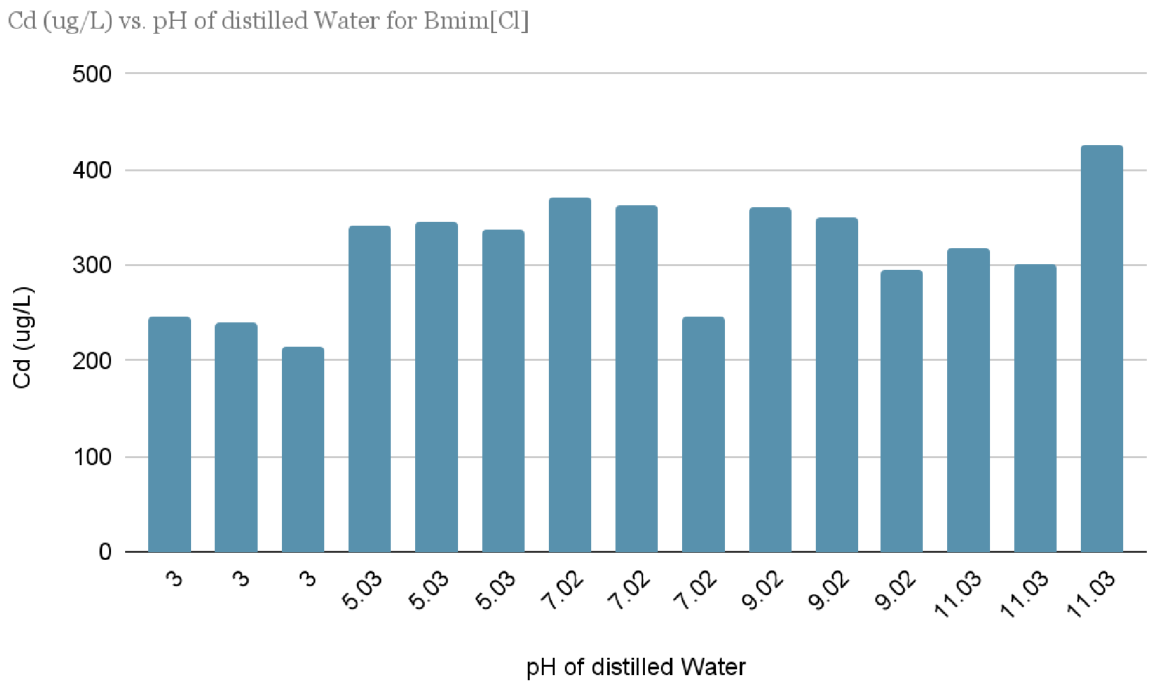


**Figure 7. Extraction of Cd under different pH with Bmim[Cl]**

The discovered experiment value at pH 3 revealed 245.97, 240.75, and 214.52 ug/L of cadmium concentration. The cadmium concentration was 340.64 ug/L, 345.23 ug/L, and 338.15 ug/L at a pH of 5.03. Next, under another pH condition of 7.02, there were 370.61 and 362.15 ug/L cadmium levels; meanwhile at pH 9.02, the cadmium concentration showed 361.41 ug/L, 349.32 ug/L, and 295.19 ug/L, respectively. The Cd concentration at pH 11.03 was 318.46 ug/L, 301.55 ug/L, and 425.1 ug/L.

### 4.2. Influence of pH values on metal extraction efficiency

This experiment is an important indication of the level of the demand for pH on the efficiency of cadmium extraction. Essentially, as the pH elevates, significant amounts of Cadmium should be seen in the solution that is extracted. On the whole, these data have been acquired over a wide range of pH, where Cd concentrations have presented an upward trend from pH 3 to pH 11.03. Such an effect can be linked to the changes in the qualification of Cd2+ ions in solution at different pHs

(Shin et al., 2007). At the lower pH, Cd ions may be put too complex or fixed on the other constituents; hence, we would have difficulty extracting them. Nevertheless, beyond the range where the complexes start dissociating, or they are weaker during extraction, it is made easier.

$CD^{2+}\,(aq) + 2Cl^{-}\,(aq) + 2Bmim^{+}\,(aq) \quad [CdCl_2]\,(s) + 2BmimCl(aq)$

The result shows that the pH in the range tested (3-11.03) can also cause the Cd to be extracted into the phase of the liquid being used. The highest Cd concentration was seen at pH 7.02 and 11.03, suggesting that these pH values could preferably be effective under the chosen ionic liquid for extractions (Sim et al., 2014). Nevertheless, these results only alter within an array of pH levels to being tested; if so, a broader overview of the favorable pH circumstances could be gained for the extraction of Cadmium from wetland biomass plants utilizing [Bmim][Cl].

Another experiment to maximize Cadmium extraction efficiency using pH level is similar to the previous experiment, except there's a marked effect of pH on the latter's performance. This is because when compared against the regularity of the last data, the fluctuation is less, although there are trends here nonetheless that should be considered. To illustrate, in the case of pH 3, 5.03, and 11.03, the Cd concentrations are more significant than what the pH 7.02 or 9.02 levels show. These results demonstrate that the contact between the ionic liquid and pH plays a vital role in the cadmium ions' chemical properties, which leads to the ionic liquid with different efficacies of extraction for various pH ranges.

$Cd^{2+}(aq) + 2BF^{-}_{4}(aq) + 2Bmim^{+}(aq) \square [Cd(BF_4)_2](s) + 2BmimBF_4(aq)$

The disparity [Bmim][BF4] to the earlier ionic liquid [Bmim][Cl] reflects some distinct outcomes. Only two experiments are similar in terms of pH dependency in cadmium removal. Nevertheless, some of them have some differences (Ghorbani et al., 2021). Thus, notice that as far as overall cadmium extraction effectiveness is concerned, the [Bmim][BF4] model is observed to have slightly lower efficiency compared to [Bmim][Cl]. Besides this, the ionic liquid operating at the range for the extraction may be different from the other. Such differences signal the necessity for choosing an agent with the applicable metal and conditions as indices of this choice.

Similar to the preceding experiments, the efficiency of cadmium extraction using [Bmim][MeSO4] shows a strong dependence on the size of pH determination. The curve depicted in the fig suggests that there is a variation in acid extraction efficiency with varying pH levels. More significantly, at pH 5.03 and 9.02, Cd concentrations were obtained higher than at pH 3, 7.02, and 11.03 (Ignat'ev et al., 2012). The variations bring to light a possible association of ionic liquid, pH, and chemical species of cadmium ions in the liquid phase.

$Cd^{2+}$ (aq) + 2$MeSO^{-}_{4}$(aq) + 2$Bmim^{+}$(aq) □ [$Cd(MeSO_4)_2$] + 2$BmimMeSO_4$(aq)

The achieved extraction efficiencies and pH dependencies of [Bmim][MeSO4] are not uniformly shown in [Bmim][BF4] and [Bmim][Cl], which were adduced before. Through the ionic liquid analysis, you are able to see that each of them exhibits its characteristics, demonstrating the need to choose the right leaching agents that will be suited to the experimental conditions as well as the particular metal you want to extract. Even more, research should investigate the mechanics of observed differences and their application in clinical practice.

This study indicates that pH is a key factor and plays an important role in the process of cadmium recovery via ([Bmim])[OTF]. Remarkably, there is a very clear difference in the efficiency of extraction across the various pH levels (PerezF et al., 2019). The fact that the maximum Cd values in solutions with pH 5.03 and 11.03 were measured while the majority of concentrations at the other pH levels were lower could be a sign of the best conditions for Cd extraction around these environments.

$Cd^{2+}$(aq) + 2$Otf^{-}$(aq) + 2$Bmim^{+}$(aq) □ [$Cd(Otf)_2$](s) + 2BmimOTf (aq)

In comparing the extraction performance determined with [Bmim][OTF] in these experiments to the previous experiments conducted with other ionic liquids, such as [Bmim][BF4], [Bmim][Cl] and [Bmim][MeSO4], we can observe significant differences in extraction efficiencies and pH dependencies. Every ionic liquid reveals its unique capabilities, making the selection of the leaching agents an important factor in terms of a successful matrix extraction (Dzulkipli et al., 2021).

### 4.3. Comparison of different ionic liquids

Every one of these ionic liquids performed distinctively for extraction and Cadmium, and a noticeable difference was obtained by pH levels**.** A plot of the effect of pH in the investigated ionic liquids shows that at pH 3.00, they all have relatively low removal capacity. Extracted cadmium concentrations were in approximately 130 to 160 µg/L range, indicating reduced effectiveness under low pH values. However, at the milder degrees of alkalinity, with a pH value of 5.03, the increased removal excess was registered with all the ionic liquids. The Cd concentrations range in the model sample solutions increased from largely moderately acidic to nearly neutral conditions, purportedly signaling the high effectiveness of acidic pHs.

Moreover, hiking the pH values to level 7.02 or 9.02 increased the removal efficiency of all other ionic liquids even further. The maximum cadmium concentration accessible to extraction was observed to occur in the alkaline pH range of both the ionic liquid species used. This suggests that alkaline conditions improved cadmium extraction significantly regardless of the ionic liquid fractions used. Nevertheless, at an extremely high pH of 11.03, there was a slight decrease in the VOC removal efficiencies where all four ionic liquids competed against each other compared to the pH of 9.02. The removal efficiency in the range of pH from 5 to 6 showed a mainly decreasing trend, and even though it was lower than at the low pH levels, its effectiveness was still obviously higher, which implied that the excessively high pH may affect the extraction process. At the same time, there was still a relatively high degree of effectiveness. Although all four imidazolium ionic liquids demonstrated the same tendency towards changing pH, these liquids may have a slightly lower extraction efficiency in the case of discrete pH values. The different results of the extracts might be connected to the various properties, and the interactions of each plant material with ionic liquid may be a possible reason.

### 4.4. Discussion of findings about research objectives

The investigation was directed to reply to some significant inquiries concerning the performance of imidazolium- cyanide- cation- ionic liquids in wetland plant leachate heavy metals, particularly Cadmium (Cd). To this end, a series of experiments were carried out by studying, specifically, the role of pH levels in the process of the leaching efficiency as well as identifying the correlation between the structure of ionic liquid and its ability to leach metals from the water. In this way, the study was able to determine the applicability of ionic liquids as green alternatives in the heavy metals' removal applications of wetland areas.

The research commenced by determining the effect of pH frequency on the removal efficacy of [Bmim][Cl] ionic liquid of Cadmium level concentration. With pH values in the acidic range, Cd removal was less efficient. This suggests that acidic conditions are likely to facilitate the leaching of Cadmium, thereby increasing concentrations. However, high pH caused the Cd removal efficiency to be greater. In contrast, the low pH indicated low efficiency, implying that the neutral or alkaline pH levels would enhance the efficiency of the Cd removal processes.

However, the pH concentration on the removed [Bmim][BF4] for Cd was found to be consistent, and the more the pH shifted up, the more the removal quantity increased as well. The rise of the pH resulted in better adsorption of Cd onto [Bmim][BF4] surfaces, being the reason for its speciation changes in the fluid and, furthermore, the formation of insoluble compounds. This represents that maximizing pH wellness is a key factor that should be addressed in making the extraction of heavy metals by ionic liquids a successful venture.

This study exceeded the elution capacity of Bmim[MeSO4] for Cd concentration under different pH conditions. Findings indicate a growing tendency as pH increases to take out the chemicals until the optimal range is reached, and further increments of pH will lead to deterioration of removal efficiency. There is a probability of the existence of a Cd removal pH range, which lies at the optimal side and under which removal inefficiency might be reduced or rise to the plateau. Knowledge of the optimal pH range becomes an invaluable tool for designing remediation strategies that are efficient in dealing with cadmium-contaminated environments.

Further, the study investigated the influence of pH value readings on the removal efficiency of Bmim[OTF] for Cd concentration. The experiment showed that the more the pH value was increased, the more the removal capacity of Cd was enhanced. In the presence of higher and positive pH, Cd extraction was more desirable. The increased precipitation or adsorption mechanisms are likely reasons for that. Consequently, it indicates the key role of pH in liquid ionic-ionic metal assimilation, especially in territories dominated by wetlands.

In addition to the results of the study above on the effects of ionic liquid structure on heavy metal leaching efficiency, the study also sheds more light on the effect of the structure of the ionic liquid. By evaluating the influence of the structure of imidazolium-ionic liquids on their leaching content, it was observed that they generally do not have significant effects on their efficacy in removing Cadamium from wetland plant biomass. If the ionic liquid used for extraction was different, or if the elements other than anion affected the extraction efficiency significantly or not, except only the presence or absence of anion in a certain ionic liquid, Cd extraction was still successful. This indicates the high removal efficiency of Cd. Thus, the importance of anion selection in ionic liquids for metal remediation is quite insignificant, which may be irrelevant.

The scientific study was linked with the applicability of imidazolium cation-based ionic liquids in cadmium removal from plant biomass in wetland habitats. The report showed that the results emphasized the significance of the pH balancing on the Cd removal efficiency and proved the effective capability of ionic liquids to use in the metal extraction processes. In addition, the research gives tips on the communication between the ionic liquid structures and metal leaching quality, resulting in the understanding that the choice of anion may not be the main cause affecting the effectiveness of the metal recovery. Therefore, research findings will undoubtedly provide invaluable data for designing effective environmentally-friendly techniques for removing heavy metals anywhere in the wetland, the implications of which include nature restorations, conservation, and other environmental efforts.

## 5. Discussion

### 5.1. Interpretation of results in the context of existing literature

The present study demonstrates synergy with other research showing the competence of ionic liquids, specifically those imidazolium salts with incorporative capability for Cadmium from different environmental matrices like wetland plant biomass. Not only does it demonstrate the viability of ionic liquids for heavy metal remediations, but it also signifies the significance of efficient treatment of heavy metals. Previous results have shown that ionic liquids with an imidazolium head group can be used successfully to extract Cadmium. The study serves to strengthen the previous findings in this field by exploring more possibilities of the application of ionic liquids in combating heavy metal contamination not only in a particular environmental context but also anywhere else where it may occur.

The pH effect on the cadmium removal efficiency is shown in a specific way. The effect is presented by the rate increase as the pH of the solution increases. This tendency confirms previous research impressions that have always demonstrated a tie between pH and the effectiveness of heavy metal detoxification. The cause of Cd ions mobility, which occurs as a result of a decrease in the pH value, lies in the speciation process in solution: at lower pH levels, more Cd ions become mobile and are, therefore, less likely to be adsorbed on the surface of the solution or precipitate out of solution. On the contrary, at a higher pH, Cd ions tend to form insoluble compounds or get attached to the surfaces, which gives another way to eliminate them from water. The importance of pH control in water treatment systems becomes evident from this understanding, and the capability of pH level correction to substantially accelerate the removal of heavy metals like Cadmium serves to facilitate necessary environmental clean-up operations.

Arguably, pH [Bmim][MeSO4] displayed the measure of [Cd] removal, which increased as pH increased. In a pH range of 3, Cd removal was rapid and dropped significantly as the pH of the solution ascended. This notion again illustrates the main function of pH adjustment in Cd-removing features where the favorability of granting Cd-contaminated waters with neutral to slightly alkaline pH levels is involved in order to achieve the desired efficiency of the Cd removal process. This study has brought forth a narrowing down of the lead factors on Cd removal effectivity as a result of pH marginalization. It suggests the need for pH control in Cd removal techniques. Thus, these are suggestions for the development and understanding of heavy metal remediation strategies with an emphasis on the aquatic environment.

As an extra feature, the observed pH values affect the leaching efficiency similarly to those published in previous scientific papers on this issue. The result of studies is that the pH is a critical factor in the concentration of metal ions between different phases, affecting the solubility and mobility of heavy metals in the solution (Fischer et al., 2011). All this is attributed to higher pH levels, which make the leaching of the heavy metals more favorable among other conditions by increasing the metal ions' solubility and promoting their release from solid matrices like plant biomass (Deng et al., 2012). Research has proceeded to provide evidence of the linearity between pH and ionic liquids pollutant-degradation demand. This finding stresses the necessity of optimizing pH when ionic liquids technologies are used as remediation strategies.

The outcomes also support us in progressing our knowledge about the arrangement of the ions and their influence on the dissolving of heavy metals. The present study has yet to identify the precise structures of the imidazolium-based ionic liquids. However, such a general trend reflects that those structural factors may have a low substantial influence on their cadmium leaching efficacy (Zhu et al., 2009). This viewpoint makes sense with prior literature, which all tend to think that the ionic liquid's cationic part seems more significant with ores metal extraction than the anionic part. Future investigations may enlighten the molecular interactions of ionic liquids with heavy metal ions by focusing on a particular mechanism that could reveal the underlying reasons for the success of metal extraction.

## 5.2. Implications of findings for phytoremediation practices and limitations

The finding, particularly so, could make the phytoremediation technology applicable for cleaning heavy metal polluted sites. Investigating imidazolium-based ionic liquids as extracting agents, the phytoremediation process can be strengthened while having high specificity to particular heavy metals, such as Cadmium (Kapahi & Sachdeva, 2019). The observed correlation between the values of pH and leaching efficiency indicates that optimizing pH conditions could help increase the uptake and translocation of heavy metals by plants, thus leading to the uptake and translocation of heavy metals by plants, which would further enhance their removal from contaminated spaces.

Furthermore, according to the preliminary information, the compatibility of imidazolium-based ionic liquids with plant biomass can be successfully integrated into phytoremediation technology (Singh et al., 2018). They have low toxicity and are usually not persistent, so they are an excellent example of a cost-efficient and environmentally friendly substitute for the chemical agents used in traditional remediation. Their capability to draw down heavy metals from vegetational tissues to grow plants and keep plant growth or health unaffected makes them suitable for biological remediation operations where maintaining the consistency of the system and the effect on ecology are the most important considerations (Yan et al., 2020).

Another way that the results have been articulated is ionic liquids, interactions between plant physiology, and the significance of including in phytoremediation designing strategy. The direct influence of pH on leachability demonstrates the call for specialized pH control practices to realize improved metal uptake efficiency by the plants and optimal recovery (Hassan & Mutelet, 2017). Furthermore, advances in future studies can investigate the additive benefits of utilizing ionic liquidcovered Phytoremediation in combination with other remediation solutions, such as microbial aid and soil amendments, to develop integrated alternative approaches for targeting multi-contamination issues. Apart from the applicability and workability of using ionic liquid in natural world settings, more research is needed. Although the laboratory experiments help reveal the fundamental mechanisms and project how the method would play out, the memorialization of the findings into full-scale implementations poses challenges that must be dealt with (Kozonoi & Ikeda, 2007). For instance, cost-benefit, legal concerns, site peculiarities, and suitability deserve a deeper look to ascertain ionic liquids-mediated Phytoremediation's applicability and viability for large-scale use.

Further research could focus on the revelation of molecular relationships between the purported ionic liquids and heavy metal ions to clarify the secret of their efficiency in the metal extraction process. The imidazolium-based ionic liquids have a chance to realize their potential for use as environmentally acceptable replacements for the remediation of heavy metals in wetlands. These ionic liquids proved efficient in the extraction of Cadmium from wetland plant biomass, and they have their own low toxicity and high biodegradability, which prove that they are suitable for waste disposal. However, adequate studies should be conducted to assess the long-term implications of using ionic liquids and the intensity and sustainability of the remediation for large-scale projects.

### 5.3 Conclusion and summary of key findings

The data from the conducted experiments reflect the usefulness of ionic liquids in Phytoremediation and also belong to the knowledge of the relationship between ionic liquids and phytomass in removing heavy metals from contaminated environments. The study findings prove that preference for the kind of ionic liquid and pH are the determining factors for the leaching efficiency of Cd coming from wetland plant biomass. Through all tested ionic liquids ([Bmim][BF4], [Bmim][OTF], [Bmim][MeSO4], and [Bmim][Cl]), a higher pH levels would facilitate the Cd biosorption process. Eventually, alkaline conditions (pH 9.02) would extract the highest Cd proportions. This hints that adjusting pH can improve the capability of ionic liquid-assisted Phytoremediation when it comes to heavy metal-contaminated sites.

Also, the study illustrates that the designer is supposed to think about the various characteristics of anionic and the structures of ionic liquids to devise a remediation plan. For leaching ability, the different ionic liquids were exhibiting different levels, with [Bmim][BF4] and [Bmim][OTF] generally presenting more through showing higher removal efficiency compared to [Bmim][MeSO4] and [Bmim][Cl]. This demonstrates the indispensability of customizable techniques for implementing remedies that align with the pollutants and site characterization. Finally, the mentioned tendencies are evidence of the advantageous contribution of ionic liquid compounds as alternatives to toxic heavy metals in the remediation of wetlands. The relative non-toxicity, rapid hydrolysis, and capacity to absorb traces of heavy metals from plant materials favor use as part of the phytoremediation protocol. Nevertheless, it is still essential to continue the studies to examine their permanence on soil and water ecosystems and ultimately to improve their practical use in the field so that one can divide their application into various remediation scenarios.

Overall, this study is a step forward in gaining knowledge of the role of ionic liquids in phytoremediation techniques and offers some promising areas for further optimization of heavy metal removal. This study shows which factors influence the leaching efficiency of Cd as a pollutant from wetland plants as a more reliable filtering material. It creates the basis for further studies and the development of sophisticated and eco-friendly methods to combat environmental pollution.

# References

Das, S., Sultana, K. W., Ndhlala, A. R., Mondal, M., & Chandra, I. (2023). Heavy metal pollution in the environment and its impact on health: exploring green technology for remediation. *Environmental Health Insights*, *17*, 11786302231201259.

Deng, Y., Long, T., Zhao, H., Zhu, L., & Chen, J. (2012). Application of porous N-methylimidazolium strongly basic anion exchange resins on Cr (VI) adsorption from electroplating wastewater. *Separation Science and Technology*, *47*(2), 256–263.

Dietz, A. C., & Schnoor, J. L. (2001). Advances in Phytoremediation. *Environmental Health Perspectives*, *109*(suppl 1), 163-168. https://doi.org/10.1289/ehp.01109s1163

Dzulkipli, M. Z., Karim, J., Ahmad, A., Dzulkurnain, N. A., Su'ait, M. S., Yoshizawa-Fujita, M., Tian Khoon, L., & Hassan, N. H. (2021). The influences of 1-Butyl-3-Methylimidazolium Tetrafluoroborate on electrochemical, thermal, and structural studies as Ionic liquid gel polymer electrolyte. *Polymers*, *13*(8), 1277. https://doi.org/10.3390/polym13081277

Fischer, L., Falta, T., Koellensperger, G., Stojanovic, A., Kogelnig, D., Galanski, M. S., ... & Hann, S. (2011). Ionic liquids for the extraction of metals and metal-containing compounds from communal and industrial wastewater. *Water Research*, *45*(15), 4601-4614.

Fuerhacker, M., Haile, T. M., Kogelnig, D., Stojanovic, A., & Keppler, B. (2012). Apply ionic liquids to remove heavy metals from wastewater and activated sludge. *Water Science and Technology*, *65*(10), 1765-1773. https://doi.org/10.2166/wst.2012.907

Förstner, U., & Wittmann, G. T. (2012). *Metal pollution in the aquatic environment*. Springer Science & Business Media.

Ghorbani, S. M., Housaindokht, M. R., & Bozorgmehr, M. R. (2021). Investigating the effect of 1-Butyl-3-methylimidazolium bromide and 1-Butyl-3-methylimidazolium methyl sulfate Ionic liquids on structure and function of Chloroproxidase by molecular dynamics simulation. *Journal of Molecular Liquids*, *332*, 115850. https://doi.org/10.1016/j.molliq.2021.115850

Hassan, E. R., & Mutelet, F. (2017). Use of Ionic liquids for the treatment of biomass materials and Biofuel production. *Carbohydrate*. https://doi.org/10.5772/67026

Ignat'ev, N. V., Barthen, P., Kucheryna, A., Willner, H., & Sartori, P. (2012). A convenient synthesis of Triflate anion Ionic liquids and their properties. *Molecules*, *17*(5), 5319-5338. https://doi.org/10.3390/molecules17055319

Jamil Emon, F., Rohani, M. F., Sumaiya, N., Tuj Jannat, M. F., Akter, Y., Shahjahan, M., ... & Goh, K. W. (2023). Bioaccumulation and bioremediation of heavy metals in fishes—A review. *Toxics*, *11*(6), 510.

Kapahi, M., & Sachdeva, S. (2019). Bioremediation options for heavy metal pollution. *Journal of Health and Pollution*, *9*(24). https://doi.org/10.5696/2156-9614-9.24.191203

Kozonoi, N., & Ikeda, Y. (2007). Extraction mechanism of metal ion from aqueous solution to the hydrophobic ionic liquid, 1-butyl-3-methylimidazolium nonafluorobutanesulfonate. *Monatshefte für Chemie-Chemical Monthly, 138*, 1145-1151.

Lebrun, M. (2001). Phytoremediation of toxic metals. Using plants to clean up the environment, edited by I. Raskin and B. Ensley, John Wiley & Sons, Inc., New York, 2000. ISBN 0-471-19254-6; £58.50, 304 pp. *Plant Science*, *160*(5), 1073–1075. https://doi.org/10.1016/s0168-9452(01)00353-3

Liu, Y., Guo, L., Zhu, L., Sun, X., & Chen, J. (2010). Cr (III, VI) was removed by quaternary ammonium and quaternary phosphonium ionic liquids functionalized silica materials. *Chemical Engineering Journal*, *158*(2), 108-114.

Pandiyan, J., Mahboob, S., Govindarajan, M., Al-Ghanim, K. A., Ahmed, Z., Al-Mulhm, N., ... & Krishnappa, K. (2021). An assessment of heavy metals pollution in the water, sediment and aquatic organisms: A perspective of tackling environmental threats for food security. *Saudi Journal of Biological Sciences*, *28*(2), 1218–1225.

PerezF, I., S. Larrea, E., Bazán, B., Barandika, G., Urtiaga, M. K., & Arriortua, M. I. (2019). Ionothermal synthesis of cadmium coordination polymers: Ionic liquid effects on the synthesis, structural, and thermal characterization. *Molecules*, *24*(22), 4059. https://doi.org/10.3390/molecules24224059

Phillips, D., Human, L., & Adams, J. (2015). Wetland plants as indicators of heavy metal contamination. *Marine Pollution Bulletin*, *92*(1-2), pp. 227–232. https://doi.org/10.1016/j.marpolbul.2014.12.038

Platzer, S., Kar, M., Leyma, R., Chib, S., Roller, A., Jirsa, F., Krachler, R., MacFarlane, D. R., Kandioller, W., & Keppler, B. K. (2017). Task-specific thioglycolate Ionic liquids for heavy metal extraction: Synthesis, extraction efficacies, and recycling properties. *Journal of Hazardous Materials*, *324*, 241-249. https://doi.org/10.1016/j.jhazmat.2016.10.054

Rai, P. K. (2008). Heavy metal pollution in aquatic ecosystems and its Phytoremediation using wetland plants: An eco-sustainable approach. *International Journal of Phytoremediation*, *10*(2), 133–160. https://doi.org/10.1080/15226510801913918

Salt, D. E., Blaylock, M., Kumar, N. P., Dushenkov, V., Ensley, B. D., Chet, I., & Raskin, I. (1995). Phytoremediation: A novel strategy for removing toxic metals from the environment using plants. *Nature Biotechnology*, *13*(5), 468-474. https://doi.org/10.1038/nbt0595-468

Salt, D. E., Smith, R. D., & Raskin, I. (1998). Phytoremediation. *Annual Review of Plant Physiology and Molecular Biology*, *49*(1), 643-668. https://doi.org/10.1146/annurev.arplant.49.1.643

Shin, H., Guo, X., & Chen, R. R. (2007). undefined. *Bioprocessing for Value-Added Products from Renewable Resources*, 351–371. https://doi.org/10.1016/b978-044452114-9/50014-1

Sim, L., Majid, S., & Arof, A. (2014). Effects of 1–butyl–3–methyl imidazolium trifluoromethane sulfonate Ionic liquid in poly(ethyl methacrylate)/poly(vinylidene fluoride–Co–

hexafluoropropylene) blend-based polymer electrolyte system. *Electrochimica Acta*, *123*, 190-197. https://doi.org/10.1016/j.electacta.2014.01.017

Singh, J. K., Sharma, R. K., Ghosh, P., Kumar, A., & Khan, M. L. (2018). Imidazolium-based Ionic liquids: A promising green solvent for water Hyacinth biomass deconstruction. *Frontiers in Chemistry*, p. *6*. https://doi.org/10.3389/fchem.2018.00548

Stojanovic, A., & Keppler, B. K. (2012). Ionic liquids as extracting agents for heavy metals. *Separation Science and Technology*, *47*(2), 189-203. https://doi.org/10.1080/01496395.2011.620587

Susarla, S., Medina, V. F., & McCutcheon, S. C. (2002). Phytoremediation: An ecological solution to organic chemical contamination. *Ecological Engineering*, *18*(5), 647-658. https://doi.org/10.1016/s0925-8574(02)00026-5

Tőzsér, D., Yelamanova, A., Sipos, B., Magura, T., & Simon, E. (2023). A meta-analysis on the heavy metal uptake in Amaranthus species. *Environmental Science and Pollution Research*, *30*(36), 85102-85112.

Vergara, M. A., Lijanova, I. V., Likhanova, N. V., Vigueras, D. J., & Xometl, O. O. (2014). The Removal Of Heavy Metal Cations From An Aqueous Solution Using Ionic Liquids†. *The Canadian Journal of Chemical Engineering*, *92*(11), 1875-1881. https://doi.org/10.1002/cjce.22053

Yadav, M., Gupta, R., Arora, G., Yadav, P., Srivastava, A., & Sharma, R. K. (2020). Current status of heavy metal contaminants and their removal/Recovery techniques. *ACS Symposium Series*, 41–64. https://doi.org/10.1021/bk-2020-1352.ch003

Yan, A., Wang, Y., Tan, S. N., Mohd Yusof, M. L., Ghosh, S., & Chen, Z. (2020). Phytoremediation: A promising approach for Revegetation of heavy metal-polluted land. *Frontiers in Plant Science*, *11*. https://doi.org/10.3389/fpls.2020.00359

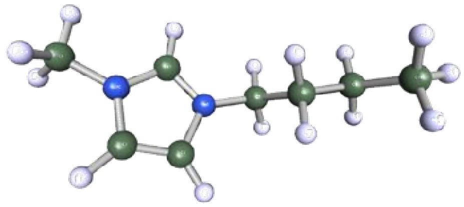
Yudaev, P. A., & Chistyakov, E. M. (2022). Ionic liquids are components of systems for metal extraction. *ChemEngineering*, *6*(1), 6. https://doi.org/10.3390/chemengineering6010006

Zhu, L., Liu, Y., & Chen, J. (2009). Synthesis of N-methylimidazolium functionalized fundamental anion exchange resins for adsorption of Cr (VI). *Industrial & engineering chemistry research*, *48*(7), 3261-3267.

# Appendices

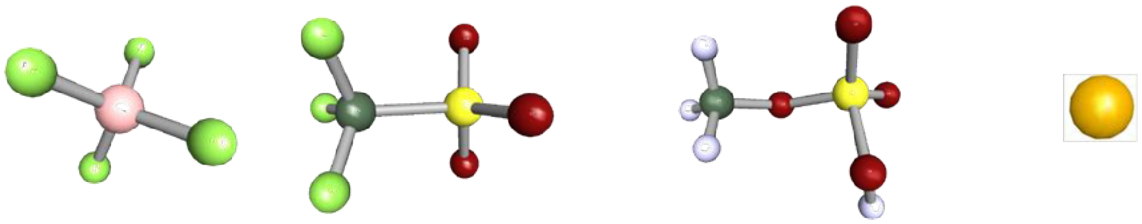
## Appendix a

Cation:



Abbreviation: [Bmim]$^+$
Formula: $C_8H_{15}N_2$
SMILES: CCCC[N$^+$](C=C$_1$)=CN$_1$C

Anions:



Abbreviation: [BF$_4$]$^-$
Formula: $BF_4$
SMILES: F[B-](F)(F)F

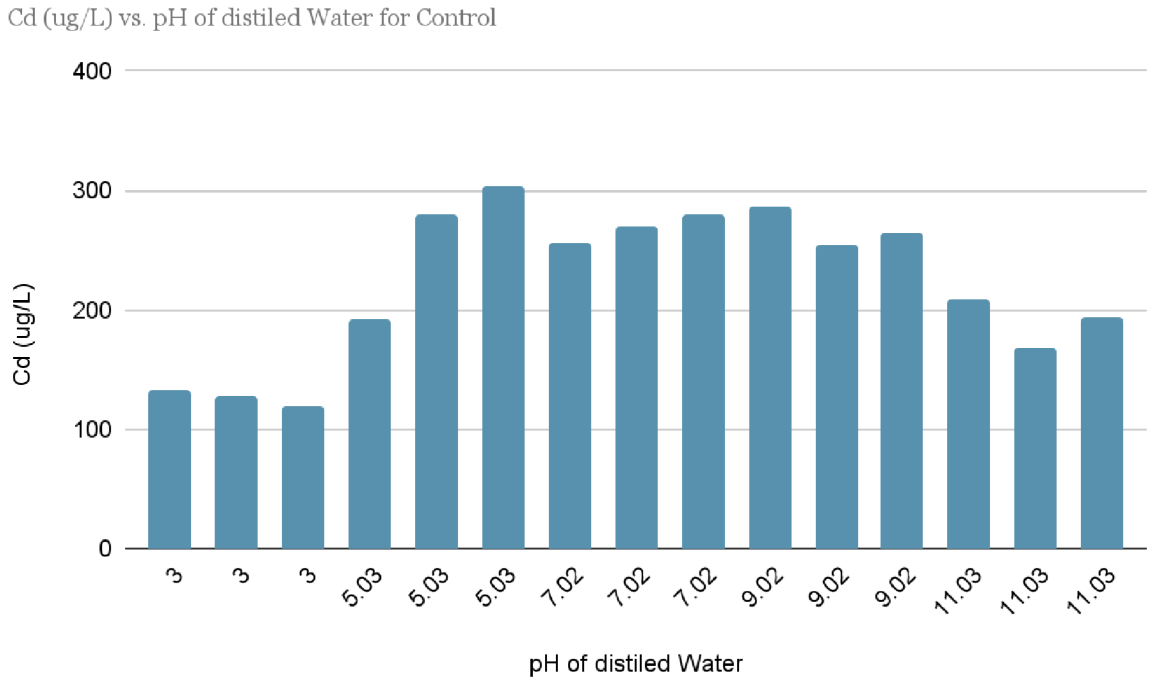
Abbreviation: [OTf]$^-$
Formula: $CF_3SO_3$
SMILES: FC(F)(F)S([O-])(=O)=O

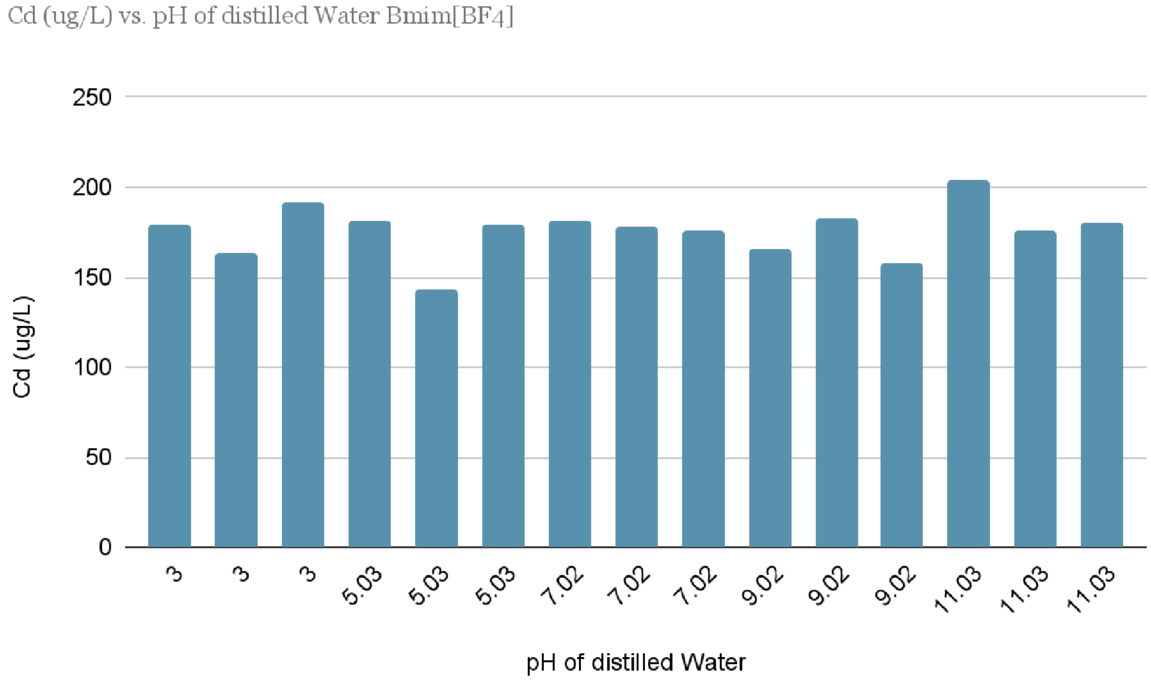
Abbreviation: [MeSO$_4$]$^-$
Formula: $CH_3SO_3OH$
SMILES: COS(O)(=O)=O

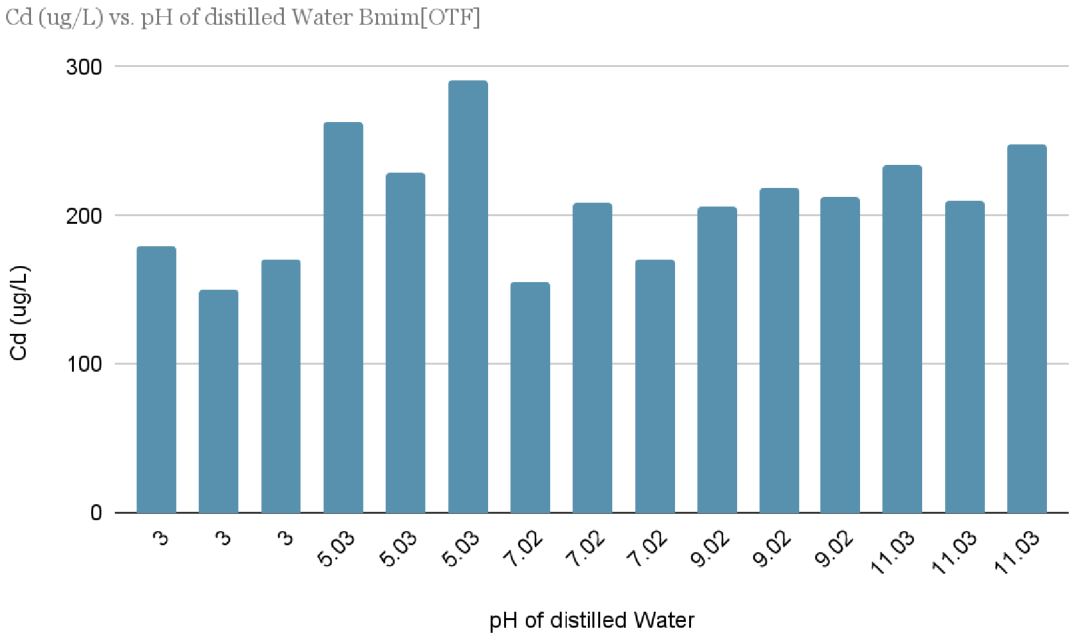
Abbreviation: [Cl]$^-$
Formula: Cl
SMILES: Cl

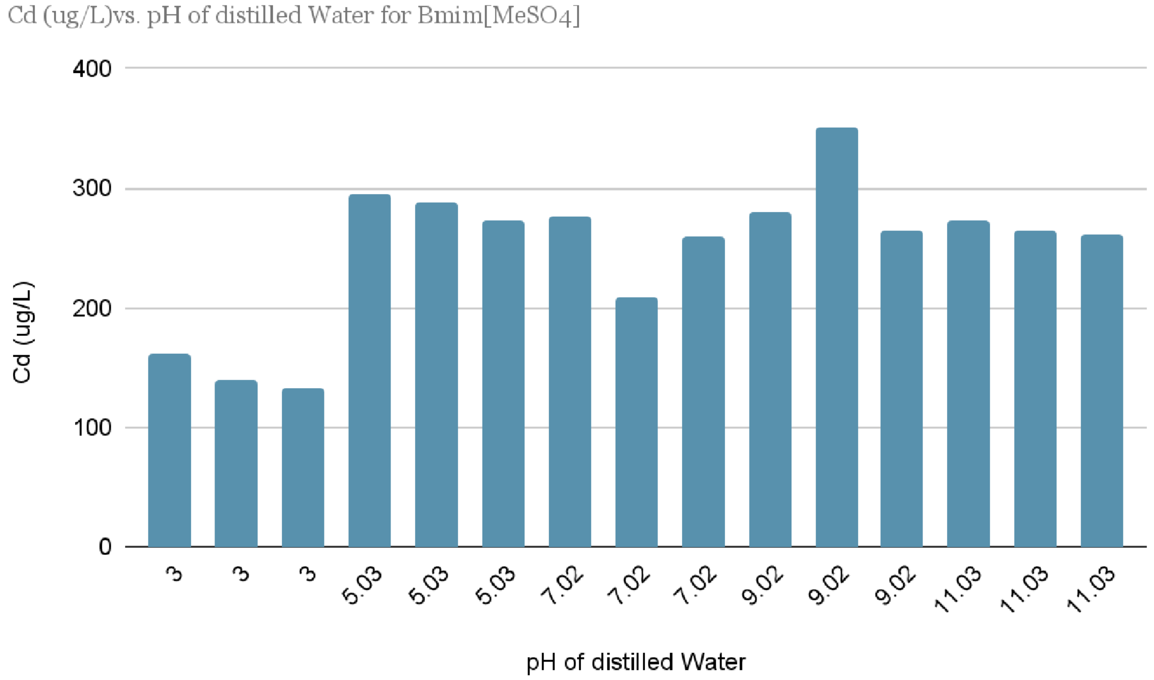
Figure 1 The structures of cations and anions in ILs used in this work

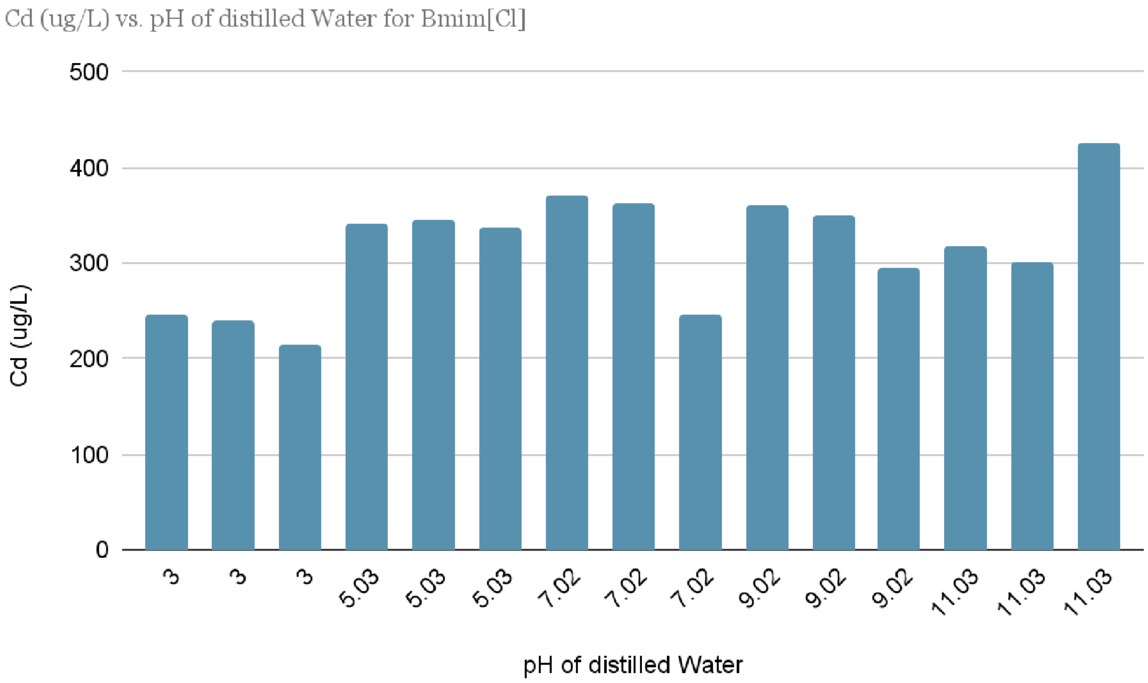
## Appendix B


Cd (ug/L) vs. pH of distiled Water for Control


Cd (ug/L) vs. pH of distilled Water Bmim[BF4]


Cd (ug/L) vs. pH of distilled Water Bmim[OTF]
300
200
100
0
Cd (ug/L)
3
3
3
5.03
5.03
5.03
7.02
7.02
7.02
9.02
9.02
9.02
11.03
11.03
11.03
pH of distilled Water


Cd (ug/L)vs. pH of distilled Water for Bmim[MeSO4]
400
300
200
100
0
Cd (ug/L)
3
3
3
5.03
5.03
5.03
7.02
7.02
7.02
9.02
9.02
9.02
11.03
11.03
11.03
pH of distilled Water


Cd (ug/L) vs. pH of distilled Water for Bmim[Cl]
500
400
300
200
100
0
Cd (ug/L)
3
3
3
5.03
5.03
5.03
7.02
7.02
7.02
9.02
9.02
9.02
11.03
11.03
11.03
pH of distilled Water