Research Progress of heavy metals remediation in soil by ionic liquids

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Abstract. At present, heavy metal pollution of soil has become increasingly serious. Soil heavy metal pollution has caused great harm to the environment and human health. Therefore, this paper reviews the sources and hazards of heavy metals in soil, the properties and applications of ionic liquids, research on the remediation of heavy metals in soil by ionic liquids and its unique advantages compared with physical remediation, chemical remediation, biological remediation and combined remediation, and put forward the future development direction.

Keywords: Heavy metal contamination; ionic liquids; applications.

1. Source and harm of heavy metals in soil
At present, the problem of soil heavy metal pollution has been widely concerned by the whole society. The sources of soil heavy metal pollution include natural pollution source and man-made pollution source, which can be divided into industrial pollution source, agricultural pollution source and domestic pollution source. Industrial pollution is the main source of heavy metal pollution. The main elements causing soil heavy metal pollution are copper (Cu), lead (Pb), zinc (Zn), cadmium (Cd), chromium (Cr), nickel (Ni), mercury (Hg), arsenic (As) and so on. Heavy metal pollution has the characteristics of long-term, concealment and irreversibility, and its treatment is very difficult. When the soil is polluted by heavy metals, the yield of crops will decrease, and the heavy metals enter the human body through the food chain, thus endangering human health.

As for soil heavy metal pollution, the relevant laws and regulations of our country are not perfect, and there are a few laws and regulations at present. The “Soil Environmental Quality Standard” formulated in 1995 stipulates the maximum allowable concentration index value of pollutants in soil and the corresponding monitoring methods. “The 12th Five Year Plan For The Comprehensive Prevention And Control Of Heavy Metal Pollution”, which was implemented in 2014, has set targets for the discharge of heavy metal pollutants. “The Soil Pollution Prevention And Control Act”, which was implemented in 2019, provides professional regulations on soil pollution as well as the responsibilities of major stakeholders [1].

2. Properties and application of ionic liquids
Ionic liquids are composed of organic cations and organic or inorganic anions that are liquid salts at or near room temperature. According to the type of cations, ionic liquids can be generally divided into...
quaternary ammonium salts, quaternary phosphorus salts, imidazoles, pyridines and so on. It is a new type of green solvent. Compared with the traditional solvents, ionic liquid has the following advantages: (1) Lower vapor pressure; (2) Better stability; (3) Higher electrochemical window; (4) Wider range of dissolution. At present, ionic liquids are mainly used in extraction and separation, organic synthesis, catalytic reaction, electrochemistry and other fields.

2.1. Application of ionic liquid in extraction separation

The traditional extraction separation uses volatile and toxic organic solvents. After the separation, these solvents will cause great harm to the environment and are difficult to handle, therefore, the choice of ionic liquids as a green solvent to replace organic solvents has become a research hotspot at present.

Ionic liquids can extract organic matter. Skoronski et al.[2] studied the extraction of phenol and 2,4-dichlorophenol in aqueous solution by phospho-based ionic liquid. The results showed that more than 99% and 89% of phenol and 2,4-dichlorophenol can be extracted respectively. The best extraction performance is obtained at lower temperatures and pH values lower than pKa values for these phenolic compounds.

Ionic liquids can be used for desulfurization and denitrification. Rogosic et al.[3] studied the desulfurization and denitritification of gasoline by using a deep eutectic ionic liquid based on choline chloride and ethylene glycol. The results showed that when the molar ratio of choline chloride to ethylene glycol was 1:3.5, the highest efficiency can reach 70.9% in the single extraction stage and the efficiency of eutectic solvent is 99% after four extraction steps.

Ionic liquids can extract biomolecules. Wang et al.[4] reported that the extraction of double helix DNA from water by hydrophobic ionic liquid [C4mim][PF6] showed that the extraction effect and the partition coefficient greatly affected the DNA content.

2.2. Application of ionic liquids in organic synthesis

Ionic liquids can be used in Friedel-Crafts, Diels-Alder, coupling, condensation, redox and other reactions.

Ludley et al.[5] studied the Diels-Alder reaction of cyclopentadiene and methyl acrylate in ionic liquid as solvent, and found that its regioselectivity was very high, and there was no waste lithium perchlorate in the system.

2.3. Application of ionic liquids in catalytic reaction

It is necessary to study the catalyst with high selectivity and activity to replace the traditional chemical reaction.

Javed et al.[6] reported that ionic liquids based on Pyridine and Piperidine were used as effective catalysts in Knoevenagel and Claisen-Schmidt condensation reactions. The results showed that ionic liquids have potential as catalysts in the formation of C = C bonds. Hou et al.[7] studied the system composed of heterogeneous catalyst of Bronsted acidity and ionic liquid 1-ethyl-3-methylimidazolium bromide (EMIMBR), which can effectively catalyze the conversion of glucose to 5-hydroxymethylfurfural, and the heterogeneous catalyst can be reused three times.

2.4. Application of ionic liquids in electrochemistry

Ionic liquids can be used in lithium metal batteries, fuel cell electrolytes, supercapacitors and other electrochemical aspects.

Widstrom et al.[8] studied high performance all-solid-state lithium metal batteries using a solid polymer electrolyte plasticized with ionic liquids. The surface-optimized ILSPE composition was able to achieve high total ionic conductivity and Li+ transfer number, and has long-term stability to the lithium metal.
3. Remediation of heavy metals in soil by ionic liquids

Ran Limin[9] reported a study on the removal of Cr from contaminated soil by 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF6] ionic liquid combined with citric acid, an oxygen chelating agent. Huang [10] reported that the toxicity of Cr (VI) in soil can be reduced by using ionic liquid 1-butyl-3-methylimidazolium chloride ([C4mim][Cl]). In this experiment, a simulation system (VI-HA) containing Cr(VI) chelated with HA was used in MCM-41 (the mobile component of substance 41) to represent the complex metal ion-organic contaminated soil, which was used for the extraction of [C4mim][Cl]. The results showed that about 70% of Cr(VI) could be extracted from MCM-41 which simulated soil pore system with after 30 minutes of extraction with [C4mim][Cl]. About 48% of the Cr(VI) species were reduced to the less toxic Cr(III) species during the extraction process.

Soumyadeep et al. [11] reported a study on the removal of Pb from contaminated soil by a mixture of natural surfactant saponin and deep eutectic solvent (DES), which is similar to ionic liquids. The polyol based DES was prepared by mixing quaternary ammonium chloride choline chloride with polyols, and then the natural surfactant saponin obtained from the pericarp of saponin fruit were mixed with DES to improve its efficiency, and the XRD spectrum analysis was carried out, the XRD value of Pb removal from contaminated soil were more than 72% when the mixture of 40% DES-Gly and 1% Saponin and the mixture of 10% DES-Gly and 2% saponin were used.

Mahmoud et al. [12] reported the surface functionalization procedure of 1 - (3-cyanopropyl) - 3-methylimidazolium-bis (trifluoromethylsulfonyl) ionic liquid [CN-C3-mim][NTF2] modified nano silica (NS amine) to form a new NS-amime-IL nanocomposites to remove Pb and Cd in soil, and the remediation rate can reach 98%-99%.

The functional ionic liquids synthesized by Kirchhecker et al. [13] can effectively extract Hg and Cd from water. Zhang Chao[14] studied the best extraction system of 1-vinyl-3-butylimidazolium tetrafluoroborate ([BVIM][BF4]) dithizone as chelating agent to extract Pb and Cd from wastewater. Zhang Yanbin [15] studied the extraction of copper from simulated wastewater by ionic liquid Aliquat (triocylmethylammonium chloride) with EDTA as a complexing agent. The extraction efficiency can reach over 85.5% .

4. Comparison with other remediation technologies

In addition to the use of ionic liquids to remediate heavy metals in soil, the commonly used techniques include physical remediation, chemical remediation, biological remediation, and combined remediation.

The commonly physical remediation technologies include engineering measures, electrokinetic remediation, thermal desorption, soil steam extraction, ultrasonic heating and so on. Douay et al. [16] carried out three times of soil exchange treatment in a French smelter, which reduced the concentration of pb (3000mg/kg) and Cd (24mg/kg) in the polluted soil and restored the polluted heavy metal soil. Wen et al.[17] showed that the overall removal efficiency of electrokinetic remediation was 0%-93.26%, and the operation time to achieve significant removal efficiency was not less than 120h.

At present, there are many chemical repair technologies, such as curing/stabilization, chemical leaching, in-situ chemical oxidation and photocatalytic degradation. According to the study of Mao Lingchen et al. [18], the method of in-situ ectopic infiltration leaching with EDTA can effectively remove Cd, Cu, Pb and Zn from the soil. Taking Pb and Cd pollution in soil as an example, three kinds of commonly used heavy metal eluents hydrochloric acid (HCl), ethylenediamine tetraacetic acid (EDTA) and calcium chloride (CaCl2) were selected to compare the leaching effects of contaminated soil. The results showed that EDTA had good and stable effect on the treatment of Pb and Cd. EDTA as a strong chelating agent, has strong binding power to these two heavy metals [19], and the leaching effect of EDTA on Pb is better than that of Cd, because the stability constant of Pb-EDTA (17.88) is slightly higher than that of Cd-EDTA (16.36).

The commonly used bioremediation technologies can be divided into three types: phytoremediation remediation, animal remediation and microbial remediation. Studies have shown that earthworms have been effective in the remediation of heavy metals and polycyclic aromatic hydrocarbon in contaminated soils.
The combined remediation technologies include plant-microbe, plant-animal, genetic engineering-plant, electrokinetic-chelate and leaching-passivation. JING et al. [20] studied that the bacteria JYX10 and JYX7 were isolated from the rhizosphere soil of phyllostachys pubescens, which were resistant to cadmium and lead, the biomass and heavy metal uptake of rape increased with the change of soil properties and heavy metal activity. Suzuki et al. [21] studied the effect of EDDS (ethylenediamine disuccinate) on the electrokinetic remediation of Pb and Cd in soil under neutral pH condition. The results showed that EDDS could improve the remediation efficiency of exchangeable lead in soil, but could not effectively remove cadmium in soil. Wang Mingxin et al. [22] showed that EGTA has a good elution effect on Cu, Zn, Cd, but a poor elution effect on Pb. KH2PO4 has good passivation effect on Pb and Cu, but weak passivation effect on Zn and Cd. Zinc contaminated soil should be remediated by single EGTA leaching. Pd contaminated soil by KH2PO4 passivation, and Cu and Cd contaminated soil by combined leaching/passivation.

Compared with these technologies, ionic liquid remediation technology has unique advantages. Because the development of green chemistry in today's world has become a hard requirement, and ionic liquids have no pollution to the environment, the preparation process is very simple and efficient, and the raw materials used are natural and green products, and the cost is low, which makes ionic liquid become a new type of green solvent.

5. Conclusion
With a lot of research on the structure, properties and functions of ionic liquids, the potential applications of ionic liquids will be developed more quickly. The remediation of heavy metal soils by ionic liquids will become a research hotspot. In order to effectively improve the ionic liquid extraction on the separation of heavy metal ions from soil, the following two points should be paid attention to. One is to study the synthesis of low viscosity, low density, high conductivity of new ionic liquids to reduce costs, the other is to study the environmentally friendly ionic liquids and make it recycled.

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