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Graphic Abstract

Sensitive and reliable method for determination of trace Cd(II) and Cu(II) in environmental water based on solid-phase extraction using a novel sorbent coupled with flame atomic absorption spectrometry.
Trace determination of cadmium (Ⅱ) and copper (Ⅱ) in environmental water samples by solid-phase extraction using novel ionic liquid-modified composite sorbent combined with flame atomic absorption spectrometry

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A sensitive and reliable analytical method for determination of trace Cd(II) and Cu(II) in environmental water was developed, based on solid-phase extraction (SPE) using a novel ionic liquid-modified composite as the sorbent combined with detection by flame atomic absorption spectrometry (FAAS). This new sorbent was prepared using a hydrophobic ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIM][PF$_6$]) immobilization onto the surface of nano-TiO$_2$ supported on fine glass beads, and characterized by Fourier transform-infrared spectrum (FT-IR) and thermogravimetric analysis (TGA). Application of the sorbent was investigated for extraction and preconcentration of Cd(II) and Cu(II) from aqueous solutions as their chelates with 2-((5-bromo-2-pyridyl)azo)-5-(diethyl-amino) phenol (5-Br-PADAP). It was found that the adsorption of these chelates on the sorbent followed Langmuir-type isotherm, and the adsorption kinetics were reasonably rapid. This novel SPE adsorbent allowed faster sample loading and higher extraction recovery than conventional nano-TiO$_2$ particles, and could be used repeatedly at...
least for 10 times without significant decrease in recovery of Cd(II) and Cu(II). The parameters that affect the SPE recovery of both metal ions were examined. The optimum conditions, including sample pH, eluent type and volume, also sample and eluent flow rates were obtained. The detection limits were 0.1 and 0.3 µg L\(^{-1}\), and the intra-day relative standard deviations (RSDs, n=6) were 2.0% and 1.4% for Cd(II) and Cu(II), respectively. The proposed method was successfully applied to the determination of trace amount of Cd(II) and Cu(II) in environmental water samples.

**Introduction**

Heavy metals have aroused considerable concern because they are generally toxic, non-biodegradable and accumulative. Therefore, determination and removal of heavy metals in aquatic environments is of tremendous interest. So far several techniques such as flame atomic absorption spectrometry (FAAS),\(^1, 2\) graphite furnace atomic absorption spectrometry (GFAAS),\(^3, 4\) inductively coupled plasma optical emission spectrometry (ICP-OES)\(^5, 6\) and inductively coupled plasma-mass spectrometry (ICP-MS)\(^7, 8\) have been utilized for detection of heavy metal elements in a variety of matrices. Although ICP-OES or ICP-MS can provide great sensitivity and selectivity for metal ion determination, the high cost of operation and maintenance of them limits their practical use. Therefore, FAAS is the most widely used technique because it is cheap, simple, rapid and precise. However, due to the low analyte concentrations and complex sample matrixes, direct determination by FAAS is very difficult in many cases. Thus, a proper sample preparation procedure is often necessary.

The most widely adopted method for separation and preconcentration of trace heavy metal ions is liquid–liquid extraction (LLE).\(^9\) But, LLE is time-consuming, laborious and requires large volumes of expensive and toxic organic solvents. To overcome the drawbacks of LLE, many new techniques for sample pretreatment have been proposed. Among them, the solid-phase extraction (SPE) technique is particularly attractive because of its high preconcentration factor, simple operation, fast phase separation and low cost.\(^10-13\) In order to achieve high recovery and good selectivity, a suitable sorbent is required for SPE procedure. Although silica gel is the most commonly used sorbent, other materials such as nano-particles (NPs) have received increasing attentions due to their higher specific surface areas.\(^14-16\) However, when static batch mode for SPE is used, naked inorganic NPs are inclined
to aggregate, and are not suitable for the complex matrix samples. Therefore, surface modification of NPs is always needed to improve extraction performance. On the other hand, when dynamic extraction mode is utilized, the sample flow rate will be very low since a NPs’s packed SPE column exhibits high back-pressure, and sometimes column blocking will occur. This problem could be alleviated by mixing NPs with some other solid substance such as fine quartz sand.

Ionic liquids (ILs), comprising a bulky cation in combination with any of a wide assortment of anions, have developed as an effective alternative to classical toxic chlorinated solvents for extraction of target analytes from solution, owing to their unique chemical and physical properties including non-volatility, good extractability for various compounds, non-flammability and high thermal stability. Recently, solid sorbent-immobilized-ionic liquids were studied and reported as solid phase adsorbents.

In the present study, a novel sorbent for SPE was prepared using a hydrophobic ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIM][PF$_6$]) immobilization onto the surface of nano-TiO$_2$ supported on fine glass beads. Among heavy metals that exist in the environment, cadmium exposure can be linked to diseases such as osteoporosis, prostate and cancer. On the other hand, copper is toxic at relatively high concentrations. Hence, Cd (II) and Cu (II) were selected for evaluation of the applicability of this new sorbent in extraction and separation of heavy metal ions from aqueous solution. Glass beads was chosen as the support due to their some possible advantages, such as good mechanical and thermal stability, low cost and environmental friendship, and ability of avoiding long sample loading time or column blocking in SPE. The parameters influencing the extraction recovery of Cd (II) and Cu (II) were investigated in detail and optimized. The developed SPE method was applied to the FAAS determination of trace Cd(II) and Cu(II) in environmental water samples with satisfactory results.

**Experimental**

**Chemicals**

2-[(5-bromo-2-pyridyl)azo]-5-(diethyl-amino) phenol (5-Br-PADAP) and glass beads (110-150 µm in diameter) were obtained from Tianjin Damao Chemical reagent Factory (Tianjin, China), and [OMIM][PF$_6$] (99%) was purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (Lanzhou, China). Purified water (18.2 MΩ cm) produced with a TKA Smart2Pure system (NiedereIlbert, Germany) was used throughout. Hydrochloric acid, nitric acid and ammonia solution (28%) were guaranteed reagent grade, and other reagents were analytical reagent grade.

5-Br-PADAP solution (0.5 g L$^{-1}$) was prepared by
dissolving 0.05 g of 5-Br-PADAP in 100 mL of ethanol-water solution (1:1, v/v) and was stored in the dark.

Stock standard solutions of cadmium and copper (1000 mg L$^{-1}$) were obtained from National Iron and Steel Material Test Center, China. Working standard solutions were prepared by appropriately diluting the stock solution with purified water.

**Apparatus**

The Fourier-transform infrared spectroscopy was recorded with a Bruker VECTOR 22 spectrometer (Bruker, Germany). The thermogravimetric analysis (TGA) was performed using a TG 209 thermal gravimeter (Netzsch, Germany). Determination of cadmium and copper was carried out using a Hitachi Z-2000 (Hitachi, Japan) flame atomic absorption spectrometer (FAAS) equipped with a deuterium background correction and an air-acetylene flame.

**Samples**

Four types of environmental water samples were analyzed to assess the applicability of the developed analytical method. These water samples were collected from the Peal River (Guangzhou, China), the Center Lake (Higher Education Mega Center, Guangzhou, China), a pond and a well (Panyu, China), respectively. All the water samples were taken into pre-cleaned polyethylene bottles, and filtered through 0.45 µm nylon membranes in order to remove suspended solids. The filtered samples were adjusted to pH 2 with 1M HNO$_3$ and stored at dark conditions at 4 °C until analysis.

**Sorbent Preparation**

**Preparation of Nano-TiO$_2$ supported on glass beads**

The glass beads were carefully precleaned prior to coating. 10 mL tetrabutyl titanate was dissolved in 12.5 mL absolute ethyl alcohol, and a mixture of 0.25 mL HCl, 12.5 mL absolute ethyl alcohol and 0.5 mL purified water was slowly added to the solution with agitation. When a sol was formed, 10 g of clean fine glass beads was soaked into the sol for 10 min. Then the beads were fished out, followed by calcination at 450 °C for 2 h.

**Preparation of [OMIM][PF$_6$] -modified nano-TiO$_2$ supported on glass beads**

10.0 g of nano-TiO$_2$ coated glass beads was first activated with 50 mL of chloride acid–water (50:50, v/v), then suspended in dry toluene (10 mL), followed by addition of 3-aminopropyl triethoxysilane (0.3 mL) and triethylamine (0.1 mL). The mixture was refluxed with agitation for 24 h at 110 °C. After filtering, the obtained material was washed successively with toluene and purified water, then dried, and thereafter placed in a flask containing [OMIM] [PF$_6$] (5.0 g) and dry toluene (10 mL). The mixture was radiated for 5 min with a
microwave output power of 230 W, followed by filtering. The resultant was washed with acetone and then purified water, and finally dried.

**Extraction and determination**

3.0 g of the prepared sorbent was packed in a short glass tube (3 mL). A 100 mL solution containing Cd(II) and Cu(II) was adjusted to pH 8 using 0.1 mol L⁻¹ NH₃·H₂O and 0.1 mol L⁻¹ HCl. Then 0.4 mL 0.5 g L⁻¹ 5-Br-PADAP was added to the solution to form chelates with Cd(II) or Cu(II). After shaking for 5 min, the sample solution was loaded to the column and passed through it at a flow rate of 2.5 mL min⁻¹. The chelates retained on the column were eluted with 5 mL 2.0 mol L⁻¹ HCl, and the concentrations of cadmium and copper in the eluent were then determined by FAAS.

**Results and discussion**

**Characterization of the sorbent**

Fig. 1 shows the FT-IR spectra of nano-TiO₂ supported on glass beads and the new composite sorbent. Significant differences in wave numbers and intensities of the absorption bands were observed in the spectra. The peak at 1556 cm⁻¹ is assigned to the C=C stretching of the imidazolium ring. The absorbance in the range of 2800-3000 cm⁻¹ is related to the C–H stretching of the octyl groups. The strong peak at 846 cm⁻¹ is attributed to the P–F stretching of the anion. These results indicated the successful modification of the nano-TiO₂ particles with [OMIM][PF₆]₂⁵.

![Fig. 1 FT-IR spectra of nano-TiO₂ supported on glass beads (a) and [OMIM][PF₆]-modified nano-TiO₂ supported on glass beads (b)](image)

![Fig. 2 Thermogram of [OMIM][PF₆]-modified nano-TiO₂ supported on glass beads](image)
The thermogram of the prepared sorbent is represented in Fig. 2, in which the mass loss at about 420 °C is associated with the thermal decomposition of the ionic liquid used, showing further confirmation of the immobilization of [DnBIM][PF$_6$] onto the surface of nano-TiO$_2$ supported on the glass beads.

From scanning electronic microscopy observation, it was found that the diameter of TiO$_2$ particles supported on glass beads was in the range of 50-100 nm.

**Adsorption properties of the sorbent**

**Adsorption isotherms**

An adsorption isotherm shows the relationship between metal ion concentration in solution and the amount of metal ion adsorbed on the sorbent at a given temperature, which can help describe the adsorption mechanism. For the adsorption isotherm experiments, 3.0 g of the developed sorbent was dispersed into 100 mL of aqueous solutions containing Cd(II) and Cu(II) of 20-200 mg L$^{-1}$ with magnetic stirring. When adsorption equilibrium was reached, the remaining content of Cd(II) and Cu(II) in the solutions were analyzed by FAAS. The amount of adsorbed Cd(II) or Cu(II) on the sorbent was calculated by the following equation:

$$q_e = (C_0-C_e)V/m$$

where $q_e$ is the amount of adsorbed Cd(II) or Cu(II) per gram of the sorbent at equilibrium (µg g$^{-1}$), $C_0$ and $C_e$ are the initial and equilibrium concentrations of Cd(II) or Cu(II) (µg L$^{-1}$) respectively, $V$ is the solution volume (L) and $m$ is the sorbent mass (g).

When the Langmuir and Freundlich models were applied to fit the adsorption data, the values of $R^2$ were found to be 0.9859 and 0.9226 for Cd(II), and 0.9727 and 0.8839 for Cu(II), respectively, suggesting that both the adsorption of Cd(II) and Cu(II) chelates with 5-Br-PADAP onto the prepared new sorbent followed Langmuir-type isotherm.

**Adsorption kinetics**

The adsorption kinetics of the new sorbent to Cd(II) and Cu(II) chelates were investigated using column experiments. The sample flow rate was set at 1.5, 2.0, 2.5, 3.0, 3.5 and 5.0 mL min$^{-1}$, respectively. The kinetic data were fitted to pseudo-second-order and Elovich models. The pseudo-second-order model gave better fit with higher $R^2$ values for both Cd(II) and Cu(II) chelates.

![Fig. 3 Kinetics of adsorption of Cd(II)-5-Br-PADAP chelate (a) and Cu(II)-5-Br-PADAP chelate (b) on [OMIM][PF$_6$]-modified nano-TiO$_2$ supported on glass beads](image-url)
variation of adsorption as a function of sample flow rate for Cd(II) or Cu(II) is shown in Fig. 3. It is evident that the flow rate in the range of 1.5–3.0 mL min\(^{-1}\) had no significant effect on the recovery of Cd(II) or Cu(II), indicating that the adsorption kinetics of the novel sorbent were reasonably fast to the Cd(II) and Cu(II) chelates.

**Reusability**

Reusability is an important factor for a sorbent in evaluation of its widespread usage in laboratory. The reusability of the prepared composite sorbent was tested after several loading and elution steps. The results showed that the sorbent could be used for SPE repeatedly at least for 10 times without significant decrease in recovery of Cd (II) and Cu (II), thus reducing the cost for batch sample pretreatment.

**Optimization of SPE conditions**

In order to evaluate the applicability of the prepared sorbent for enrichment and separation of Cd(II) and Cu(II) from aqueous samples, parameters that might affect the solid phase extraction efficiency for Cd(II) and Cu(II) were examined and optimized, such as sample pH, sample flow rate, eluent type and volume, and coexisting ions. All the optimization experiments were conducted three times, using spiked purified water samples.

**Selection of sample pH**

The effect of sample pH was studied in the range of 6-11. Fig. 4 shows the dependence of extraction recoveries of Cd(II) and Cu(II) on sample pH. As can be seen, the recoveries enhanced drastically with the increase in pH from 6 to 8 and then decreased gradually at pH 9-11. In this work, pH 8.0 was selected for further works.

**Selection of 5-Br-PADAP concentration**

The effect of 5-Br-PADAP concentration on the extraction recoveries for Cd(II) and Cu(II) was tested in the range from 0.00005 % to 0.0005 % (w/v). The results showed that the recovery for each ion increased along with 5-Br-PADAP concentration from 0.00005 % to 0.00015 %, and then kept almost unchanged up to 0.0005 %. Based on these results, 0.0002 % (w/v) was employed as the optimal 5-Br-PADAP concentration.

![Fig. 4 Effect of sample pH on recovery of Cd(II) (a) and Cu(II) (b)](image-url)
Selection of sample flow rate

The influence of sample flow rate on the recovery for Cd(II) and Cu(II) was examined in the range of 1.5–5 mL min⁻¹. The results shown in Fig.3 demonstrated that quantitative recovery of Cd(II) and Cu(II) could be achieved when sample flow rate was less than 2.5 mL min⁻¹. Thus, all subsequent experiments were performed at a flow rate of 2.5 mL min⁻¹.

Selection of eluent type and volume

It can be seen from Fig.4 that an acid reagent could be used as the eluent for Cd(II) and Cu(II) chelates of 5-Br-PADAP. Therefore, various concentrations of HCl and HNO₃ were studied for elution of the retained chelates from SPE column at a flow rate of 1.0 mL min⁻¹. The results revealed that HCl was more suitable than HNO₃ as the eluting reagent, and the complete desorption of the chelates of Cd(II) and Cu(II) could be obtained when 2 mol L⁻¹ HCl was adopted. The effect of eluent volume on recovery of the analytes was also examined. It was found that 5 mL of 2 mol L⁻¹ HCl could efficiently elute off the adsorbed chelates of Cd(II) and Cu(II) with 5-Br-PADAP.

Interference study

In order to demonstrate the selectivity of the developed SPE protocol for determination of Cd(II) and Cu(II) at trace levels, the effects of common coexisting ions on the analytical signals of Cd(II) and Cu(II) were studied. In these experiments, solutions of 10 µg L⁻¹ of Cd(II) and Cu(II) containing the interfering ions were treated according to the procedure described in 2.4. The results indicated that within a ±5% error range, 400 mg L⁻¹ K⁺ and Na⁺, 200 mg L⁻¹ Ca²⁺ and Mg²⁺, 150 mg L⁻¹ SO₄²⁻ and Cl⁻, 10 mg L⁻¹ Al³⁺ and V(⁵⁺), 5 mg L⁻¹ Fe³⁺, 2 mg L⁻¹ Co²⁺ and Ni²⁺, and 1 mg L⁻¹ Pb²⁺ and Zn²⁺, had no significant interferences with the analysis of Cd(II) and Cu(II).

Analytical performance

Under the optimized experimental conditions, the performance of the proposed analytical method was evaluated. It was found that the calibration curve was linear in the range of 0.3–60 and 1–100 µg L⁻¹, with the R² value of 0.9979 and 0.9986 for Cd(II) and Cu(II), respectively. These results indicated that a good linear regression was established between the absorbance and the concentrations.

The limit of detection (LOD, defined as 3 S_b/k, where S_b and k are the standard deviation of the blank measures and the slope of the calibration curve, respectively) were 0.1 and 0.3 µg L⁻¹, while the limit of quantification (LOQ, defined as 10 S_b/k) were 0.3 and 0.9 µg L⁻¹ for Cd(II) and Cu(II), respectively.
The reproducibility of the developed method was studied by repeated determination of 10.0 µg L\(^{-1}\) of Cd(II) and Cu(II) six times in a day (intra-day precision), whereas inter-day precision was tested for 6 days. The results showed good precisions with relative standard deviation (RSD) of 1.4–2.0 % (intra-day precision) and lower than 4.0 % (inter-day precision). The results showed that the developed method had good precision for quantitative analysis.

Analytical characteristics of the developed method are shown in Table 1. It is obvious that the proposed approach has a high sensitivity and good reproducibility for detection of trace cadmium and copper in aqueous samples.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Cd</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear dynamic range (µg L(^{-1}))</td>
<td>0.3—60</td>
<td>1.0—100</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.9979</td>
<td>0.9986</td>
</tr>
<tr>
<td>LOD (µg L(^{-1}))</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>LOQ (µg L(^{-1}))</td>
<td>0.3</td>
<td>0.9</td>
</tr>
<tr>
<td>Intra-day RSD (%; n=6)</td>
<td>2.0</td>
<td>1.4</td>
</tr>
<tr>
<td>Inter-day RSD (%; n=6)</td>
<td>3.9</td>
<td>3.0</td>
</tr>
</tbody>
</table>

spiked with 1.00 µg L\(^{-1}\) of Cd(II) and 2.50 or 10.0 µg L\(^{-1}\) of Cu(II) were analyzed using the same procedure. The average recoveries for Cd(II) and Cu(II) were 90.5% and 87.7% for river water sample, 88.0% and 92.4% for lake water sample, 93.3% and 92.7% for pond water sample, and 88.9% and 97.9% for well water sample, respectively. Therefore, the matrix effect from river water, lake water, pond water and well water on the accuracy of the developed method was not significant. These analytical results show that the developed sorbent can be used for effective extraction and detection of trace Cd(II) and Cu(II) in aqueous samples.

For comparison, a SPE column packed with naked nano-TiO\(_2\) particles was also prepared and used for pretreatment of the water samples. It was found that it

### Table 1  Analytical characteristics of the proposed method
would take more than 60 min to pass 100 mL river water through the column, and the average spiked recovery for Cd(II) and Cu(II) were 59% and 78%, respectively. Therefore, the new composite sorbent allowed faster sample loading and higher solid-phase extraction recovery for the chelates of Cd(II) and Cu(II) than commonly used nano-TiO$_2$ particles.

**Comparison with other methods**

Table 3 compares the dynamic linear ranges, LODs, RSDs for the proposed method and other previously reported techniques for determination of trace Cd(II) and Cu(II) in environmental water samples. All of them employ SPE for sample separation and preconcentration, followed by FAAS determination. However, the sorbents used for SPE are different, including ionic liquid–modified nano-TiO$_2$ supported on glass beads (this work), diphenylcarbazide-modified nanoporous silica, gallic acid-modified silica gel, diaminobenzidine-coated silica gel, pyridinedicarboxaldehyde-functionalized resin and thiourea-modified silica gel. As listed in Table 3, compared to the existing techniques, the developed method has the lowest LODs, wider linear ranges and comparable RSDs. Therefore, the new sorbent is a powerful alternative to other sorbents for extraction and determination of Cd(II) and Cu(II) at low levels in water samples.

**Conclusions**

[OMIM][PF$_6$]–modified nano–TiO$_2$ supported on glass beads has been synthesized as a novel reusable sorbent for solid phase extraction, which exhibits great potentiality for the enrichment and separation of trace Cd(II) and Cu(II) from aqueous solutions as chelates with 5-Br-PADAP. SPE column packed with this new sorbent can overcame some drawbacks of common nanoparticle-packed column such as slow sample loading, column blocking, and low extraction recovery for heavy metal ions. Coupled with FAAS, a sensitive, reliable, cheap and environmentally friendly method for trace determination of Cd(II) and Cu(II) was established and applied to environmental water samples with satisfactory results, indicating that the developed method can act as an alternative to some techniques with expensive instrumentation and operation such as ICP-MS.

**Acknowledgements** The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (No.20875018).
Table 2 Analytical results of Cd(II) and Cu(II) in environmental water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cd</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Added (µg L(^{-1}))</td>
<td>Found (µg L(^{-1}))</td>
</tr>
<tr>
<td>River water</td>
<td>0</td>
<td>0.68±0.02</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.52±0.05</td>
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<tr>
<td>Lake water</td>
<td>0</td>
<td>nd(^b)</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.88±0.04</td>
</tr>
<tr>
<td>Pond water</td>
<td>0</td>
<td>0.35±0.01</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.26±0.04</td>
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<tr>
<td>Well water</td>
<td>0</td>
<td>0.52±0.01</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.35±0.05</td>
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</table>
Table 3  Comparison with other previously reported techniques

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Linear range (µg L⁻¹)</th>
<th>LOD (µg L⁻¹)</th>
<th>RSD (%)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Cd</td>
<td>Cu</td>
<td>Cd</td>
</tr>
<tr>
<td>Diphenylcarbazide-modified nanoporous silica</td>
<td>1-100</td>
<td>1-150</td>
<td>0.15</td>
</tr>
<tr>
<td>Gallic acid-modified silica gel</td>
<td>0.2-1.0</td>
<td>0.4-2.6</td>
<td>0.65</td>
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<tr>
<td>Diaminobenzidine-coated silica gel</td>
<td>0.1-10</td>
<td>0.5-100</td>
<td>4</td>
</tr>
<tr>
<td>Pyridinedicarbboxaldehyde-functionalized resin</td>
<td>1.0- 4.0</td>
<td>2.0-8.0</td>
<td>0.13</td>
</tr>
<tr>
<td>Thiourea-modified silica gel</td>
<td>–</td>
<td>–</td>
<td>0.81</td>
</tr>
<tr>
<td>Ionic liquid-modified nano-supported on glass beads</td>
<td>0.3-60</td>
<td>1-100</td>
<td>0.1</td>
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</table>

References

361.


