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Environmental Hazards of Phenanthrene and Extraction using Ionic Liquid

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Abstract

In order to improve the quality of the environment and minimise pollutants and other environmental and health hazards, industrial activities require adequate monitoring to determine the pollutant levels in the environment. Polycyclic aromatic hydrocarbons are toxic organic pollutants that can pose severe threats to man and the environment. This study aims to determine the potential of ionic liquid in extracting phenanthrene, a polyaromatic compound, to promote a clean environment whilst recovering material for reuse in other industrial applications. The research methodology comprises a literature review of journals and laboratory research. This involves developing a novel method to investigate the potential use of 1-propyl-3-methylimidazolium bromide (propylMIMBr), an ionic liquid synthesised by microwave technology, to recover the pure aromatic compound selectively. Though phenanthrene is toxic to the environment, it can be of value in the manufacturing industry for making dyes, plastics, pesticides and drugs. Findings from this study reveal that >1g of phenanthrene is soluble in 2g of propylMIMBr ionic liquid at 74°C and can be isolated as a viscous pale yellow liquid in 90% yield for reuse and recycling. Thus, novel technologies should be explored to isolate pollutants such as phenanthrene from contaminated environments.

Keywords: environmental hazards, ionic liquids, phenanthrene, polycyclic aromatic hydrocarbons

Introduction

Industrial activities can interact with the environment and potentially cause varying impacts, including emissions into the air and water and the discharge of hazardous wastes (Goetsch & Davis, 2001). Some of these hazardous wastes are high in polycyclic aromatic hydrocarbons (PAHs), hydrophobic pollutants commonly found in contaminated soils and groundwater (Zabar et al., 2023). Indeed, PAHs have diverse sources and acute toxicity and thus are categorised as high-priority pollutants by the US Environmental Protection Agency (Peng et al., 2016 & Hussar et al., 2012). They can also be found in spent drilling fluid (Iwegbue, 2011). Plants that grow in PAH-contaminated soils can easily be contaminated with these compounds because of their uptake, especially root crops, which can harm man as they consume them and stand the risk of sicknesses attributed to these pollutants (Zhan et al., 2010). Amongst these persistent PAHs, phenanthrene is one of the most abundant PAHs in the environment, and long-term exposure levels can lead to chronic kidney injury and fibrosis (Ruan et al., 2021). Studies have shown that in adult mouse offspring, in-utero phenanthrene exposure caused glucose intolerance and decreased insulin levels in females while causing elevated fasting blood glucose and insulin levels in males (Guo et al., 2021). In soils, accumulation of phenanthrene can potentially threaten soil invertebrates, including earthworms, and the toxicity is also high (He et al., 2022). Others reveal that phenanthrene induces cardiotoxicity by interfering with excitation-contraction coupling (Sørhus et al., 2023), disrupting the fish heart's contractile and electrical function (Yaar et al., 2023). Hence, it is necessary to investigate the extraction of phenanthrene using an organic solvent that can enable its separation under prescribed conditions.

Ionic Liquids in Material Recovery

Room temperature ionic liquids (RTILs) are liquids containing very large, irregularly shaped positive ions that prevent the crystallisation of anion–cation mixtures (**Figure 1**) as ionic solids at room temperature (Benedetto, 2017). RTILs are colourless, have low viscosities and are easy to handle and, therefore, have attractive properties for use as solvents as researchers continue to improve their properties and potential for extraction of materials in various industries (Sharma et al., 2023).

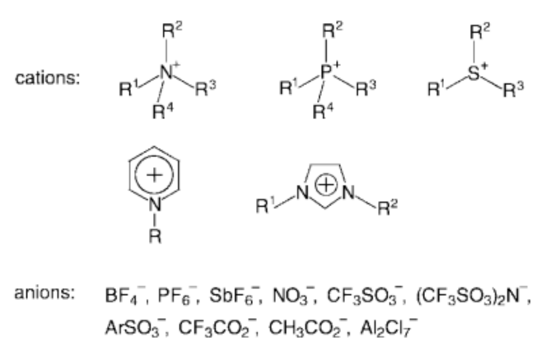

Figure 1: Structure of Ionic Liquid (Sheldon, 2001)

No single ionic liquid possesses all the unique properties such as low or negligible vapour pressure, the ability to dissolve a wide range of inorganic and organic compounds, high thermal stability, large electrochemical windows, high conductivity, high heat capacity and low flammability. Hence, systematic changes to the structure of the ionic liquid enable them to be effectively applied (Wasserscheid & Welton, 2003; Forsyth et al., 2004). The selectivity of a specific aromatic compound is influenced by anion volume and hydrogen bond strength between the anion and the imidazolium alkyl side chain. Therefore, the proper combination of imidazolium cations and anions can lead to highly selective materials for the extraction of aromatic compounds (Cassol et al., 2007), such as phenanthrene, which is a low molecular weight compound with three aromatic rings (Boldrin et al., 1993; Cerniglia, 1993 & Varanasi, 1989). There is evidence that tailor-made ionic liquids can act as catalysts in selectively extracting valuable components from wastes in an environmentally safe manner, compared to traditional volatile organic solvents (Lateef et al., 2009).

Characteristics of Phenanthrene

Phenanthrene comprises three benzene rings (**Figure 2**) (Yang et al., 2019). There is no production of phenanthrene as a pure product; however, just like most polycyclic aromatic hydrocarbons (PAHs), phenanthrene is present in fossil fuels and derived products (Verbruggen &van Herwijnen, 2011). Phenanthrene can persist in aquatic and terrestrial environments, posing a severe threat to the environment and human health (Chen et al., 2017).

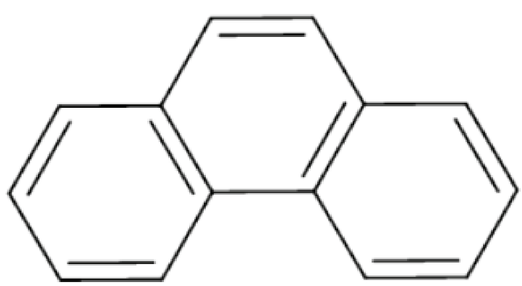

Figure 2: Structure of Phenanthrene (Kwofie & Gupta, 2021)

A study by Cortet et al. (2005) reveals that phenanthrene affects the population dynamics of mesofauna and soil biological functioning depending on exposure duration, type of community, or both (Cortet et al., 2005). Sojinu et al. (2011) reveal that the average half-life of phenanthrene ranges from 16 to 126 days in soil (Sojinu et al., 2011). Wilson and Jones (1993) assert that phenanthrene is mutagenic in bacterial and animal cells and carcinogenic in rodents (Wilson & Jones, 1993)

Environmental Hazards of Phenanthrene

PAHs are significant sources of global environmental pollution (Ruiz-Santaquiteria et al., 2022) and are frequently associated with light, non-aqueous-phase liquids in soil (Lee et al., 2003). Phenanthrene is profusely present in aquatic environments and poses a higher risk to animals, causing genotoxicity, cardiotoxicity, transgenerational toxicity, neurotoxicity, and developmental toxicity, and potentially inducing oxidative stress and behavioural alterations (Bhuyan & Giri, 2020). Phenanthrene has high lipoafinity and is known to be environmentally persistent, tending to accumulate in benthic ecosystems, causing severe impacts to marine organisms, from nematodes to fish (Pontes et al., 2020). Wei et al. (2014) investigate the effects of phenanthrene on seed germination and various physiological changes in wheat seedlings and discover that phenanthrene has the potential to exert oxidative damage in the early development stage of wheat, especially at high concentrations (Wei et al., 2014). Thus, several studies investigate the removal of these pollutants from the environments, and these approaches include coagulation, precipitation, ozonation, adsorption, ion exchange, and advanced oxidation processes (Nzila et al., 2018).

Case Studies of Extraction of Phenanthrene

Microbial degradation is the principal practice for effectively eliminating and abolishing polycyclic aromatic hydrocarbons (PAHs) from polluted environments (Murthy et al., 2016). Several environmental challenges are linked to PAHs, especially their potential to accumulate in soils (Roelofs et al., 2016). According to Zhao et al. (2021), some root-associated bacteria could degrade PAHs in contaminated soil (Zhao et al., 2021). Phenanthrene is recalcitrant to biodegradation (Liu et al., 2019). Some methods for extracting phenanthrene include biodegrading phenanthrene in soil and water in cloud point systems using *Sphingomonas polyaromaticivorans* (Pan et al., 2019). Also, a study on the novel removal of phenanthrene from a plant, clover (Trifolium pratense L.), grown in a contaminated site, demonstrates the use of *rhizobacterium Sinorhizobium meliloti P221* to colonise the rhizosphere soil and enhance phenanthrene degradation (Sun et al., 2014). Furthermore, Stavrinou et al. (2022) demonstrate the removal of phenanthrene from water matrices through adsorption onto natural organic substances (NOSs) and natural inorganic compounds (NICs) (Stavrinou et al., 2022). Meng et al. (2017) demonstrate using biosynthesised *schwertmannite* for phenanthrene degradation, illustrating its stability and reusability as a Fenton-like catalyst (Meng et al., 2017).

Potentials of Ionic Liquids in Material Extraction

With increasing legislation targeting the reduction of PAH concentrations in the environment, an adaptation of ionic liquids in selective extraction of these pollutants is gaining broader interest and extensive trials for the removal of aromatics compounds, especially in base oils and synthetic crude oil (Arenas-Fernández et al., 2022). Ionic liquids possess exclusive properties such as nonvolatility and adequate viscosity, qualifying them as extraction solvents in direct-immersion and headspace liquid-phase microextraction (Liu et al., 2003). Li et al. (2022) demonstrate the successful use of ionic liquids in extracting polycyclic aromatic hydrocarbons (PAHs) from fluid catalytic cracking (FCC) diesel (Li et al., 2022).

MATERIALS AND METHODS

Synthesis of 1-propyl-3-methylimidazolium bromide ionic liquid

For the synthesis of 1-propyl-3-methylimidazolium bromide ionic liquid *(*propyIMIMBr), the reagents 1-methylimidazole (5.0 g, 0.06 mol) and 1-bromopropane (10.2 g, 0.08 mol) were mixed and heated by microwave for a total time of 30 s at 10, 10, 5 and 5 s intervals at 40, 20, 20 and 20% microwave power, respectively. The washing of the resulting reaction mixture 4 times with 20ml of diethyl ether enables the removal of un-reacted starting material and residual ether evaporated under vacuum. The temperature of the rotary evaporator is set at 40°C, gradually scaled up to 60°C, and allowed to run for an hour at a rotation speed of 10rpm. The solubility tests of phenanthrene were experimented with in propyIMIMBr ionic liquid. **Table 1** shows the prescribed condition for the solubility of phenanthrene in ionic liquid. The potential of propyIMIMBr for liquid-liquid extraction and the miscibility of the ionic liquid with the organic solvents were investigated at room temperature by adding 2g of ionic liquid to 5ml of organic solvent, stirring at 600rpm for a duration of 20mins (see **Table 2**).

Table 1: Solubility of Phenanthrene in propyIMIMBr Ionic Liquid

Components	Measurement	Heating profile	Solubility Value/°C
Phenanthrene	IL- 2g Solute – 0.2g	Temperature: 20-25°C, 30-36°C, 40-52°C, 60°C, 70-74°C Duration: 20 min	>lg at 74°C

	Stirring:	600-1000rpm

Table 2: Solubility of Pure Components and Ionic Liquid in Organic Solvents

Starting Materials	Measurement	Protocol
Phenanthrene	Solute – 0.5g	Heating: None
	Solvent – 5ml	Stirring 600-1000rpm
		Duration 20 min
propyIMIMBr	IL- 2g	Heating: None
	Solvent – 5ml	Stirring 600-1000rpm
		Duration 20 min

RESULTS

The solubility of phenanthrene in propyIMIMBr at 74°C (**Figure 2**) occurred at >1g. For the miscibility of propyIMIMBr with organic solvents, a wide range of options for liquid-liquid extraction were discovered (**Table 3**).

Table 3: Summary of Solubility Test Results

S/N	IL: Pure Component	phenanthrene	propyIMIMBr
	Solvent: Pure Component	>1g	2g
1	Ethanol	Insoluble	Soluble
2	methanol	Insoluble	Soluble
3	ethyl acetate	Soluble	Insoluble
4	water	Insoluble	Soluble
5	Ethanolamine	Insoluble	Soluble
6	Toluene	Soluble	Insoluble
7	Xylene	Soluble	Insoluble
9	1-bromopropane	Soluble	Insoluble
10	1-chlorobutane	Soluble	Insoluble
11	1-propanol	Insoluble	Soluble
12	1-butanol	Insoluble	Soluble

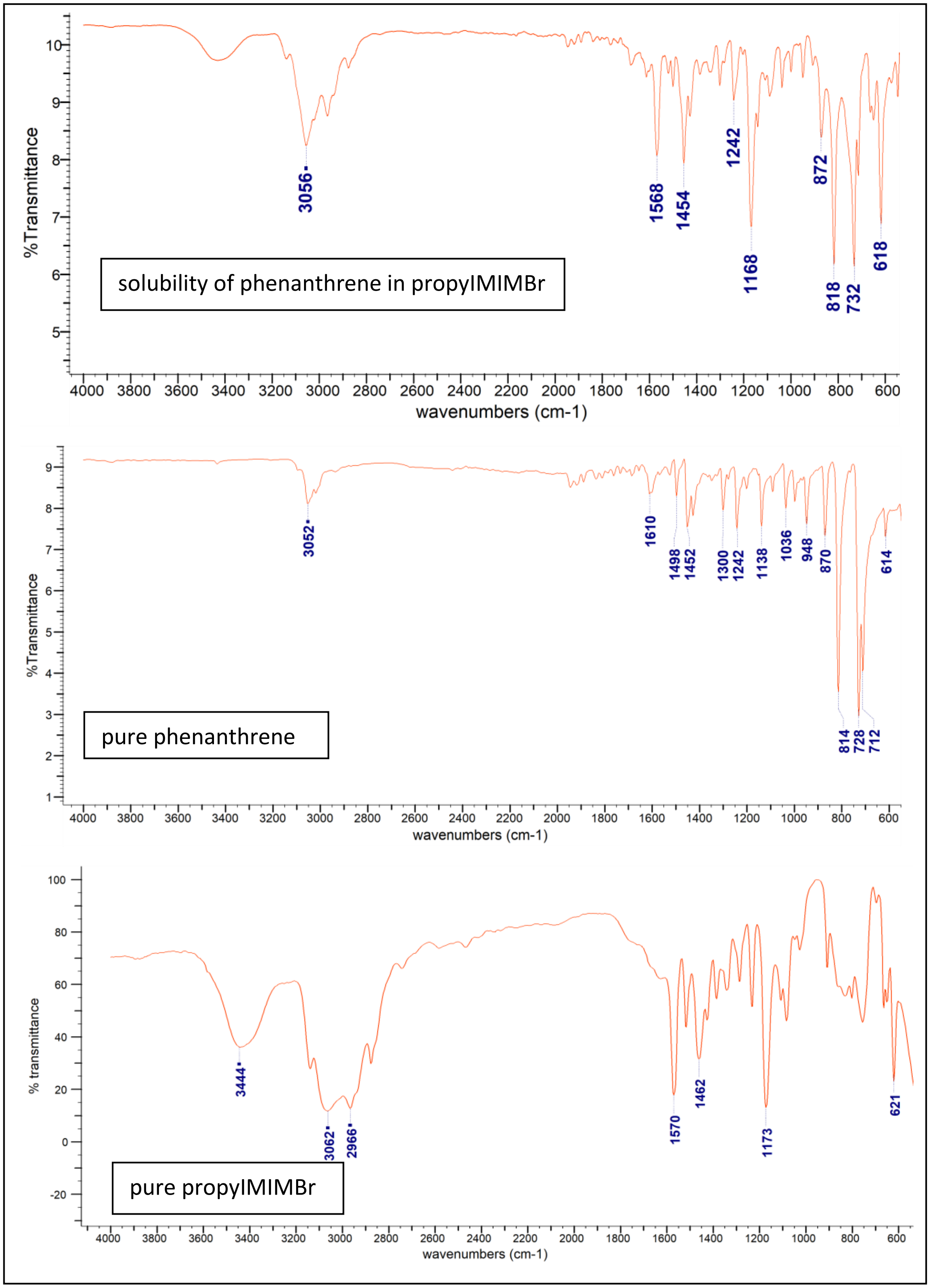

Figure 2: Solubility of Phenanthrene in propyIMIMBr

DISCUSSION

Phenanthrene is a high-priority pollutant that can contaminate soils and water mediums, posing a risk of illnesses. There are many methods of extraction of phenanthrene; among them is the novel use of room temperature ionic liquids such as propyIMIMBr to extract this aromatic compound selectively from wastes (soils and water), where they are commonly found. Room temperature ionic liquids are mild to work with and thus can be further investigated for extraction of phenanthrene from complex waste streams.

CONCLUSION

For ionic liquids to be used successfully in the recovery of aromatic compounds, it is not only crucial that the components be soluble in the ionic liquid but also that the components can be extracted from the ionic liquid solution and that the ionic liquid can be recycled and reused in the overall recovery process. This study demonstrates this and can be further explored to isolate phenanthrene from hazardous wastes intelligently.

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