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Short Communication

Ionic liquid as extraction agent for detection of volatile phenols in wastewater and its regeneration

Volatile phenols in the wastewater provide a basic parameter of the pollution. Spectrophotometric method based on the reactions of the individual phenols with 4-aminoantipyrine in the presence of an oxidizing agent is the current official analytical method in many countries. In this paper, we propose a method for extracting the resultant colored dye with ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate instead of chloroform. The results revealed excellent extraction efficiency, and the used ionic liquid could be regenerated easily. The method with small volume green reagent could be potentially applied in portable devices for *in situ* environmental analysis.

Keywords: Extraction reagent / Ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate / Regeneration / Volatile phenols
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1 Introduction

Phenol and substituted phenols are used widely in many industrial processes, such as coking plants, paper, cosmetic and dyes industries. They are released in industrial wastewater and domestic water, and may be a threat to human health and aquatic life [1–4]. Due to their toxicity and persistence in the environment, some volatile phenols were included in monitoring programs list of priority pollutants.

Current official analytical methods for phenolic compounds extraction are liquid–liquid extraction (LLE) for liquid samples, and Soxhlet extraction for solid samples (US EPA Methods 604, 605, 8041 and 3540 B, respectively). These methods require expensive and hazardous organic solvents, which are undesirable for health and disposal reasons; in addition, the analysis takes a long time. Many other methods for determination of phenols in wastewater have been proposed, such as chromatography [5, 6], spectrophotometry [7, 8] and flow injection analysis [9, 10]. The most frequently used is the reaction of 4-aminoantipyrine (4-AAP) [11]; meanwhile, it is a classical and official method in many countries such as China. This method is based on alkaline solution and the phenol in wastewater is reacted with 4-AAP in the presence of hexacyanoferrate, the

resultant colored dye (RCD) is extracted into chloroform for preconcentration and the absorbance is measured at 460 nm [12, 13]. However, chloroform as the extraction agent in this method has certain drawbacks associated with toxicity and volatility.

Ionic liquids have received attention as green solvents for a variety of applications [14–16], such as electrochemistry [17], organic synthesis, chromatography analysis [18, 19], and LLE [20–22]. A detailed account was reported on ionic liquids in separations [23] and some researches on extraction of phenols have been published [24, 25]. Ionic liquids exhibit unique properties, including low volatility, high thermal stability, nonflammability, and can dissolve a number of organic and inorganic compounds [26].

In this paper, ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆) was used as a replacement for chloroform to extract the RCD, RCD was extracted but not the phenols in water as the references reported. Aliquots of 3 mL of [BMIM]PF₆ were applied to extract 50 mL of RCD solution, 20 min was enough for extraction and absorbance measured at 470 nm wavelength, the results of the determination were consistent with that of chloroform. And regeneration of ionic liquid after extracting the RCD was investigated. [BMIM]PF₆ has the same extraction efficiency after five cycles.

2 Materials and methods

2.1 Reagents and apparatus

Phenol and potassium ferricyanide were purchased from Tianjin Kermel Chemical Reagent (Tianjin, China). 4-AAP was obtained from Sinopharm Chemical Reagent

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Abbreviations: 4-AAP, 4-aminoantipyrine; [BMIM]PF₆, 1-butyl-3-methylimidazolium hexafluorophosphate; LLE, liquid–liquid extraction; RCD, resultant colored dye

(Shanghai, China). Ammonia and ammonium chloride were provided by Yixing Second Chemical Reagent Factory (Yixing, China). Chloroform was purchased from Shanghai Shenxiang Chemical Reagent (Shanghai, China). All the reagents were of analytical grade quality. Ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆) was obtained from Lanzhou Institute of Chemical Physics (Lanzhou, China).

UV-vis spectra were recorded on a UV-2100 spectrophotometer (Shimadzu, Kyoto, Japan).

2.2 Preparation of standard solutions

Two percent (w/v) of the 4-AAP solution and 8% w/v of the potassium ferricyanide solution were prepared; ammonium chloride-ammonia buffer solution was prepared by dissolving 2.0 g of ammonium chloride in 100 mL of ammonia. All solutions were prepared using distilled water, and were stored in the dark at 4°C until analysis. Phenol reference solutions from 2 to 100 µg/L were prepared daily by appropriate dilutions of 1.00 g/L stock solution.

2.3 Procedure of the extraction

Aliquots of 2 mL of ammonium chloride-ammonia buffer solution were added to 50 mL of phenol solution for adjusting pH 10, the mixture was treated successively with 1.5 mL of 4-AAP solution and 1.5 mL of K₃[Fe(CN)₆] solution, and this mixture was set aside for a certain period of time. Then, the RCD was extracted with 3 mL of ionic liquid, and measured in 1 cm cell at the optimum wavelength, against a blank of double distilled water treated in the same manner.

2.4 Regeneration of ionic liquid [BMIM]PF₆

Aliquots of 3 mL of [BMIM]PF₆ after extraction of RCD were taken to the separatory funnel, and 10 mL of chloroform were added, surged and set aside for certain period of time, then retained in the ionic liquid layer; this method was repeated three times. Finally, the ionic liquid layer was collected for reuse.

3 Results and discussion

3.1 Characteristics of ionic liquid [BMIM]PF₆

Ionic liquids are ionic media formed from combination of organic cations and various anions; they possess adjustable hydrophobicity-hydrophilicity, their unique properties of nonvolatility, low toxicity and dissolving a number of organic and inorganic compounds may be of importance in their application as extractive media in LLE processes.

Ionic liquids have been applied in sewage treatment and used for recycling the volatile phenols in industry [27–29].

In this paper, ionic liquid [BMIM]PF₆ was used as extraction agent for detection of volatile phenols in waste water. [BMIM]PF₆ is a viscous, colorless, hydrophobic and non-water soluble ionic liquid; it is one of the most widely studied ionic liquids and is commercially available from most of the major international suppliers of chemicals. It is known to very slowly decompose in the presence of water. It may be obtained in two steps: BMIM-Cl is synthesized by alkylating 1-methylimidazole with 1-chlorobutane. A metathesis reaction with potassium hexafluorophosphate gives the desired compound; the tetrafluoroborate may be prepared by analogously using potassium tetrafluoroborate [30, 31].

3.2 [BMIM]PF₆ as extraction reagent for detection of volatile phenols

The color is different with RCD in dissimilar solutions. In this study, ionic liquid after extracting the RCD was measured at different wavelengths from 440 to 550 nm. Absorbance data are shown in Fig. 1. It indicated that the highest absorbance was in the vicinity of 470 nm.

The volume of extraction solvent is an important parameter for obtaining higher preconcentration factor and better extraction efficiency. The volume ratio of ionic liquid and the solution containing RCD was investigated with 1:10, 1:15, 1:20, 1:25, 1:30 (shown in Fig. 2). The absorbance was increased with the volume of mother solution containing RCD, but after the ratio 1:20, the absorbance was not effectively increased with the increasing of volume of mother solution, extraction efficiency was the best when the volumetric ratio was 1:20. Extraction time is another important factor in achieving equilibrium between two phases. The extraction yield can be increased with longer extraction times, which provide longer contact time between the extracting phase and sample. The results are shown in

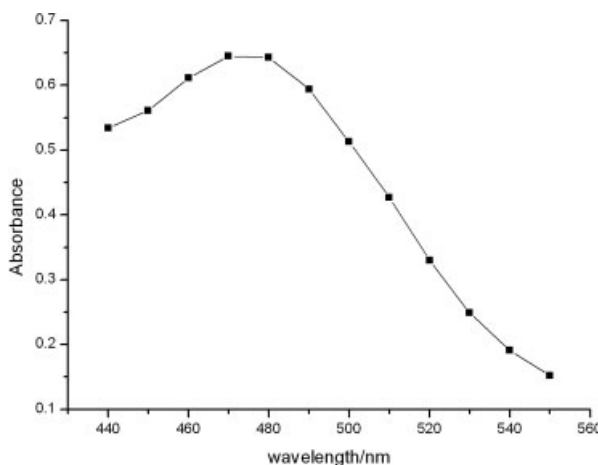


Figure 1. Absorbance of RCD in ionic liquid.

Fig. 2. As can be seen, the absorbance of ionic liquid containing RCD increases between 0 and 20 min; after 20 min, a platform was formed due to RCD saturation in ionic liquid.

Many parameters affect extraction efficiency such as pH, ionic strength and temperature. Because this extraction procedure followed by the phenols in wastewater was reacted with 4-AAP in the presence of hexacyanoferrate, and the operation was performed at room temperature, we did not investigate the other conditions such as pH, ionic strength and temperature. Fortunately, the extraction efficiency with ionic liquid is equivalent to that of chloroform. RCD residue in the mother solution with ionic liquid and chloroform was investigated. The results showed that the extraction rate of ionic liquid was 97%, while the extraction rate of chloroform was 98%.

The developed method was applied to determine volatile phenols of wastewater in two chemical industry parks. Standard phenols were applied for calibration (Fig. 3). A good linear relationship was in the range of 5–100 $\mu\text{g/L}$.

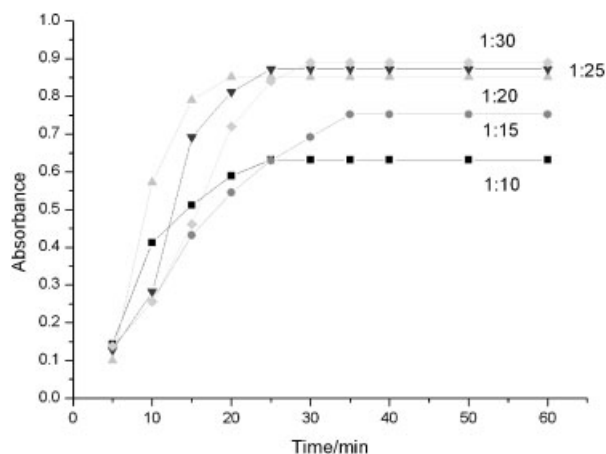


Figure 2. Relationship between absorbance and volume ratio of ionic liquid and the solution containing RCD.

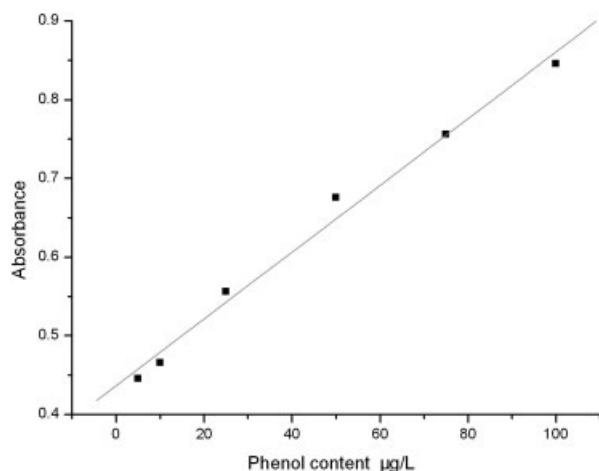


Figure 3. Relationship between absorbance and concentration of phenols.

Table 1. Concentration of volatile phenols in wastewater measured with proposed and conventional methods

Wastewater samples	Ionic liquid extraction method (mg/L)	Chloroform extraction method (mg/L)
Xiangshui Chemical Industry Park	0.052	0.050
Binhai Chemical Industry Park	0.436	0.427

Table 2. RCD content in [BMIM]PF₆ after different extraction times with chloroform

Extraction times	RCD content in [BMIM]PF ₆ (%)
1	21.6
2	4.15
3	1.37

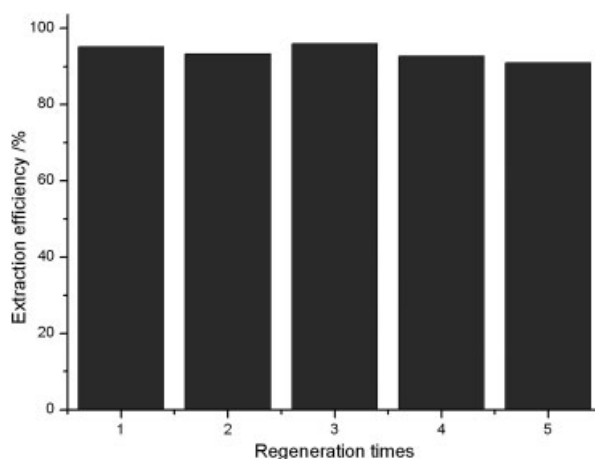


Figure 4. Extraction efficiency of the regenerated ionic liquid [BMIM]PF₆.

Accuracy was validated by traditional chloroform extraction method. Data are listed in Table 1. The results with the proposed method exhibited agreement with that of the traditional method.

3.3 Regeneration of [BMIM]PF₆ after extraction of the RCD

For the purpose of achieving reuse of ionic liquid, we should select a kind of solvent whose extraction rate must be not lower than that of ionic liquid [BMIM]PF₆, and they are immiscible with each other. In this study, chloroform was chosen to extract the RCD in [BMIM]PF₆, because RCD was well dissolved in chloroform. In order to improve the efficiency of [BMIM]PF₆ regeneration, 30 mL of chloroform was used to extract RCD for three times on average in

sequence to regenerate 3 mL of [BMIM]PF₆. The results are presented in Table 2. The data indicated that 98.6% of RCD was removed.

It is necessary to test the dynamic adsorption and desorption. Continuous adsorption-regeneration runs of an identical ionic liquid were also performed to test its applicability. Figure 4 indicated that ionic liquid [BMIM]PF₆ can be completely regenerated for reuse without any significant capacity loss. After five cycles, the extraction efficiency for RCD in aqueous solution was more than 92%.

Ionic liquid was applied as extraction solvent instead of chloroform. It could avoid damaging health from hazardous organic solvents in regular determination. The used ionic liquid could be collected and regenerated periodically. Actually, chloroform as regeneration solvent is the main disadvantage for this method and further research is focused on a green one.

4 Concluding remarks

Comparing the extraction efficiency of the two extraction agents of chloroform and [BMIM]PF₆, extraction rate of ionic liquid [BMIM]PF₆ for the RCD was equal to that of chloroform, the extraction efficiency was best when [BMIM]PF₆/RCD solution volumetric ratio was 1:20; 470 nm was selected as detection wavelength and a good linear relationship in the range of 5–100 µg/L was observed. Ionic liquid as green solution was more environmentally friendly compared with chloroform. The results for volatile phenols detection with the proposed method exhibited agreement of traditional method, and the used ionic liquid could be regenerated easily. The used ionic liquid could be collected and regenerated periodically. Further research is needed for finding a green regeneration solvent. Due to the merit of less dosage and low toxicity, ionic liquid could be used instead of chloroform for volatile phenols detection and be potentially applied in portable devices for *in situ* environmental analysis.

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5 References

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