Article

A review on determination of heavy metal ions in wastewater using ionic liquids

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Abstract

Water pollution and water scarcity is considered worldwide as a severe problem. It has motivated researchers to develop more effective wastewater treatment techniques for their reuse. Many governmental agencies are cataloging the increase of complex metals and compounds in industrial wastewater because of their toxicity and tenacity. Traditional extraction methods of industrial wastewater can appreciate the mending of some parts of heavy metals with clean production and less efficient resource recovery. In recent decades, there has been research on emerging the methods of heavy metal ions from wastewater. To overcome the limitations of traditional extraction treatment methods by introducing the enchanted material called ionic liquid, that is considered to be anew green solvent (neoteric solvent, designer solvent, ionic fluid, molten salt), that substitutes the conventional solvents with many advanced and better properties that is not available in traditional extractors. Ionic liquid has evident advantages over traditional organic solvents and has a wide range of applications in various areas especially as a kind of extracting agent for heavy metal ions. The research and application status of ionic liquid is reviewed and discussed the extraction processes of traditional technologies for the removal of heavy metals from wastewater. This review summarizes the applications of ionic liquids in the determination of heavy metals in wastewater. Also, study the future developments and prospects of ionic liquid for the extraction of heavy metals. According to the results, the application of ionic liquids is likely to be increase in the future.

Keywords extraction methods; heavy metal ions; ionic liquid; wastewater.

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1 Introduction

In the 21st century, depleted natural resources and environmental protection have got attention for sustainable development (Sarwar et al., 2019). Heavy metals pollution in wastewater has long-term toxic effects on human health and aquaculture. Heavy metals toxicity even in trace quantities is very harmful, and their tendency for bioaccumulation in the food chain makes it necessary to develop schemes for the removal of heavy metals from wastewaters (Hultberg et al., 1998; Antochshuk, 2002; Rozada et al., 2008). Some common heavy metals such as cadmium, zinc and copper sources and its effect on human health are mentioned in table 1. Due to excessive intake a metal species culminate to noxiousness symptoms, disorder the cellular functions, indoctrinate devastating disabilities in living organism, and eventually results in the form of death (Garbarino, 1995). Bioaccumulation of heavy metals through the food chain can cause cancer and other bone diseases, and damage the plant's tissues. To overcome heavy metals pollution in the water, mitigation measures must be needed for industrial wastewater and domestic water (Sarwar et al., 2019).

In 1914, the first organic salt, ethyl nitrate ([EtNH3]NO_3), found to be liquid at room temperature, with a melting point of 12 degrees Celsius, was the first ionic liquid to be discovered. In general, organic cations (such as pyrrolidinium, imidazolium, pyridinium and ammonium) and inorganic anions (such as chloride, bromide, tetrafluoroborate, and hexafluorophosphate) consist of ionic liquids (Singh and Savoy, 2020) shown in Fig. 1.

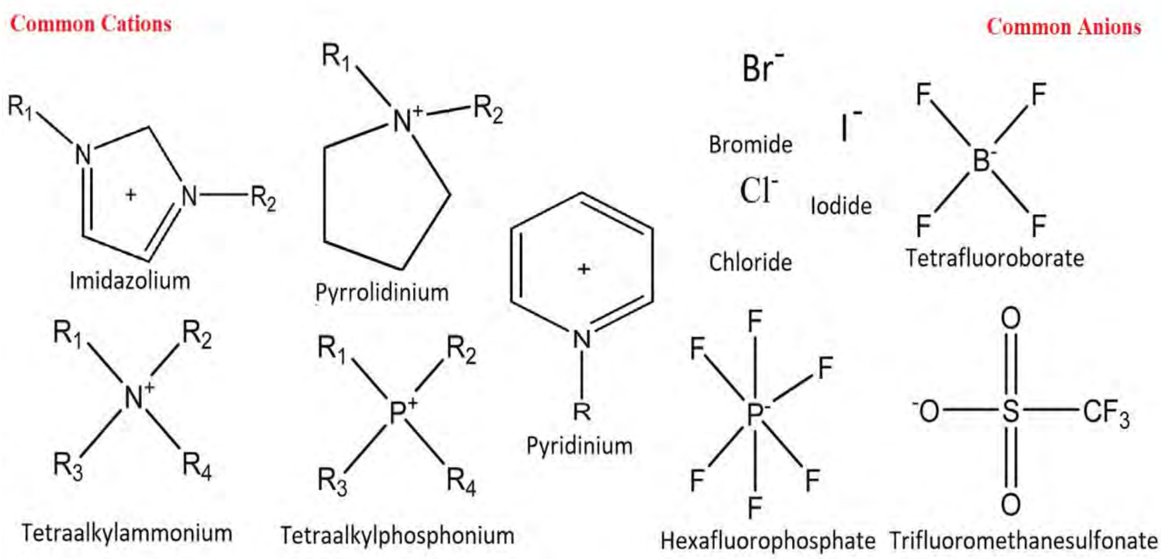

Fig. 1 Structure of some common anions and cations of ILs.

Many industrial and analytical separation processes have been applied to ionic liquids, but their applications in the treatment of waste water, particularly in the removal of organic pollutants, are still not well studied. In 1951, Hurley and others added N-alkylpyridine to $AlCl_3$ to heat the two solid mixtures and found that it formed a clear, transparent liquid. Ionic liquids have recently been introduced as attractive clean alternatives to traditional organic solvents in an extensive range of chemical and biochemical processes (Toral et al., 2007). They also function effectively in extraction processes, such as separation of metal species (Marsousi et al., 2019; Germani et al., 2007), organic compounds, and even macromolecules (Marsousi et al., 2019). Over the past few years, extraction of several metal ions using ionic liquids containing suitable complexing agents such as crown ether (Marsousi et al., 2019), dithizone (Phuong et al., 2010), and other organic ligands has been carried out (Isosaari et al., 2019). Depending on the nature of the extraction agent in the extraction system, the extraction system can be roughly summarized into three types: acidic or negative extractors (e.g. organophosphate, bisulfur); neutral extraction systems (e.g. crown ether, cup aromatics, etc.), functional extractors (ionic liquids both as solvents and extractors). Although ionic liquid is considered a green solvent, which is relatively safe, there is some toxicity in the entry environment. Therefore, while developing and utilizing ionic liquids, it is necessary to strengthen the recycling, ecotoxicology, degradation treatment technology and other related research to ensure that the environment does not cause secondary pollution. This review paper introduces the research progress of ionic liquid extraction and separation of heavy metal ions and also illustrates the use of various ionic liquids in the treatment of waste water and suggests the versatility of ionic liquids in the development of rapid, efficient and selective removal processes.

Table 1 Sources and health effect of heavy metals.

Metals	Major Sources	Health effect
Cadmium	Electroplating and Batteries	Harms kidney function, Gastrointestinal disorder, Bone defects (itai-itai, osteomalacia, osteoporosis), Nephrotoxicity, Anemia, Anosmia, Ulceration, Carcinogenesis effects
	Dyes and Paint pigments	
	Pesticide and Fertilizer	
	Nuclear plant and Coating operations	
Copper	Mining Metal and Electrical manufacturing	Hemodialysis (Kidney Damage), Nausea, Vomiting, Bloody diarrhea, Fever, Stomach pain, Low blood pressure, Anemia
	Agriculture and domestic pesticides and fungicides	
	Finishing and Leather Processing	
Zinc	Electroplating, Smelting and Mining	Effect calcification of bone Alzheimer’s disease, Corrosive and harmful to themucous membranes, Adverse effect ongastrointestinal tissue, Throat burning, Abdominal pain and diarrhea, Hematological changes, Anemia
	Galvanizing and Metal processing	
	Rodenticides and Herbicide	
	Dyes and Paint pigments	
	Wood preservative and Solubilizing agents	

2 Scope of Ionic Liquids

The frontier of investigation in ILs has highlighted the development of green and sustainable chemistry over the past decades. Basic and applied studies have developed significantly and illustrated the value of ILs to science in the fields of chemistry, biology, physics, etc. with its wide spectrum of applications. Yearly based number of publications demonstrated from 2009 to 2020 in Fig. 2 related to ionic liquids (Sourced from ISI Web of Science).

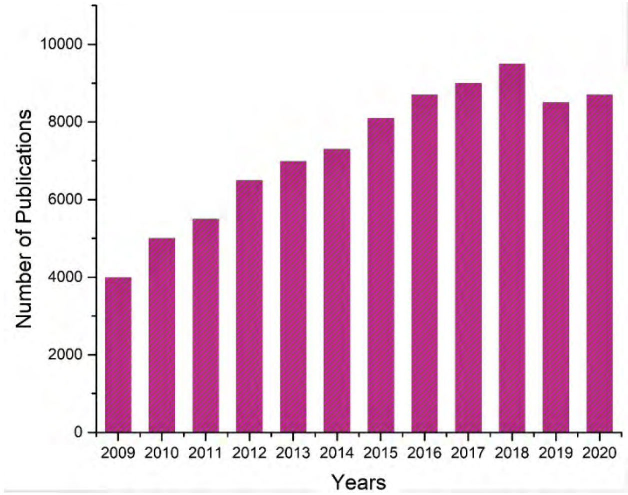

Fig. 2 Publications related to ionic liquids.

In particular, ILs have been considered a green solvent that can usually be used to replace conventional organic volatile solvents. In addition, ILs reflect several viable perspectives on the industrial and laboratory scales in the areas of synthesis, catalysis, material science, physical chemistry, electro chemistry, nuclear physics, medicinal chemistry, engineering and many more. The main focus of ILs is on physical chemistry, chemical engineering, material science and multidisciplinary chemistry, as they are prevalent in different IL applications. Due to their continued expansion, addressing ILs physico-chemical properties and many more significant properties could be beneficial. The number of research publication according to different field/subject categories demonstrated in Fig. 3 (Sourced from ISI Web of Science).

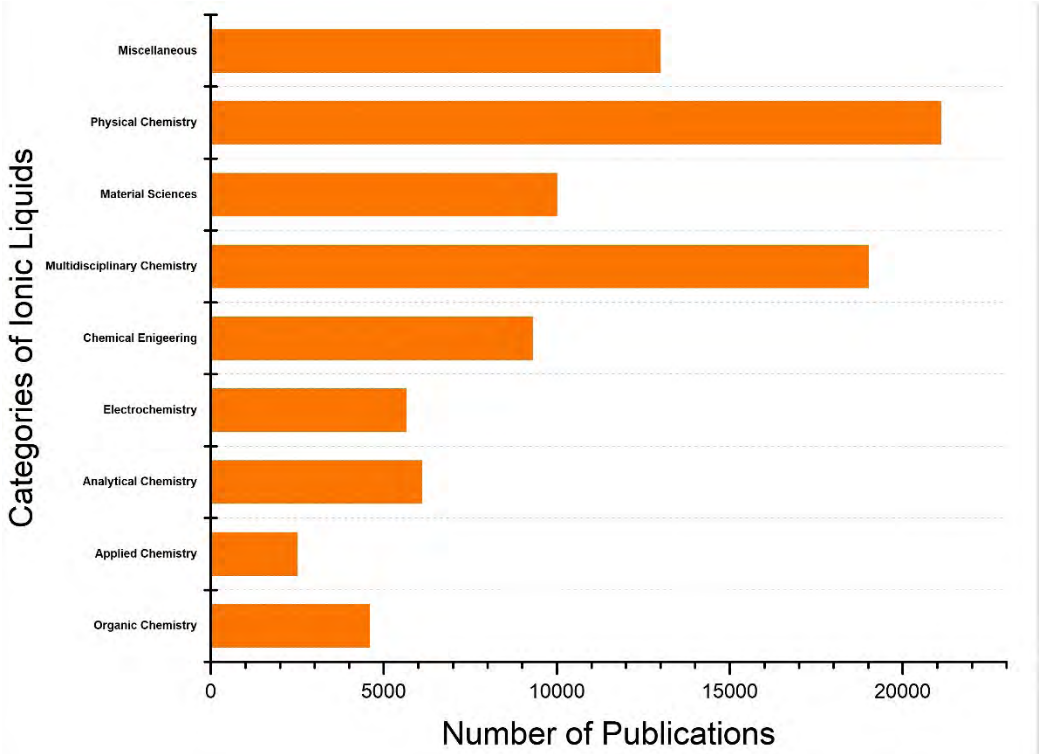

Fig. 3 Subject Related Categories of Ionic Liquids.

3 Wastewater Treatment Methods

Heavy metal pollution produced by industrial enterprises that have long-term, dynamic, cumulative and complex types of heavy metal ions in wastewater, their contents and its existence differs from industry to industry production processes (Long et al., 2018). Heavy metal wastewater differs from other wastewater, regardless of any means, the heavy metals cannot be broken down to destroy, but only by changing its position or changing its physical, chemical form to reduce its toxicity and the content of wastewater. At present, the treatment of heavy metal wastewater can be divided into two main categories:

(1) The specific methods of removing insoluble heavy metal compounds from water by precipitation and floating include the precipitation method, sulphides precipitation method, floating separation method, ion floating method, electrolysis precipitation or electrolytic floating method, diaphragm electrolysis method, etc. (Hendricks, 2006).

(2) The concentration and separation of heavy metals in wastewater without changing their chemical morphology, specifically the adsorption method (biosorption method), extraction method, reverse osmosis method, electrodialysis method evaporative enrichment method, "ion exchange method, etc (Gunatilake, 2015). Based on the first type of method which is mainly used to remove heavy metal ions from wastewater to make discharge become standardized, widely used because of simple operational method and other characteristics but this method has some drawbacks of handling heavy metal sludge disposal and heavy metal resource waste which caused or generate the secondary pollution(Wang et al., 2019). Although the second type of method is relatively complex in-process and cumbersome in operation, heavy metals can be concentrated in their original form, which can be used directly in the production process to realize the closed cycle of heavy metals and the purpose of resource utilization (Wei et al., 2010). Compared with the first type of method that needs to make heavy metals go through a multi-step chemical morphology transformation to be used, the second method has incomparable advantages. Of course, in the actual treatment process, the method should be taken according to the comprehensive consideration of heavy metal type and concentration in wastewater(Khalid et al., 2018).

4 Heavy Metals Contaminated Wastewater Extraction Method

The ideal method of heavy metal wastewater treatment is to realize the utilization of heavy metal resources in wastewater and the discharge of wastewater(Sarwar et al., 2019). Therefore, heavy metal wastewater treatment has tended to the direction of the clean production process, resource recycling, and closed-cycle direction (Lommelen et al., 2019).

Extraction is a materialization treatment scheme, which is an important process in heavy metal treatment technology. Recovery and extractions of heavy metals are widely used in soil, sludge, solid waste disposal(He et al. 2020). Used HCL, Na_2-EDTA, citric acid as an extractor in different extraction conditions of manganese contaminated soil heavy metals Mn, Pb, and Cd for extraction experiments, in which EDTA to Pb extraction rate reached 57.14% and extraction effects are susceptible to other substances in the soil (Liu et al., 2018). Used of ammonia-based complexes EDTA and DTPA to MSW urban solid waste incinerators for the extraction of these heavy metals Zn, Pb, Cu has been studied, and extraction rate of Zn can reach 90%, the extraction rate of Pb is 80%, the extraction rate of Cu is 60%, and the fly ash after the complex agent treatment can meet the requirements of landfill (Ferreira et al., 2002). The extraction of heavy metals in sludge was studied using green polymer poly schemata as an extractor, The extraction rate of Pb, Ni, Cu ions is more than 92% and Cr, Cd, Zn's extraction rate is about 70% (Gaber et al., 2011). In recent years, the extraction method for the treatment of heavy metal wastewater has also been gradually carried out, used extracting solution with kerosene Agent, TBP extractor and Ammonium tri methyl bromide co-extractor in analog electroplating wastewater for Cr removal rate up to 83.4% (Ye et al., 2019). Used of butanol as an extractor, liquid-liquid triphasic extraction method to treat heavy metal wastewater, the extraction rate of butanol to nickel is achieved 95% and the use of hydrochloric acid as an anti-extraction that enhanced the extraction rate up to 99%.

5 Extraction of Heavy Metals by Ionic Liquids

Ionic liquid (IL) is a new medium and soft functional material developed in the green frame in recent years, with a low melting point, a wide liquid temperature range, not easy to volatile, strong solubility, design ability, electrochemical window width and other unique properties (Ghandi, 2018). Ionic liquid sits on the synthesis of organic and polymeric substances because of its matchless advantages of many traditional solvents and its application as a green solvent. The ionic liquids in organic synthesis has evolved rapidly in the last 20 years (Kennepohl et al., 2020). Today ILs are examined and implemented in various industrial fields. Due to their interesting properties, ILs have a large potential for a wide variety of application in industry. Well established applications are shown in figure 4 which elaborates the application of ionic liquids in gas separation (Althuluth et al., 2014; Romanos et al., 2013) and purification (Abai et al., 2015) electrolytes for batteries (Armand et al., 2009) dissolution of cellulose (Swatloski et al., 2002) or dissolving metal oxides (Nockemann et al., 2006; Vander Hoogerstraete and Binnemans, 2014).

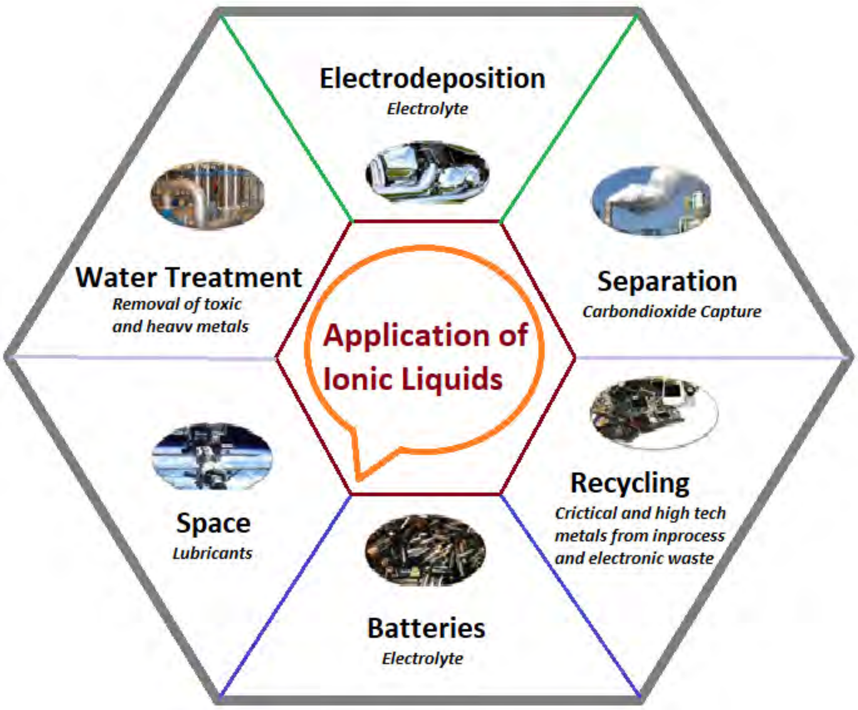

Fig. 4 Application of ionic liquids.

A lot of research has been done on the use of ionic liquids as extraction phases and the addition of various other extractors to the extraction of metal ions. They studied ionic liquids [Bmim][PF_6], [Hmim][PF_6] for extraction phase, with 1-pyridyl-azo-2-naphthol (PAN), 1-thiazolyl-azo-2-naphthol (TAN), Halogen ions, Pseudo halide ions (CN^-, OCN, SCN^-) as other extractors, that extract Cd, Hg, etc heavy metals from water. The study found that the distribution coefficient (D) was<1 when extracting a Cd. PAN and TAN were added as an extractor, the distribution coefficient increased by at least two orders of magnitude after pH increased from 1 to 13 (Domanska et al., 2005; Lertlapwasin et al., 2010; Messadi et al., 2013). Using alkyl ionic liquids [Bmim][PF_6], [Hmim][PF_6], [Omim][PF_6] and add 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (Htta)extracted divalent heavy metal ions Cd, Co, Pb, extraction efficiency can reach more than 95%.The use of 1 mol/L nitric acid solution for back-extraction, 95% of heavy metal ions can be effectively anti-extraction, thus avoiding the use of organic solvents in the back-extraction process of environmental pollution (Hirayama et al., 2005). The study of its extraction mechanism holds that ionic liquid and Pb form a neutral pal, and Cd, Co form alkaline compound. The extraction properties of hydrophobic (Fig. 5) ionic liquids ([Bmim][PF_6], [Hmim][PF_6] and [Omim][PF_6]) were studied, and the extraction rate of ionic liquids to Cu and Ni increased from 2.31% and 2.18% to 99.89%, respectively, by the addition of chelating agents. And 98.64% the anti-extraction of Ni is achieved by changing pH (Li et al., 2008).

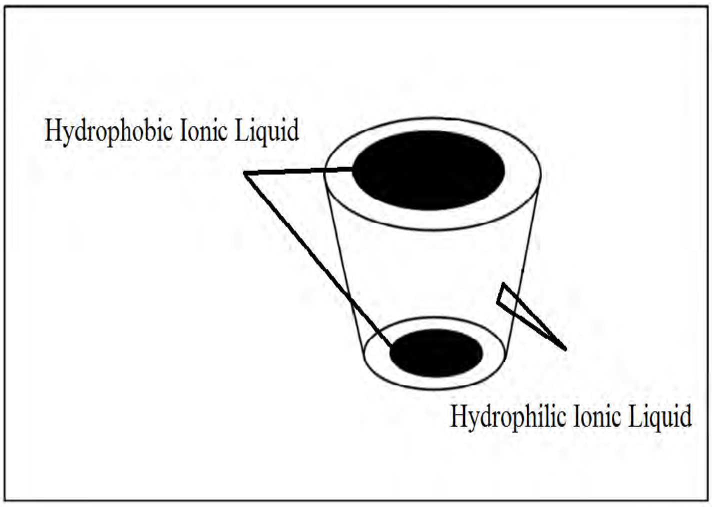

Fig. 5 Sketch of ionic liquid types.

1-(ethyl-3-Oxybutycomine)-3-Methylmitoxylene hexafluorophosphate, studied its extraction properties on Zn, Cu, Ni, Fe, extraction efficiency reached 97%, 84.9%, 88.1%, 60.9% respectively (Cai, 2011).Take advantage of the new extractor 1-benzene-3-methyl-4-benzoyl-ketone-5 to shrink 2-amino benzene pyrite using Ionic liquid dual water phase system to extract heavy metal ions, the extraction system of heavy metal ions extraction capacity from strong to weak: Cu, Pb, Co, Ni, Zn (Chen et al., 2010). For the first time, liquid-phase micro-extraction was applied to the industrial wastewater treatment of ionic liquid, and the results showed that the concentration of metal ions was significantly reduced after ionic liquid extraction and the removal efficiency of heavy metal ions was related to the initial concentration of heavy metals and the pH value of the solution and the concentration of suspended matter were greatly related (Fischer et al., 2011).

6 Conclusions

In general, for the treatment of heavy metal wastewater, the extraction methods can achieve the primary recovery of heavy metals and able to reuse water for further process directly, but laborious its pre-treatment time, high use of organic solvents that can easily cause the secondary pollution. Also, they have a lot of limitations in traditional extraction methods and can’t tunable according to the desire for better extraction results. On the other hand, ionic liquids have many advanced and magnetic properties that are not available in traditional extractors. Themost attractive merits of ionic liquids are non-volatile, hydrophobic, non-flammable, stable at high temperature, green solvent, have task-specific design ability (easily tunable) and many other advantages that solve the limitation point of heavy metal in the treatment of wastewater by extraction method. The use of ionic liquid for the extraction of metal ions can effectively avoid environmental pollution caused by traditional extraction methods, and also have high extraction efficiency. Ionic liquids also need to be modified and study its effective anti-extraction method that will allow ionic liquid as a better extractant and ability to be recycled completely and then to achieve the application of industrialization.

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