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Adsorption efficiency of pentafluorobenzene on ionic liquids-based silicas

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The adsorption of pentafluorobenzene on nine ionic liquid-based silicas was investigated using solid phase extraction. The effects of several variables such as the type of ionic liquid groups, adsorption time, temperatures and water ratio in the solution system were experimentally evaluated. The imidazole-chloride ionic liquid group based silica exhibited the highest adsorption efficiency under the optimized conditions of 5 min adsorption at 30°C in water/methanol (30:70, vol%) solution. In addition, the effects of pH, as well as type and concentrations of chloride salts were investigated. At pH values other than neutral and high salt concentration, the adsorption efficiency was reduced. Finally, the relative standard deviation of less than 5.8% over a 5-day period showed a high precision for the nine tested sorbents.

Keywords: ionic liquids based silica, pentafluorobenzene, adsorption, solid-phase extraction.

INTRODUCTION

Fluorobenzene and its derivatives are widely used as raw materials in pharmaceuticals, agricultural chemicals, and polymer syntheses[1, 2]. However, during the production process and waste discharge, fluorinated organic compounds can enter the ambient environment and can be absorbed through the skin or inhaled. Their toxicities are similar to that of benzene and they are harmful for the liver, kidney and even nervous system[3]. Thus, these harmful chemicals should be removed before entering environment. However, the C-F covalent bonds in fluorobenzene and its derivatives are extremely stable so most chemical oxidants are not strong enough to induce decomposition.

Previous studies have reported the degradation of fluorobenzene by bacteria or photodissociation[4–6]. Although these techniques are accurate, they have several disadvantages including the need for the expensive equipment, high cost operations and well-controlled experimental conditions. For these reasons, the most favorable technique is sorbents adsorption[7–9]. A widely used sorbents is silica, and it has been applied for the adsorption of styryl pyridinium dyes and several organic compounds[10–12]. To increase its adsorption capacity, a silica surface modifier can be introduced[13–16].

Ionic liquids (ILs) are well-known green reaction medias with excellent chemical properties. ILs are receiving significant attention in the fields of analytical chemistry, sample preparation, organic synthesis, extraction and separations[17–21]. Their hydrophobicity, miscibility with several inorganic/organic solvents, and π-π interactions between functional groups are allow ILs to be widely applied as solvents for sorbents modifications[22, 23]. Some studies regarding the preparation of IL modified silica and the extraction of benzene and its derivatives by IL modified materials have been reported in the literatures[24–28]. However, no reports regarding the adsorption of pentafluorobenzene by IL-based sorbents have been published to date.

To investigate the interaction and adsorption mechanism between IL groups and pentafluorobenzene, nine ILs with different polarities and functional groups were modified on a silica surface. The adsorption capacities of all sorbents were evaluated using solid-phase extraction (SPE) under various times, temperatures and pH values. Furthermore, chloride salts are common interferences which can change the ionic strength in aqueous solution and influence the adsorption capacity of sorbents. In addition, the anion of the ILs groups modified on silica in this study is Cl-, so the influence of the type and concentration of chloride salts were considered.

EXPERIMENTAL

Material

Silica (40 μm), (3-chloropropyl)trimethoxysilan, (3-aminopropyl)trimethoxysilane, imidazole, methylimidazole, ethylimidazole, butylimidazole, hexylimidazole, 1-(3-aminopropyl)imidazole, 1,2-dichlorobutane, 1,4-dichlorobutane, 1,6-dichlorohexane and pentafluorobenzene were purchased from Aladdin Inc. (Shanghai, China) and all grades of purity were higher than 98.0%. Organic solvents such as acetone, ethanol, toluene, triethylamine et al. were supported by Beilian Company (Tianjing, China) and purities were higher than 99.0%. Ultrapure water was produced by a purification machine (UPH--I-5, Youpu, China) and all organic solvents should be filtered before use.

Preparation of IL-based silica

Silica was activated by stirring in 10.0% vol HCl aqueous solution for 24 hr and washed by water until pH = 7.0. Then the activated silica was synthesized by following steps shown in Fig. 1. Firstly, chlorine was modified on silica surface by adding (3-chloropropyl) trimethoxysilane as a coupling compounds. Subsequently, 50.0 g of activated silica, 65.0 mL of (3-chloropropyl) trimethoxysilane and 200.0 mL of toluene were well stirred and heated to 100°C in a flask for 12 hr. The obtained powder (3-chloropropyl based silica, Cl-Sil) was then washed with ethanol and fully dried. Then Cl-Sil was separated into two parts. For the aliquot, five flasks were prepared and 5.0 g of Cl-Sil was mixed with 50.0 mL of toluene in each flask. Then 5.0 g of imidazole, methylimidazole, ethylimidazole, butylimidazole, hexylimidazole and 1-(3-aminopropyl)imidazole

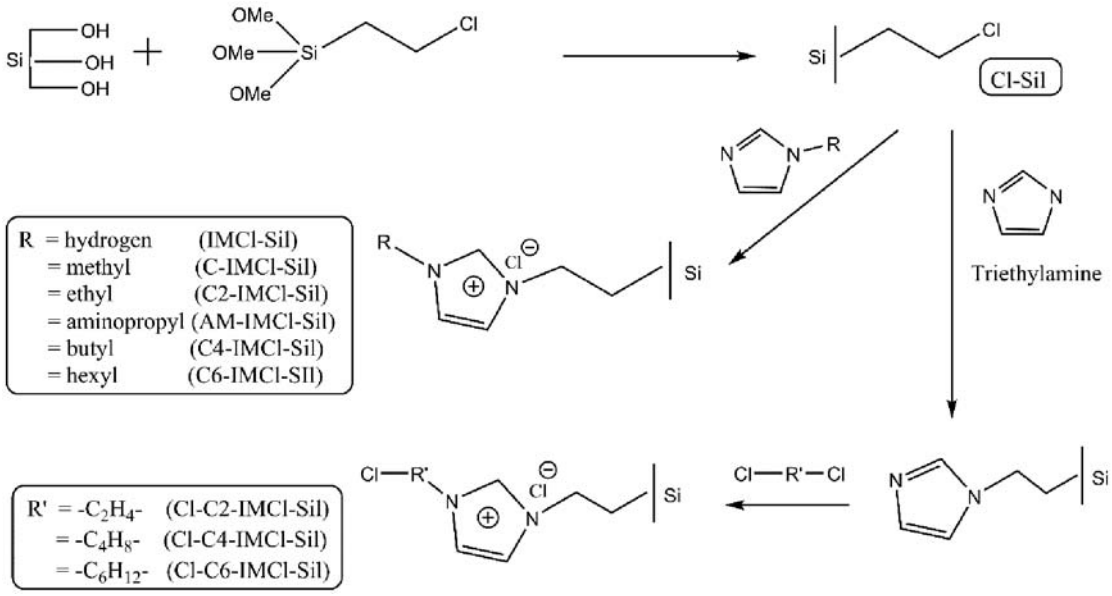

Figure 1. Synthesis process of nine IL-based silicas

were added into each flask respectively. All flasks were heated and refluxed for 12 hr, then different IL group (-IMCl-, imidazole as cation and Cl- as anion) based silicas were obtained and named IMCl-Sil, C-IMCl-Sil, C2-IMCl-Sil, C4-IMCl-Sil, C6-IMCl-Sil and AM-IMCl--Sil. In addition, 10.0 g of silica was mixed with 10.0 mL of (3-aminopropyl)trimethoxysilane in 100.0 mL of toluene for 12 hr under 100°C. The powder of NH_2-Sil was obtained after washing with ethanol.

For the second aliquot, 20.0 g of Cl-Sil, 25.0 g of imidazole, 10.0 g of triethylamine and 100.0 mL of toluene were mixed in a flask. After the mixture was heated to 100°C for 12 hr, the obtained imidazole-based silica was dried at 80°C for overnight. Subsequently, three flasks were prepared with each of them containing 5.0 g of imidazole-based silica, 50.0 mL of toluene and 5.0 g of chloralkane (1,2-dichlorobutane, 1,4-dichlorobutane and 1,6-dichlorohexane, respectively). Afterwards, all flasks were heated and refluxed for 12 hr and three additional IL-based silicas (Cl-C2-IMCl-Sil, Cl-C4-IMCl-Sil and Cl-C6-IMCl-Sil) were obtained. All IL-based silicas were washed with diluted water, ethanol and acetone, and then fully dried for further experiments.

Comparison of adsorption efficiency by SPE

0.2 g of each IL-based silica was packed into SPE cartridge (Ø 0.9 cm, Alltech, Deerfield, IL, USA) and all sorbents were cleaned by water, methanol and acetone alternately. 25.0 mL of pentafluorobenzene solution (0.1 mg/mL) was slowly poured into each SPE cartridge. After fully adsorption, filtrated solutions from cartridges were collected and analyzed by HPLC (LC3000, CXTH, Beijing, China). The chromatographic conditions were: a commercial Wondasil C_{18} column (4.6×250 mm, 5 μm, SHIMADZU, Japan) with methanol/water (80:20, v/v) as mobile phase. The flow rate, UV wavelength, and injection volume were 0.8 mL/min, 250 nm and 5.0 μL, respectively. At last the sorbents were washed by methanol/HCl (99.0:1.0, vol%) solution to remove all adsorbates and initialized by methanol.

Change of adsorption time and temperature

In SPE cartridges, the adsorption time was changed from 0.5 min to 30.0 min by controlling the flow rate of pentafluorobenzene solution. After the adsorption time was confirmed, the temperature was changed from 5°C to 70°C. All experiments were repeated 5 times and analyzed by HPLC.

Effect of water ratio, pH and several chlorine salts

During the adsorption process, 0.1 mg/mL of pentafluorobenzene was prepared in 25.0 mL methanol/water solution, and in it the water ratio was increased from 5.0 vol% to 70.0 vol%. When the ratio was decided, the pH value of the solution was changed from 3.0 to 10.0 by adding HCl or NaOH. Finally the effects of types and concentrations of chlorine salts were evaluated.

RESULTS AND DISCUSSION

Adsorption efficiencies of different sorbents

First of all, the calibration curves were constructed using the chromatographic peak areas measured at seven increasing concentrations ranging from 0.001–0.1 mg/mL. Good linearity was obtained and the correlation equation was $y = 5.48x + 0.10$ ($R^2 = 0.92$) (y is peak area and x is the concentration in solution).

In the SPE process, after reaching adsorption equilibrium of the pentafluorobenzene on the sorbents, the adsorption amounts were detected and the results are shown in Fig. 2. IMCl-Sil exhibited the highest adsorption amount because of the interactions between pentafluorobenzene and the IL group which include electrostatic, π-π, weak hydrogen-bonding and dipole--dipole interactions. With increasing carbon chain length, the adsorption efficiencies of C-IMCl-Sil, C2-IMCl-Sil, C4-IMCl-Sil and C6-IMCl-Sil gradually decreased. The carbon chains had a lower polarity than the IL group, so the increasing carbon chain length weakened the hydrogen-bonding and dipole-dipole interactions. In addition, long carbon chain likely covered the surface of the sorbent and blocked the bonding between the

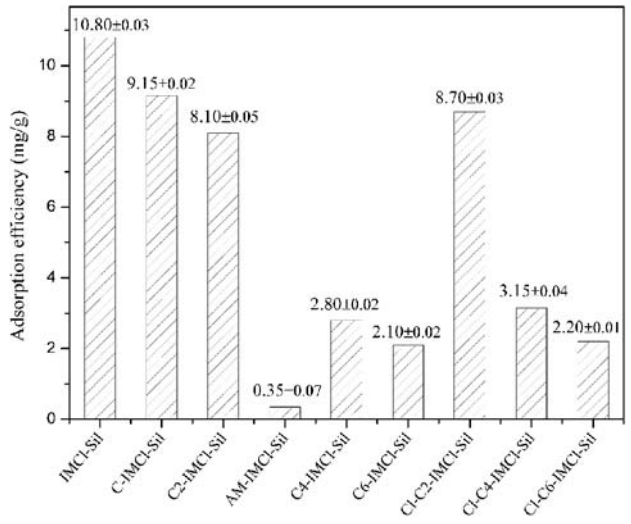

Figure 2. Adsorption efficiencies of pentafluorobenzene on different sorbents. (Methanol solution, adsorption time: 10 min, room temperature)

pentafluorobenzene and IL group. Thus, C4-IMCl-Sil and C6-IMCl-Sil exhibited significantly lower efficiencies than the other sorbents. Furthermore, Cl-C2-IMCl-Sil, Cl-C4-IMCl-Sil and Cl-C6-IMCl-Sil were more efficient compared to the C2-IMCl-Sil, C4-IMCl-Sil and C6-IMCl--Sil. Because both chlorine and fluorine at the end of the carbon chain are electron-withdrawing, a weak interaction between them was established. AM-IMCl-Sil exhibited the lowest adsorption efficiency because the amino group on the IL was highly polar and alkaline, reducing the interaction with pentafluorobenzene. Under the same conditions as AM-IMCl-Sil, no adsorption amount on NH_2-Sil was observed and confirmed this explanation. Therefore, IMCl-Sil, C-IMCl-Sil, C2-IMCl-Sil and Cl-C2-IMCl-Sil were selected for further testing.

Effect of adsorption time and temperature

In Fig. 3, at actual temperature the adsorption amounts on the four sorbents increased with increasing time. For IMCL-Sil and C-IMCl-Sil, stronger interactions with pentafluorobenzene resulted in higher adsorption after 5.0 min. For C2-IMCl-Sil and Cl-C2-IMCl-Sil, which had longer carbon chains, the highest adsorption amounts

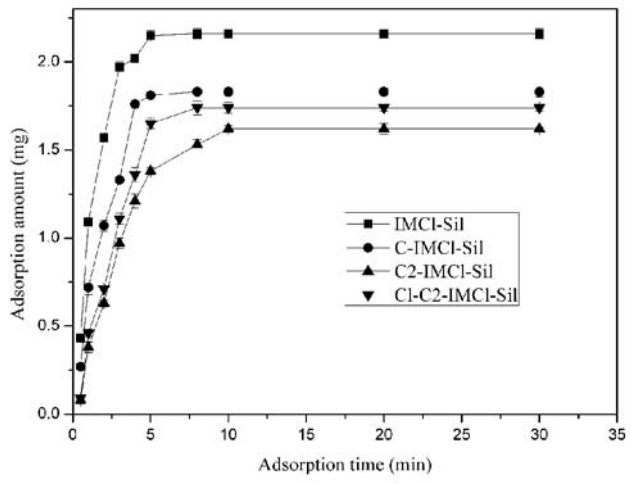

Figure 3. Adsorption amounts of pentafluorobenzene on four sorbents with different time. (Methanol solution, room temperature)

was obtained after 8.0 min (10.0 min for C2-IMCl-Sil). In this case, 5.0 min was selected as the optimal time.

The temperature was also varied and the results are shown in Fig. 4. When temperature increased, pentafluorobenzene contacted the sorbents more frequently resulting in increased adsorption. The higher temperature also caused desorption of the pentafluorobenzene from the sorbents so the overall adsorption amounts decreased. IMCL-Sil and C-IMCl-Sil exhibited the highest adsorption at 30°C and 20°C compared to that of C2-IMCL-Sil and Cl-C2-IMCl-Sil. This indicated that the stability of the adsorption properties of IMCL-Sil and C-IMCl-Sil were better than the other sorbents. Therefore, adsorption with IMCL-Sil and C-IMCl-Sil for 5.0 min at 30°C was selected as the optimized adsorption condition.

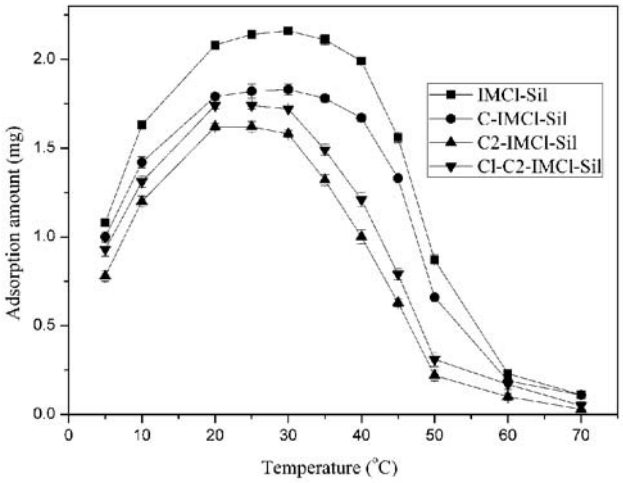

Figure 4. Adsorption amounts of pentafluorobenzene on four sorbents with different temperature. (Methanol solution, adsorption time: 10 min)

Effect of the water ratio and pH of solution system

In previous studies pentafluorobenzene was dissolved in pure methanol, so when water is added the polarity and solubility of the solution system will changed. In Fig. 5, it can be seen that the adsorption on IMCl-Sil and C-IMCl-Sil increased when the water ratio was increased from 5.0 vol% to 30.0 vol%, and at ratio higher than 30.0 vol%, both adsorptions decreased. This could be explained by the polarity of system increasing with higher water ratios and pentafluorobenzene, as a hydrophobic compound, tended to concentrate on the IL groups. However, when the water ratio was higher than 30.0 vol%, more IL groups interacted with water because of their hydrophilicity and desorbed the pentafluorobenzene into solution. Furthermore, the more hydrophobic C-IMCl--Sil can retain more pentafluorobenzene than IMCl-Sil at high water ratios (≥60%). In summary, 30.0 vol% of water in the solution system is optimal for enhanced adsorption efficiency.

Additionally, pH of the water/methanol system was changed from 3.0 to 10.0. In Fig. 5, the best adsorption of IMCl-Sil and C-IMCl-Sil was obtained when pH = 6.0~7.0. When the pH was less than 6.0 the solution included large amount of H^+ and reduced the electrostatic and hydrogen-bonding interactions. When the pH was higher than 7.0, similar to the AM-IMCl--Sil, the basic groups in solution reduced the adsorption

stability. So the neutral solution would not affect the adsorption efficiency.

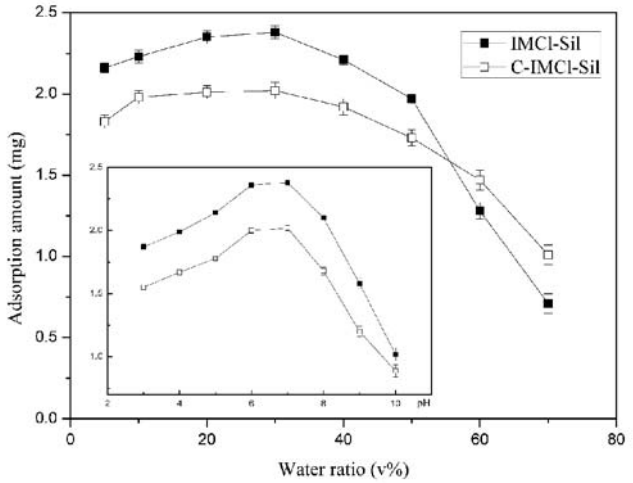

Figure 5. Adsorption amounts of pentafluorobenzene on IMCl-Sil and C-IMCl-Sil with different water ratio and pH. (Water/methanol solution, adsorption time: 5 min, 30°C)

Effect of the type and concentration of salts

Because the anion of IL is Cl^-, chlorine salts in the solution may disturb the adsorption process. Firstly, six inorganic chlorine salts (0.1 mol/L) were added into the pentafluorobenzene solution system with IMCl-Sil (Fig. 6A). NaCl and KCl exhibited almost no effect on the adsorption amount but with increasing concentration of chloride, the adsorption amounts decreased. In addition, NaCl, $MgCl_2$ and $FeCl_3$ from 0.1 to 1.0 mol/L were added (Fig. 6B) and the adsorption amounts showed a significant decreased with the increasing concentration of the three salts. The likely occurred because the interaction between Cl^- and pentafluorobenzene was disturbed when a large amount of Cl^- was present from additional salts (for example three chlorine atoms in $AlCl_3$ molecular or high concentration of $MgCl_2$). Especially for $FeCl_3$, as an acid salt in water solution, the adsorption efficiency was significantly decreased. These results in Fig. 6A and 6B revealed that the additional interfering salts were detrimental to adsorption efficiency.

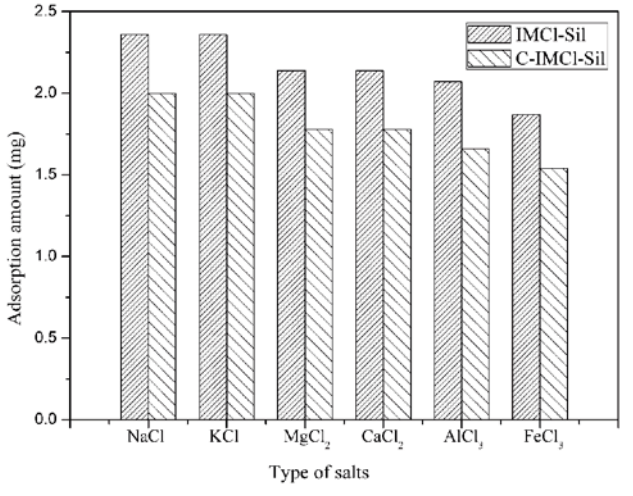

Figure 6a. Effect of different salts on adsorption amounts of IMCl--Sil and C-IMCl-Sil. (Water/methanol (30:70, vol%), adsorption time: 5 min, 30°C)

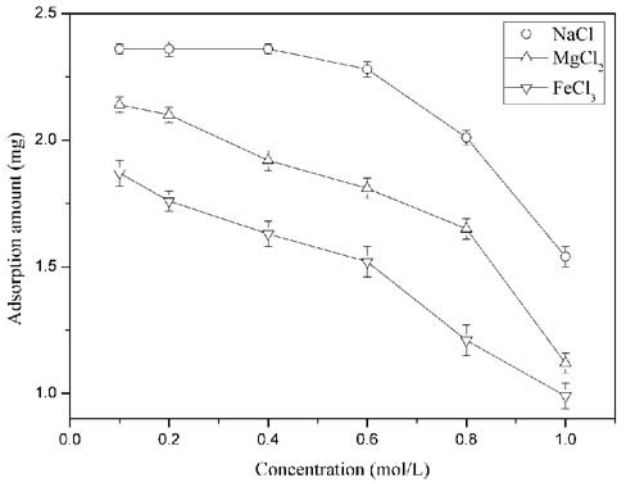

Figure 6b. Effect of different concentration of three salts on adsorption amounts of IMCl-Sil. (Water/methanol (30:70, vol%), adsorption time: 5 min, 30°C)

Analysis method validation

Assays of repeatability calculated as relative standard deviations (RSDs) were performed with all sorbents by SPE process 5 times in a 5-day period. The standard solutions of pentafluorobenzene were diluted and injected until the limit of detection (LOD) was obtained at a signal/noise ratio of 3. The RSD of precision tests and the limit of detections (LOD) on standard solutions were presented in Table 1.

Table 1. RSD and LOD of adsorption amount on nine IL-based silicas

Sorbent	RSD [%]		LOD [μg/mL]
	Intra-day	Inter-day	
IMCl-Sil	2.4±0.2	4.0±0.4	0.03
C-IMCl-Sil	2.3±0.1	4.1±0.5	
C2-IMCl-Sil	2.5±0.3	4.3±0.4	
C4-IMCl-Sil	2.6±0.3	4.8±0.5	
C6-IMCl-Sil	4.0±0.3	5.1±0.6	
Cl-C2-IMCl-Sil	2.6±0.2	4.3±0.4	
Cl-C4-IMCl-Sil	3.1±0.3	4.7±0.5	
Cl-C6-IMCl-Sil	3.7±0.3	5.1±0.6	
AM-IMCl-Sil	4.5±0.2	5.8±0.6	

Table 2 provided a comparison of the proposed IL--based silica with other commonly used methods for adsorption of fluorobenzene compounds. Some studies used theoretical calculations with vibrational analysis to predict chemical bonds between fluorobenzenes and polar solvents, nonpolar solvent even on metal[29–31]. Liquid-solid adsorption was used to adsorb fluorobenzene by active carbon[8]. Although the capacity was high, the interaction mechanism was not explained. Then SPE with different sorbents were applied to adsorb several fluorobenzene compounds[32, 33]. However with simple form of interaction on fiber and silane modified silica, the adsorption capacities were obviously low. The proposed IL-based silicas presented several interactions on pentafluorobenzene with a series of advantages such as green aspect, high sensitivity, high stability and so on. Thus, the proposed IL-based silicas has great potential for adsorption of pentafluorobenzene with a wide range in several fields.

Table 2. Comparison of the proposed method with the previous studies on fluorobenzene compounds

Method	Sorbent/solvent	Target	RSD [%]	LOD	Capacity	Ref
Theoretical calculation	Polar solvents	1,3-DFB, FB	–	–	–	29
Theoretical calculation	Chloroform	FB	–	–	–	30
Theoretical calculation	Copper	Benzene, FB, 1,3-DFB	–	–	–	31
Adsorption	Active carbon	FB	–	–	37.00-388.00 mg/g	8
SPME	Monolithic fiber	FB, 1,2-DFB, 1,2,4-TFB, 1,2,4,5-TEFB, PFB and HFB	4.40-10.80	1.09-5.88 μg/L	1153.00 μg/g	32
SPE	Silane modified silica	56 flavor compounds	1.10-6.10	2.00-77.00 μg/L	-	33
SPE	IL modified silica	PFB	2.30-5.80	0.03 μg/mL	10.80 mg/g	This work

CONCLUSIONS

Adsorption of pentafluorobenzene on nine IL-based silica sorbents by using SPE was investigated. Under 5.0 min at 30°C in water/methanol (30:70, vol%) solution, the order of adsorption efficiencies of nine IL-based silicas were: IMCl-Sil > C-IMCl-Sil > Cl-C2-IMCl-Sil > C2-IMCl-Sil > Cl-C2-IMCl-Sil > Cl-C4-IMCl-Sil > C4-IMCl-Sil > Cl-C6-IMCl-Sil > C6-IMCl-Sil > AM--IMCl-Sil. Also effects of pH and different chlorine salts on adsorption efficiency were evaluated, the results showed that pH lower or higher than neutral and high concentration of salts would reduce the adsorption efficiency. At last the relative standard deviations (RSDs) were tested in a 5-day period and the result less than 5.8% showed a high precision with the nine sorbents.

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