

The Investigation of Adsorption Behaviors of Nine Ionic Liquid-Immobilized Silicas on Two Phenols in Water and Soil Samples

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An experimental study on adsorption of phenol and o-cresol using ionic liquid-immobilized silica contained different functional groups was carried out. The effects of various operating parameters such as type of ionic liquid group, different adsorption time and ambient temperatures, different solvents in solid phase extraction (SPE) process and several aqueous ion solutions on adsorption of two phenols had been experimentally investigated. It was found that amino ionic liquid-immobilized silica had the highest adsorption efficiency and stability. The optimized adsorption conditions were 15 min under 35 °C. In SPE, the acidity solution such as ethanol-HCl (0.1 % vol.) and NaH₂PO₄ could reduce the adsorption efficiency of sorbents. Finally, the sorbent was applied to determining two phenols in real samples and relative standard deviation (RSD) less than 6.14 % showed the high precision.

Keywords: ionic liquid, immobilized silica, phenols, water, soil.

1. INTRODUCTION

Along with the development of the industry, pollution of water and soil from inorganic and organic compounds has increased rapidly in recent decades. Large amount of aqueous pollutions has toxicological effects in humans and animals [1]. Phenols are one of the major organic compounds used in several chemical manufacturing processes, also they are used as an antiseptic or added in disinfectant [2]. Phenols are toxic and had a carcinogenic effect, therefore of considerable health concern to human and aquatic lives when released to the environment. The concentrations of phenol in industrial effluents are normally in a range of 2.8–6800.0 ppm which is much higher than the LD50 for aquatic lives [3]. For these reasons, removing phenols is one of the main aims in water and soil treatment.

Various treatment methods like ozonation, distillation, liquid extraction, pervaporation, membrane extraction, biological based processes and different kinds of electrochemical methods were currently practiced for phenolic compounds removal [4–8]. Kalle et al. used iron oxidation to remove phenolic compounds with pH in the range between 2 and 4, the maximum value removal is at the level of 92 % [4]. Chedeville et al. used ozonation to treat wastewater under pH = 5, after process the abatement of phenolic compounds reached 80 % [5]. Parida and Pradhan removed phenolic compounds by adsorption onto manganese nodule leached residue, under 4 h equilibrium time 28.5 mg/g of phenol can be adsorbed at pH = 3 [6]. Yavuz et al. treated wastewater by electrochemical oxidation. 99.5 % phenol was removed at 40 min of electrolysis with density of 5 mA/cm² [8].

Although these techniques provide accurate results, they have several disadvantages, such as the requirement of expensive apparatus, complicated operation with high

costs, and the requirement of well-controlled experimental conditions. In the case, the most favourable technique is adsorption using sorbents.

Ionic liquids (ILs), a green reaction media with excellent chemical properties, are employed as a modifier. ILs are receiving a lot of attention in the fields of analytical chemistry, sample preparation, organic synthesis, liquid-phase extraction, and chromatographic separations [9–13]. The characteristics, such as hydrophobicity, miscibility with several inorganic/organic solvents, π - π interactions between analyte and functional groups of the ionic liquids, are widely applied [14]. Some researches were already published using IL or IL based materials to extract phenols from water solutions [15–19]. Balasubramanian and Venkatesan removed phenolic compounds using IL in tributyl phosphate solution, the result was observed that 0.02 % (v/v) of IL [BMIM][PF₆] can remove 99.5 % of phenols at pH = 6.5 [17]. Rao et al. synthesized a cyclodextrin-ionic liquid polymer, and the sorbent adsorbed 29.6 mg/g of phenolic compound under pH = 6 and 180.0 min [18].

Solid-phase extraction (SPE) is one of the most convenient and high-performance separation technologies that can help minimize the use of organic solvents, which are regulated as priority pollutants. Li et al. [20] and Wang et al. [21] successfully applied SPE in separation of harmful compounds. So in this research, adsorption of o-cresol and phenol from aqueous solutions using IL-immobilized silica contained different groups was evaluated using SPE method. IL groups were based on imidazole which contained different carbon chains and side groups. In SPE process, aqueous ions solution and several organic solvents were used in washing and elution steps. Also the effect of adsorption time and ambient temperature were investigated.

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2. EXPERIMENTAL DETAILS

2.1. Chemicals

Silica (40 μm), (3-chloropropyl)-trimethoxysilan, imidazole, 1-methylimidazole, 1-ethylimidazole, 1-butylimidazole, 1-hexylimidazole, 1,2-dichloroethane, 1,4-dichlorobutane, 1,6-dichlorohexane, 2-chloroethylamine, phenol and *o*-cresol were purchased from Aladdin Inc. (Shanghai, China) and all grades of purity were higher than 98 %. Organic solvents such as ethanol, toluene, triethylamine et al. were supported by Beilian Company (Tianjing, China) and purities were higher than 99.7 %. Water, all organic solvents and samples should be filtered before use.

2.2. Preparation of IL-immobilized silica

Silica was first washed by distilled water and ethanol, and activated in a vacuum oven under 120 $^{\circ}\text{C}$ for 4 h. Then two groups of activated silica were synthesized by following steps shown in Fig. 1.

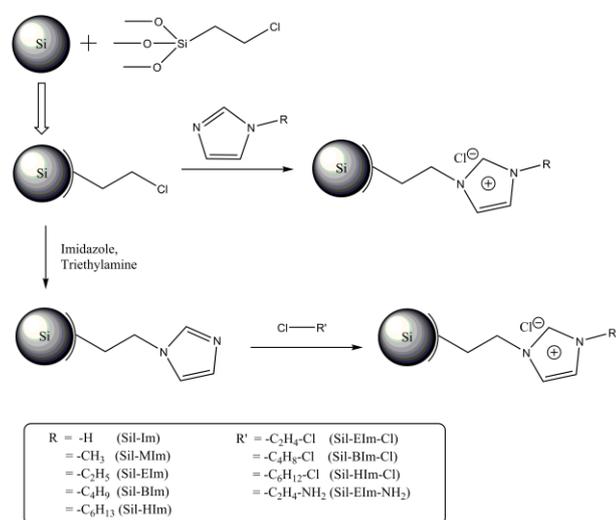


Fig. 1. Synthesis process of nine IL-immobilized silicas

For the first group, 25.0 g of silica, 25.0 mL of (3-chloropropyl)trimethoxysilane and 100.0 mL of toluene were well mixed in a flask, and the mixture was heated to 100 $^{\circ}\text{C}$ for 12 h. When the powder was washed by ethanol and fully dried, chloropropyl silica (Si-Cl) was obtained. Then five flasks contained 5.0 g of Si-Cl and 50.0 mL of toluene were prepared, 5.0 g of imidazole, 1-methylimidazole, 1-ethylimidazole, 1-butylimidazole and 1-hexylimidazole were added into flask respectively. After all flasks were heated and refluxed for 12 h, IL-immobilized silicas such as imidazole chloride-silica (Si-Im), 1-methylimidazole chloride-silica (Si-MIm), 1-ethylimidazole chloride-silica (Si-EIm), 1-butylimidazole chloride-silica (Si-BIm) and 1-hexylimidazole chloride-silica (Si-HIm) were obtained. For the second group, 25.0 g of Si-Cl was prepared as well and it mixed with 28.0 g of imidazole (15.0 g of triethylamine as a catalyst) in 200.0 mL of toluene. After the mixture was heated to 100 $^{\circ}\text{C}$ for 12 h, the obtained imidazole-silica was dried at 80 $^{\circ}\text{C}$ for overnight. Then four flasks contained 5.0 g of imidazole-silica and 50.0 mL

of toluene were prepared, 5.0 g of 1,2-dichloroethane, 1,4-dichlorobutane, 1,6-dichlorohexane and 2-chloroethylamine were added into flasks respectively. After all flasks were heated and refluxed for 12 h, IL-immobilized silicas such as Si-EIm-Cl, Si-BIm-Cl, Si-HIm-Cl and Si-EIm-NH₂ can be obtained. All IL-immobilized silicas were washed by diluted water, ethanol and acetone, and fully dried for further experiments. The characteristics of all obtained silicas were analyzed by FT-IR (Nicolet 6700, Thermo Fisher, Waltham, USA) in the range of 400-4000 cm^{-1} with a scan rate of 20 scans/min and TGA (Labsys evo, Setaram, Caluire, France) with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under N₂.

2.3. Preparation of silica-physically adsorbed-ILs

Three 100 mL flasks contained 10.0 g of 1-methylimidazole were prepared and 17.0 g of 1,2-dichloroethane, 23.0 g of 1,4-dichlorobutane and 28.0 g of 1,6-dichlorohexane were added into each flask. Three mixtures were stirred and heated until refluxing for 24 h. Then the mixtures were evaporated to remove excess alkyl halides and washed by diethyl ether. After fully drying in oven, three ionic liquid 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl), 1-butyl-3-methylimidazolium chloride ([BMIm]Cl) and 1-hexyl-3-methylimidazolium chloride ([HMIm]Cl) were obtained. Each obtained IL was added into 1.0 g of activated silica and the adsorption equilibrium would be achieved completely in 2 h. Then three silica-physically adsorbed-IL sorbents Si/[EMIm]Cl, Si/[BMIm]Cl and Si/[HMIm]Cl were prepared.

2.4. Adsorption efficiency of sorbents with SPE

0.3 g of each IL-immobilized silica was packed into nine SPE cartridges (\varnothing 0.9 cm, Alltech, Deerfield, IL, USA) and two groups of such cartridges were prepared. Then water, methanol and acetone were alternately added into cartridges to clean the materials. After pretreatment, loading, washing, elution and cleaning steps with different solvents were orderly applied into SPE process. In loading step, 0.1 mL of 0.01 mg/mL of *o*-cresol and phenol solutions were dropwised into each cartridge group. After the solutions were well dispersed into sorbents, the cartridges were placed for 30 min until adsorption equilibrium obtained. Then in washing step 3.0 mL of water was dumped into each cartridge according to the amount of sorbents, after through the materials washing water were collected and analyzed by HPLC. In elution step, several organic solvents with different polarities (methanol, ethanol, acetonitrile, hexane and chloroform) were selected as elution solvent to remove phenols after washing step. Then 3.0 mL of solvent contained 0.1 % (vol.) HCl which had higher elution ability was used in cleaning step to remove rest of phenols from materials. Solutions from each process were analyzed by HPLC (LC3000, CXTH, Beijing, China). The chromatographic conditions were: a commercial C₁₈ column (4.6 \times 250 mm, 5 μm , RStech Co., Daejeon, Korea) with methanol/water (80:20, v/v) as mobile phase. The flow rate, UV wavelength, and injection volume were 0.5 mL/min, 270 nm and 20.0 μL , respectively.

2.5. Change of adsorption time and temperature

o-Cresol and phenol had similar adsorption behaviors on sorbents, so *o*-cresol was selected. Firstly, under room temperature 0.3 g of Sil-EIm-NH₂ was mixed with 0.1 mL of 0.01 mg/mL *o*-cresol within different adsorption time from 0.3 min to 30 min. Then same amount of Sil-Im-NH₂ and *o*-cresol solution was mixed under increasing temperature from 15 °C to 70 °C. At different time and temperature points, 3.0 mL of ethanol-HCl (0.1 % vol.) was used to remove unadsorbed *o*-cresol. Each point was repeated 7 times and analyzed by HPLC.

2.6. Effect of adsorption by several ions

0.1 mol/L of several salt aqueous solutions such as NaCl, KCl, MgCl₂, AlCl₃, CaCl₂, FeCl₃, Na₂CO₃, NaHCO₃, Na₂HPO₄ and NaH₂PO₄ were prepared. In order to evaluate the effect of salt after fully equilibrium, the adsorption and desorption time were increased by adding more volume of solvents. After loading the 1.0 mL of 0.01 mg/mL of phenol in SPE cartridges with 3.0 g of Sil-Im, Sil-EIm-Cl and Sil-Im-NH₂ as sorbents, 10.0 mL of salts aqueous solutions were used in SPE and amounts of unadsorbed phenol were analyzed.

2.7. Preparation of real water and soil samples

Four environmental water samples were obtained from the Yangtze River, a lake, a well and plant effluent. After filtration, 10.0 mL of four water samples were loaded into SPE cartridges. Three soil samples were taken from different places near a plant and each of them was stirring with 10.0 mL of pure water for 30 min, then the filtered water layers were also loaded into SPE cartridges with 3.0 g of sorbents. After loading process, elution and washing processes were followed the previous optimized steps.

3. RESULTS AND DISCUSSION

3.1. Adsorption ability of commercial resins

First of all, the calibration curves were constructed using the chromatographic peak areas measured at seven increasing concentrations, ranging from 0.001–0.025 mg/mL for *o*-cresol and 0.005–0.1 mg/mL for phenol. Good linearity was obtained and the linear correlation equations were $y = 53.491x + 0.0413$ ($R^2=0.997$) for *o*-cresol and $y = 15.463x + 0.0453$ ($R^2=0.999$) for phenol (y is peak area and x is the concentration of phenols in solution).

Normally macro-resin was widely used in waste water treatment with materials adsorption technology. However adsorption efficiencies and stabilities under high temperature were partially unsatisfactory. In order to prejudge the effect of adsorption efficiency between functional group and phenols, commercial silica (0.1 g), two base properties resins (0.2 g of each, Amberlite® IRA402 and 717, Dow Chemical Company, Michigan, USA) and one acid property resin (0.2 g, Amberlite® 732, Dow Chemical Company, Michigan, USA) were static mixed with 3.0 mL of 0.05 mg/mL phenols aqueous solution for 60 min.

After analysis, the adsorption amounts for *o*-cresol were 0.12 mg/g on silica, 0.23 mg/g and 0.17 mg/g on two base properties resins, nothing was adsorbed on acid property resin. For phenol the amounts were 0.076 mg/g, 0.47 mg/g, 0.76 mg/g and 0.00 mg/g respectively. The results showed that the materials contained base group had much stronger interaction with phenols. Although adsorption efficiency of silica was a little far from base groups, it had large surface area and supplied hydrogen bonds. So in the following researches IL-silicas with/without base group should be investigated.

3.2. Characterization

In the FT-IR spectra (Fig. 2), except silica the other nine sorbents showed the appearance of peaks nearby 1572.3 cm⁻¹ which is the finger print region of IL groups. Sil-BIm and Sil-HIm showed a peak at 1481.4 cm⁻¹ which belongs to -C-C- bond. Sil-EIm also showed this peak but quite smaller because of less amount of -C-C- bonds. The vibration range of -C-H group in alkanes is 2850.0–3000.0 cm⁻¹ so the peaks at 2942.2 cm⁻¹ belong to the carbon chain [22, 23]. Obviously, Sil-BIm and Sil-HIm with longer carbon chain showed larger peak area than Sil-MIm and Sil-EIm. The finger print region of the -C-Cl group ranges from 690.0 to 704.0 cm⁻¹, so Sil-EIm-Cl, Sil-BIm-Cl and Sil-HIm-Cl showed one more conspicuous peak at 694.8 cm⁻¹ than Sil-EIm, Sil-BIm and Sil-HIm. Compared Sil-EIm-Cl and Sil-EIm-NH₂, the peak of -C-Cl was disappeared and the peak at 660.6 cm⁻¹, which was attributed to the -NH₂ group proved that -C-Cl was replaced as -C-NH₂.

Thermogravimetric analysis can determine the thermo stability of the additional groups on silica with the weight loss and Fig. 3 shows the results from 200 °C to 600 °C. In Fig. 3 a, with same amount of sorbent, more weight was lost from 12.33 % of Sil-Im to 22.09 % of Sil-HIm because of the increasing of carbon chain on IL group. However, although the carbon chain of Sil-BIm and Sil-HIm were longer than Sil-EIm, the lost weight did not increased much. This is because the hydrophobic property of long carbon chain influenced the synthesis efficiency, especially Sil-HIm. Fig. 3 b showed that with the same IL group of Sil-EIm, 1.27 % and 4.94 % more weight lost belong to the additional -NH₂ and -Cl groups. Both FT-IR and TGA results indicated the successful immobilization of IL groups on silica.

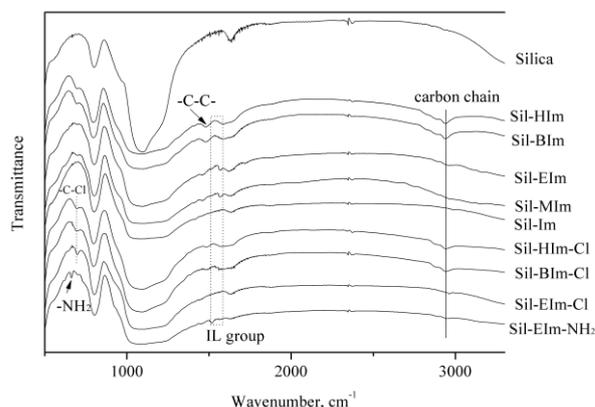
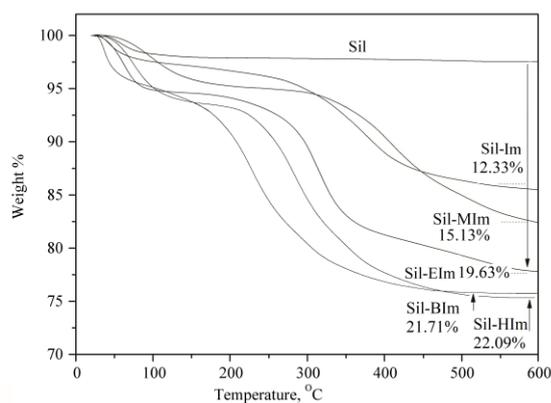
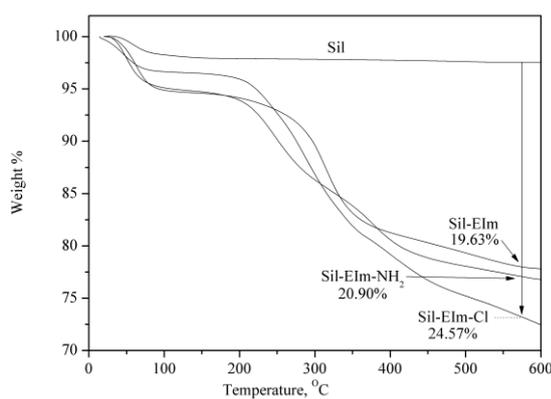


Fig. 2. FT-IR spectra of silica and IL-immobilized sorbents



a



b

Fig. 3. TGA analysis: a– Sil, Sil-Im, Sil-MIm, Sil-EIm, Sil-BIm and Sil-HIm; b– Sil, Sil-EIm, Sil-EIm-NH₂, Sil-EIm-Cl

3.3. Adsorption abilities of different sorbents

In SPE process, after adsorption equilibrium of two phenols arrived on sorbents, several solvents were used to investigate the strength of interaction by detecting the amount of two phenols in collected solutions. Firstly loading and washing steps were evaluated. Because *o*-cresol and phenol had solubility in water, and the purpose of this research was to remove phenols in water, so water was selected as washing solvent and amounts of removed phenols are shown in Fig. 4 and Fig. 5.

Among Sil-Im, Sil-MIm, Sil-EIm, Sil-BIm and Sil-HIm, amounts of *o*-cresol and phenol removed by 3.0 mL of water from Sil-Im and Sil-MIm (less than 0.14 μg and 0.024 μg respectively) were not much because of hydrogen bonds. With increasing the length of carbon chain on ionic liquid group from Sil-EIm to Sil-HIm, both amounts of *o*-cresol and phenol in washing solvent increased. The phenomenon could be explained with two mechanisms. First, with increasing of carbon chain, the hydrophilic properties of IL groups increased, as well the difference of polarities between IL groups and phenols increased [24]. Second, when the structural volume of IL groups increasing, in an unit surface area the number of effective IL groups which would be bonded phenols was reduced. In this case, water can wash most part of both phenols (more than 0.79 μg) from Sil-BIm and Sil-HIm. In addition, polarity of *o*-cresol was a little lower than phenol, the results showed that *o*-cresol was more trended to Sil-BIm

and Sil-HIm although the distinction of adsorption amount had almost no difference.

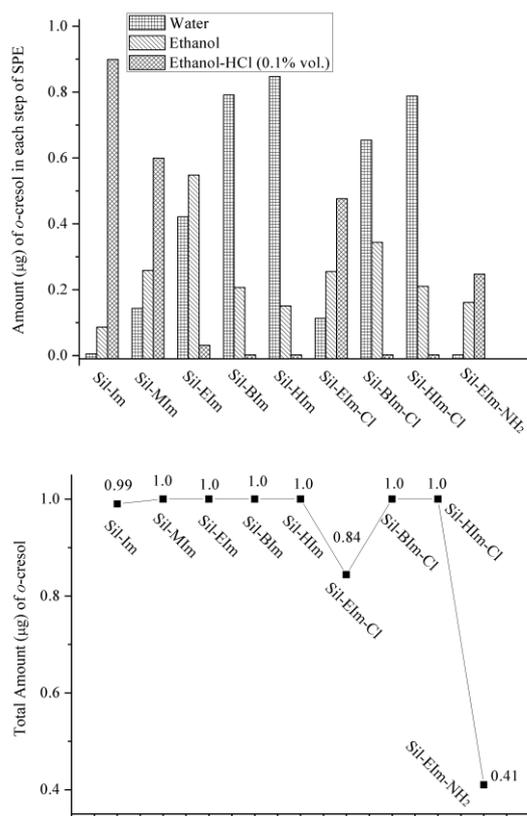


Fig. 4. Detected amount of *o*-cresol from nine sorbents in collected solutions after washing, elution and cleaning step of SPE

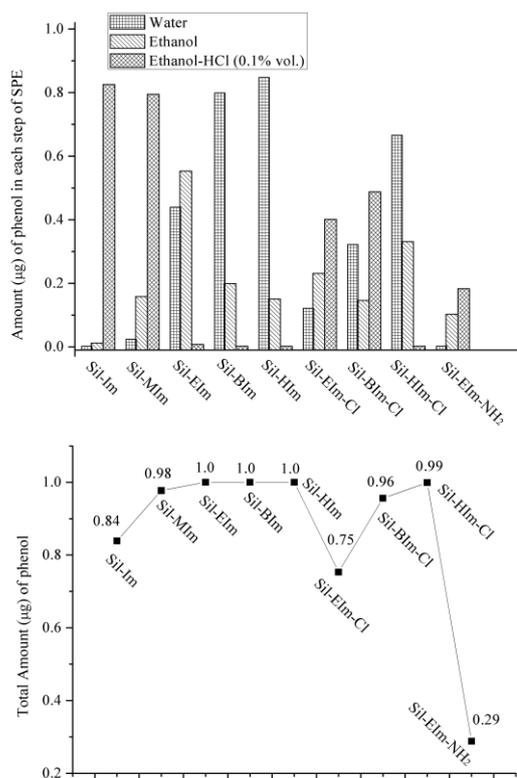


Fig. 5. Detected amount of phenol from nine sorbents in collected solutions after washing, elution and cleaning step of SPE

Effect of the interaction between -Cl and phenols was also shown in the two figures. -Cl group is an electron-withdrawing group. Because of conjugative effect, -OH groups on *o*-cresol and phenol were electron-donating group [25]. So compare the ILs contained same carbon chain, the -Cl on IL had more interaction with -OH groups. As the results shown in two figures, washing amount of phenol from Sil-BIm was 0.79 μg but from Sil-BIm-Cl the amount decreased to 0.32 μg . Moreover, washing amount of *o*-cresol from Sil-BIm-Cl was larger than phenol (0.65 μg), that because the stereo-effect of methyl group weakened the electron-donating of -OH. For Sil-Im-NH₂, no phenols were detected in washing solvent revealed that IL and amino groups can bond with phenols strongly enough.

Elution and cleaning steps were followed. First of all, elution abilities of different organic solvents were tested on Sil-MIm using phenol as target. 3.0 mL of methanol, ethanol, acetonitrile, hexane and chloroform eluted the Sil-MIm and 0.16 μg , 0.16 μg , 0.63 μg , 0.013 μg and 0.66 μg of phenol were detected in eluates respectively. The results showed that the elution ability was lower for hexane, similar for methanol and ethanol, higher for acetonitrile and chloroform. However in consideration of the toxicities of methanol, acetonitrile and chloroform, so ethanol was selected as elution solvent to remove phenols which were adsorbed on materials.

Because the solubility of phenols in ethanol was larger than water, 3.0 mL of ethanol can elute almost all phenols from Sil-EIm, Sil-BIm, Sil-Him, Sil-BIm-Cl and Sil-Him-Cl. For Sil-Im, Sil-MIm, Sil-EIm-Cl and Sil-Im-NH₂, the eluted amounts of *o*-cresol were less than 0.26 μg and of phenol were less than 0.16 μg . The results revealed that three groups such as short chain ionic liquid, -Cl and -NH₂ had stronger interaction with phenols. Also in this step Sil-Im showed more advantage of adsorption on phenol than *o*-cresol as well as than other sorbents.

From the results of commercial sorbents, acid environment was against adsorption, so in final cleaning step ethanol-HCl (0.1 % vol.) was used to remove rest of substances from sorbents. The total amounts of two phenols in Fig. 4 and Fig. 5 showed that within 3.0 mL of cleaning solvent, only 0.41 μg of *o*-cresol and 0.29 μg of phenol were washed out. More volume (≥ 15.0 mL) of ethanol-HCl solution should be needed to elute all phenols from Sil-Im-NH₂. In conclusion, IL-NH₂ group had the highest interaction with these two phenols.

3.4. Comparison of IL-immobilized silica and IL-physical adsorbed silica

In previous research ionic liquid was physically adsorbed on silica, and then the sorbent was used in separation [26]. In this research, Sil/[EMIm]Cl, Sil/[BMIm]Cl and Sil/[HMIm]Cl were packed into three SPE cartridges. *o*-Cresol was used as the target and the SPE process was the same as previous. After loading, 3.0 mL of water was washed each sorbent and the amount of *o*-cresol in eluates were 0.66 μg , 0.32 μg and 0.12 μg respectively. When the sorbents were eluted using ethanol, all *o*-cresol were removed.

These three ILs had hydrophilic properties, although the property was decreased with the carbon chain increasing. When they adsorbed on silica only weak hydrogen bonds were formed. In loading step, three sorbents had different behaviors. On Sil/[EMIm]Cl, most of *o*-cresol was bonded with [EMIm]Cl, which had short carbon chain. But the behavior on Sil/[HMIm]Cl was quite different. Because of long carbon chain of [HMIm]Cl, silica could not adsorb it well but directly bonded *o*-cresol. In washing step water washed out most of ILs from sorbents, *o*-cresol was taken by IL from Sil/[EMIm]Cl but stayed on silica in Sil/[HMIm]Cl. Then hydrogen bonds were destroyed by ethanol so all *o*-cresol were eluted out. The results revealed that IL-immobilized silicas were quite more stable and could be applied for further tests.

3.5. Effect of different ambient conditions

According to Fig. 6, under room temperature the adsorption amounts of *o*-cresol increased with time increasing, and there was no obviously increasing after 15 min. The result showed that the adsorption equilibrium was obtained at 15 min. Then the temperature of equilibrium system was increased. As shown in Fig. 7, the adsorption amounts increased with increasing temperature until 35 °C. After that it decreased rapidly under higher temperature. The result means high temperature was unprofitable for adsorption. However, under high temperature the test was repeated for 7 times and the adsorption efficiency of Sil-EIm-NH₂ was decreased less than 2 %. The good repetition revealed the high stability of ionic liquid-immobilized silica sorbents.

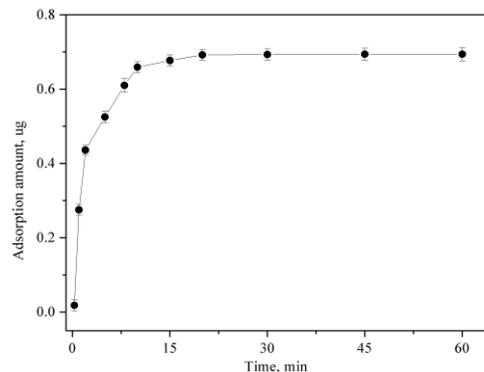


Fig. 6. Effect of adsorption of *o*-cresol with different time on 0.3 g of Sil-EIm-NH₂ under room temperature

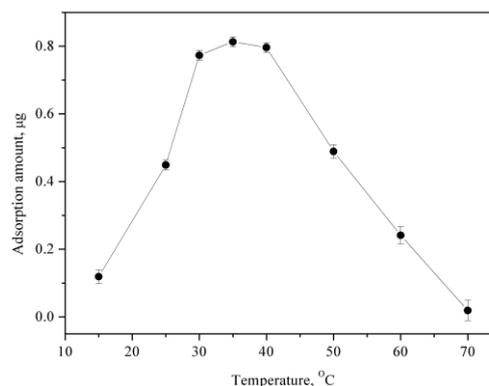


Fig. 7. Effect of adsorption of *o*-cresol under several temperature on 0.3 g of Sil-EIm-NH₂ at 15 min

3.6. Effect of different ions

In waste water, except phenols there were lots of other substances such as high concentration of ionic salts which may affect the efficiency of sorbents. So several ionic salts were dissolved in water, and larger volume of solutions were used to wash phenol from Sil-Im, Sil-EIm-Cl and Sil-EIm-NH₂. The results are listed in Table 1.

Table 1. Effect of different ions on adsorption of phenol

Loading amount	Ion aqueous solutions	Unadsorbed amount of phenol, μg		
		Sil-Im	Sil-EIm-Cl	Sil-EIm-NH ₂
10 μg	H ₂ O (Ref)	0.01	1.21	0.00
	NaCl	0.014	2.42	0.010
	KCl	0.015	2.44	0.010
	MgCl ₂	0.24	3.22	0.021
	AlCl ₃	0.31	3.38	0.023
	CaCl ₂	0.38	3.71	0.031
	FeCl ₃	0.96	5.13	1.22
	Na ₂ CO ₃	0.020	2.45	1.33
	NaHCO ₃	0.010	1.22	0.52
	Na ₂ HPO ₄	0.010	1.24	0.57
NaH ₂ PO ₄	0.52	4.11	6.98	

Firstly, salts with different cation ions were investigated. Compared amount of phenol with pure water,

NaCl and KCl solution washed same amount from Sil-MIm and Sil-EIm-NH₂. For MgCl₂, AlCl₃ and CaCl₂, the aqueous solutions were quite weak acid, so washed amounts were a little more than pure water. For aqueous solution of FeCl₃ the acidity was much higher than other chloride salts [27], so the washing ability was stronger according to the results in Table 1. Additionally, ionic salts which included Cl⁻ anion effect the adsorption ability of Sil-EIm-Cl because the -Cl anions in water blocked the interaction between the sorbent and phenol. Secondly, sodium salts with different anions were tested. When NaHCO₃ and Na₂HPO₄ were used, the pH of aqueous solutions was no changed too much, so washing amounts with these two salt solutions were not difference from pure water. Na₂CO₃ was a base so there was large concentration of -OH group in aqueous solution, and they had competition adsorption with phenol on sorbents. Moreover, the aqueous solution of NaH₂PO₄ was an acid it can wash out the highest amount of phenol from sorbents.

3.7. Comparative evaluation on the analytical performance

Table 2 provides a comparison of the proposed IL-based silica with other commonly methods for the determination of phenols in environmental water samples.

Table 2. Comparison of the analytical performance of the proposed ionic liquid material with literature reported work

Sorbent	Analyte	Sample	Detection method	Spiked concentration, $\mu\text{g/L}$	Recovery, %	Intra-day RSD, %	Inter-day RSD, %	Ref.
IL-based silica (SiO ₂ -ClPrNTf ₂)	1-NAA, 4-CA, 4-CP, 4-MP, 4-NP, isatin and phenazone	Drinking, ground, lake, sea and waste water	Liquid-solid adsorption	25.0–75.0	82.1–99.5	Average 4.9		28
IL-based surfactants (C ₁₂ C ₁₂ Im-Br, et al.)	Phenol, 2-CP, 2,4-DMP, 4-t-BP, 4-OP, 4-CuP, BPA, 4-NP	Waste and tap water	SPME	15.0 and 50.0	85.4–123.0	1.6–13.0	5.8–17.0	29
IL organic-inorganic hybrid nanomaterial (LDH/DABCO)	Phenol, 4-CP, 2,4-DP, 2,6-DP, 2,4,6-TP, 3-AP, 4-AP, 3-NP, 4-NP	Chichih river, Polsangi bridge	SPME	0.01 to 500.0	–	0.02–5.3	–	30
IL-based silica (SilprMimPF ₆)	Phenol, 2,4-DP, 2,4,6-TP, PCP	Tap and river water	SPE	10.0–100.0	47.8–101.4	–	3.7–8.8	31
Silica-titania oxide sol-gel based IL (Si-Ti@CN/IL)	2-CP, 3-CP, 2,4-DP, 2,4,6-TP, 2,3,4,6-TTP, PCP	Tap and lake water, leachate from landfill site	SPE	5.0 and 1000.0	73.4–105.5	2.3–4.7	1.6–4.3	32
Nine IL-silicas (Sil-EIm-NH ₂ , et al.)	Phenol, <i>o</i> -cresol	Seven water and soil samples	SPE	0.0–200.0	86.0–110.0	3.8–5.9	4.1–6.2	This work

1-NAA: 1-naphthylacetic acid; 4-CA: 4-chloroaniline; 4-CP: 4-Chlorophenol; 4-MP: 4-methoxyphenol; 4-NP: 4-nitrophenol; 2-CP: 2-Chlorophenol; 3-CP: 3-Chlorophenol; 2,4-DMP: 2,4-dimethylphenol; 4-t-BP: 4-tert-Butylphenol; 4-OP: 4-octylphenol; 4-CuP: 4-cumylphenol; BPA: bisphenol A; 4-NP: 4-nonylphenol; 4-CP: 4-Chlorophenol; 2,4-DP: 2,4-Dichlorophenol; 2,6-DP: 2,6-Dichlorophenol; 2,4,6-TP: 2,4,6-Trichlorophenol; 2,3,4,6-TTP: 2,3,4,6-tetrachlorophenol; 3-AP: 3-Aminophenol; 4-AP: 4-Aminophenol; 3-NP: 3-Nitrophenol; 4-NP: 4-Nitrophenol; PCP: Pentachlorophenol; SPME: solid phase microextraction, SPE: solid-phase extraction

Normal liquid-solid adsorption method with SiO₂-ClPrNTf₂ material achieved recoveries of 82.1–99.5 % and average RSD of 4.9 % for seven phenols in five water samples [28]. Solid-phase microextraction can detect small amount of phenols in water samples. Trujillo-Rodríguez et al. used the method to extract eight phenols with C₁₂C₁₂Im-Br material from two water samples although the RSD was higher than other researches [29]. Abolghasemi et al. used LDH/DABCO nanomaterial to extract nine phenols from two water samples with RSD of 0.02–5.3 % [30]. Solid-phase extraction was the most widely used method. Su et al. used SilprMimPF₆ and Bakhshaei et al. used Si-Ti@CN/IL to extract several phenols from water and leachate with similar recoveries, and RSDs of Si-Ti@CN/IL were higher than SilprMimPF₆ [31, 32]. Thus, RSDs of all researches in Table 2 were slightly different, the effects of necessary factors-different inorganic salts-were investigated in this work.

3.8. Analysis of phenols in real water and soil samples

Finally the proposed method was applied to determination of two phenols in real water and soil samples. By HPLC detection, the amount of phenols in

10.0 mL of real samples were lower than 2.0 µg. In this case, 0.0–2.0 µg amounts of phenols were added to the samples and analyzed for recovery experiments. Also according to previous results, Sil-Em-NH₂ which exhibited higher adsorption ability and interaction strength was selected as the optimized sorbent. The results in Table 3 showed that except water from Yangtze River, a lake and plant effluent, phenols were not detected in other samples. The recoveries are from 82.00 % to 110.00 %. Moreover, the intra-day and inter-day relative standard deviation (RSD) which were less than 6.14 % showed the high precision of the method.

4. CONCLUSIONS

In this study, nine ionic liquid immobilized silicas were prepared and applied as sorbents in SPE to adsorb two phenols in real water and soil samples. FT-IR and TGA results revealed that the IL groups were successfully immobilized. The performance of IL-immobilized silicas was compared with IL-physically adsorbed on silica, and Sil-ILs were quite more stable. The adsorption abilities of all sorbents were evaluated by SPE with 3.0 mL of water, ethanol and ethanol-HCl (0.1% vol.) as washing, elution and cleaning solvent, respectively.

Table 3. Determine of phenol and *o*-cresol in four water samples and three soil samples by SPE with Sil-EIm-NH₂ as sorbent

Sample	Analyte	Added, µg	Founded, µg	Recovery, %	Intra-day RSD, %, n = 3	Inter-day RSD, %, n = 3
Yangtze River water	Phenol	0.00	0.03 ± 0.001	–	3.87	4.12
			0.51 ± 0.09	96.00	4.35	4.56
			1.05 ± 0.15	102.00	4.58	4.63
			1.49 ± 0.19	97.33	4.44	4.86
			2.01 ± 0.23	99.00	4.87	5.03
Lake water			0.00	–	–	–
			0.49 ± 0.05	98.00	4.68	4.89
			0.98 ± 0.12	98.00	4.21	4.97
			1.43 ± 0.15	95.33	4.45	4.68
Well water			1.87 ± 0.16	93.50	5.01	5.58
			0.00	–	–	–
			0.46 ± 0.04	92.00	4.38	4.38
			0.89 ± 0.13	89.00	4.25	4.99
Plant effluent			1.53 ± 0.13	102.00	4.44	4.68
			1.88 ± 0.12	94.00	4.79	5.02
	0.43 ± 0.02	–	5.01	5.53		
	0.98 ± 0.11	110.00	5.24	5.50		
#1 soil sample	1.32 ± 0.23	89.00	5.12	5.21		
	1.83 ± 0.34	93.33	5.47	5.55		
	2.40 ± 0.12	98.50	5.43	5.64		
	0.00	–	–	–		
#2 soil sample	0.45 ± 0.02	90.00	5.36	5.62		
	0.99 ± 0.13	99.00	5.12	5.38		
	1.47 ± 0.21	98.00	5.66	5.63		
	1.80 ± 0.15	90.00	5.80	5.92		
#3 soil sample	0.00	–	–	–		
	0.43 ± 0.05	86.00	5.38	5.77		
	0.94 ± 0.15	94.00	5.33	5.87		
	1.44 ± 0.14	96.00	5.78	6.00		
#3 soil sample	1.95 ± 0.28	97.50	5.91	6.21		
	0.00	–	–	–		
	0.41 ± 0.03	82.00	5.73	5.91		
	0.91 ± 0.12	91.00	5.23	5.55		
#3 soil sample	1.51 ± 0.17	101.67	5.88	6.01		
	1.99 ± 0.27	99.50	5.76	6.02		

Table 3. Continuation

Sample	Analyte	Added, μg	Founded, μg	Recovery, %	Intra-day RSD, % , n = 3	Inter-day RSD, % , n = 3
Yangtze River water	<i>o</i> -Cresol	0.00	0.12 \pm 0.02	–	5.03	5.17
			0.63 \pm 0.09	102.00	5.02	5.41
			1.11 \pm 0.08	99.00	5.11	5.36
			1.53 \pm 0.21	94.00	5.32	5.78
			2.08 \pm 0.35	98.00	5.32	5.69
Lake water			0.06 \pm 0.002	–	4.88	5.02
			0.56 \pm 0.05	100.00	5.36	5.46
			1.07 \pm 0.12	101.00	5.59	5.66
			1.45 \pm 0.15	92.67	5.45	5.89
			1.97 \pm 0.16	95.50	5.88	5.93
Well water			0.00	–	–	–
			0.44 \pm 0.03	88.00	4.18	4.36
			0.86 \pm 0.14	86.00	4.28	4.69
			1.49 \pm 0.12	99.33	4.24	4.64
			1.85 \pm 0.13	92.50	4.81	4.82
Plant effluent	0.58 \pm 0.12	–	5.23	5.75		
	1.10 \pm 0.21	104.00	5.46	5.73		
	1.61 \pm 0.22	103.00	5.34	5.43		
	2.01 \pm 0.43	95.33	5.69	5.77		
	2.43 \pm 0.20	92.50	5.65	5.86		
#1 soil sample	0.00	–	–	–		
	0.46 \pm 0.03	92.00	5.16	5.42		
	0.89 \pm 0.14	89.00	5.14	5.40		
	1.49 \pm 0.20	99.33	5.46	5.43		
	1.78 \pm 0.14	89.00	5.82	5.95		
#2 soil sample	0.00	–	–	–		
	0.45 \pm 0.01	90.00	5.33	5.83		
	0.99 \pm 0.10	99.00	5.27	5.82		
	1.47 \pm 0.09	98.00	5.83	5.95		
	2.00 \pm 0.23	100.00	5.86	6.11		
#3 soil sample	0.00	–	–	–		
	0.46 \pm 0.02	92.00	5.62	5.78		
	0.95 \pm 0.11	95.00	5.34	5.42		
	1.50 \pm 0.16	100.00	5.76	5.98		
	1.95 \pm 0.23	97.50	5.87	6.14		

Sil-Im-NH₂ showed the highest adsorption ability and under 35 °C for 15 min the largest amount of two phenols was adsorbed and was stable with 7 times repetition. Also the effect of different ions on adsorption efficiency was evaluated, as well as the result of HCl in ethanol, the acidity of FeCl₃ and NaH₂PO₄ solution was reduced the performance of sorbents. Finally, two phenols in water and soil samples were detected using SPE with a 0.0–2.0 μg spiked amount. From the result of recoveries 86.0–110.0 % and RSD less than 6.14 %, Sil-EIm-NH₂ was found as a high efficiency and better selectivity sorbent to separate two phenols from water sample. Also this type of sorbents has a potential for separation of phenol samples with complicated matrices. Therefore, ionic liquid-immobilized silica with SPE can substantially separate phenols from environmental samples and it has a great application value in the detection of a wide range pollutants.

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