Preparation and Characterization of Activated Carbon Based Rice Husk and Its Use for Preconcentration of Pt(II)

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Article history: Received 9 September 2013, Received in revised form 29 September 2013, Accepted 8 October 2013, Published 10 October 2013.

Abstract: Activated carbon based rice husk (KLC) was prepared using chemical activation method which consisted of potassium hydroxide treatment. It was employed as a low cost and effective solid phase material for the separation and preconcentration of Pt(II), prior to determination by electrothermal atomic absorption spectrometry (ETAAS). Pt(II) was collected on KLC after complexation with allyl thiosemicarbazide at pH 4. The complex was then desorbed with dimethylformamide and determined by ETAAS. KLC sorbed Pt (II) at pH 4 with preconcentration factor of 100 fold in less than one minute (t1/2). Common other ions did not interfere except Co(II) which was eliminated by EDTA. The linear calibration range for the proposed method was 0.15-120 µg L⁻¹. The limit of detection (LOD) is 0.11 µg L⁻¹ and the relative standard deviation (RSD) for 10 replicate measurements at 10 µg L⁻¹ Pt(II) was 1.82%. The method was successfully applied to the extraction and determination of Pt in spiked water and geological samples.

Keywords: Activated carbon, rice husks, solid phase extraction, platinum.
1. Introduction

The increased medical and industrial use of platinum has led to a growing need for its determination in biological and environmental materials. Platinum is mainly used in automobile exhaust catalytic converters and a catalyst in a wide variety of processes such as nitric acid production and petroleum reforming. Platinum also finds applications in chemical and glass industries as cladding on account of anticorrosion properties and in electronic industry as material for electrodes, contacts and resistance wires.

Another field of application of platinum is the manufacture of jewelers. Some platinum coordination compounds are used in chemotherapy for some types of cancer. Soluble platinum compounds are toxic and chronic industrial exposure to them is responsible for the syndrome called platinosis. Release of platinum from automotive catalytic converters has given rise to environmental and health concerns. Small concentration changes of platinum in the environment and human body must be closely monitored since its environmental and biological impacts are still unclear and have been the object of several studies [1, 2]. Therefore, ultra-sensitive analytical methods are very desirable, since normal concentrations of the metal in biological samples are below the limit of detection of most analytical techniques [3]. A separation/preconcentration step is often applied in order to remove matrix interferences and preconcentrate the analyte to a level which can be reliably determined.

Various methods have been developed for platinum separation and preconcentration from environmental and biological matrices, e.g., liquid–liquid extraction [4,5], sorption on XAD-4 resin [6–8], on aminopyridine resin [9], on activated charcoal [10], on activated alumina [11,12], on C18-bonded silica gel [13] or on silica gel functionalised with aminopropyltriethoxysilane [14]. Most of these methods are off-line and require considerable sample manipulation and long analysis time.

Activated carbon (AC) has been widely used for the removal of metal ions from aqueous samples. AC is a good adsorbent as it has high surface area and porous structure, high adsorption capacity and a certain degree of reactivity due to the presence of appropriate functional groups [15]. However, production of commercial AC is still expensive and increasing attention has been given by researches in order to investigate more economical methods for its preparation. As AC can be produced from any carbonaceous materials that are rich in elemental carbon and low proportion of inorganic components, natural materials or certain easily-available agricultural by-products may have potential to be used as the precursors of AC. Research has been conducted on rice husk to produce AC [16,17]. Considering the availability of agricultural by-products, rice husk is a good alternative for the production of cheap AC as adsorbent.

Rice husk is the by-product of the rice milling industry. It represents about 20% of the whole rice produced, on weight basis of the whole rice [18]. Rice husks have been used in manufacturing block
employed in civil construction as panels and was used by the rice industry itself as a source of energy for boilers [19]. However, the amounts of rice husk available are so far in excess of any local uses and have posed disposal problems. The rice husk compositions [18] are: 32.24% cellulose, 21.34% hemicellulose, 21.44% lignin, 1.82% extractives, 8.11% water and 15.05% mineral ash. The mineral ash is 94.5–96.34% SiO₂.

The aim of the present study is to produce a low-cost KOH-activated carbon based rice husk (KLC) and to evaluate the feasibility of its use for removal of Pt(II) from aqueous solution.

2. Experimental

2.1. Reagents and Solutions

All aqueous solutions were prepared with ultrapure water that had been obtained by Milli-Q water purification system (Millipore, Bedford, MA, USA). Reagents used were of analytical grade from Sigma-Aldrich (St. Louis, MO, USA) or Merck (Darmstadt, Germany). The laboratory glassware was kept overnight in 10 % v/v HNO₃ solution. Before the use, the glassware was washed with deionized water and dried in a dust free environment. The stock standard solution (1000 µg mL⁻¹) of Pt(II) was prepared by dissolving the appropriate amounts of Na₂PtCl₄ in 1 mol L⁻¹ HCl. Working standard solutions were prepared daily from the stock solution by the dilution with 1 mol L⁻¹ HCl. One mol L⁻¹ solution of allyl thiosemicarbazide (ATSC) was prepared by dissolving appropriate amount in 100 mL ethanol. Buffer solution was prepared with 0.5 mol L⁻¹ sodium acetate and the pH (1-6) was adjusted using 0.1 mol L⁻¹ NaOH and/or HCl.

2.2. Preparation of KOH-activated Carbon from HF-leached Rice Husks

Rice husks (RH) from the rice mill of Damanhour City (Egypt) was used as a raw material. Firstly, rice husks was washed with distilled water to remove dust and other impurities, and then dried at 110 °C for 24 hr, and finally the dried product was ground. Dried RH was leached with hydrofluoric acid, HF, the acid solution volume (25%AR) to mass ratio was 3:1, the slurry was stirred for 2 hr, and then the solid was separated and washed with distilled water followed with drying at 110 °C for 24 hr. The last dried leached RH was then carbonized in stainless steel tube (40mmx500mm) in absence of oxygen at 600 °C for 4hr., after cooling carbonized product soaked in KOH with ratio 1:3 (weight of carbonized sample: weight of KOH), in presence of least amount of water able to dissolve KOH, soaking process for 48hr. The last mixture was then dried, followed by calcinations at 800 °C for 3 hr in the stainless steel tube in closed system. After cooling to room temperature, the activated product was
washed with distilled water several times, dried, ground and sieved to the fraction of size 0.3-0.5 mm, and stored in clean dry glass bottles.

2.3. Instrumentation

Micrograph of KLC sample was obtained using SEM model Quanta 250 FEG (Field Emission Gun) attached with EDX unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 kV., magnification 14x up to 1000000 and resolution for Gun. Prior to sample analysis, the sample were dried and out gassed at 120 °C for 4 hr. The IR spectra were recorded using a Mattson 5000 FTIR Spectrophotometer. The pH was adjusted using Hanna instrument model 8519 digital pH meter. The Perkin-Elmer® AAAnalyst™ 800 atomic absorption spectrometer (Shelton, CT, USA), with a longitudinal Zeeman background correction furnished with a transversely heated graphite atomizer (THGA) was used for determination of Pt. The operating parameters were set according to the manufacturer recommendation.

2.4. Textural Characterization of the Activated Carbon Sample

The textural characterization of activated carbon sample (KLC) was based on the corresponding N2-adsorption isotherms, determined at -196 °C using a conventional volumetric apparatus. Prior to adsorption the carbon sample was heated at 200 °C and a reduced pressure of 10^-5 torr for 4 hr.

_Determination of pHPzc:_ initially, 40 mL of NaCl (0.01 mol L^-1) was placed in several closed flasks. The pH within each flask was adjusted to a value between 2-12 by adding either 0.1 mol L^-1 HCl and/or 0.1 mol L^-1 NaOH. Then, 120 mg of KLC was added to each flask, the flasks were agitated for 48hr, the final pH was then measured. The pHPzc is defined as the point where the curve pH_{final} versus pH_{initial} crosses the line pH_{final} = pH_{initial} [20].

2.5. Water Samples

Tap, river, brackish, sea and industrial waste water samples were collected in polytetrafluoroethylene containers, filtered using a 0.45 μm Millipore cellulose nitrate membrane to remove suspended particulate matter, and stored in the dark at 4 °C. Tap water was obtained from the laboratory, and river water was collected from river Nile water from Mansoura city (Egypt). Brackish water was taken from Damietta Bridge (Egypt). Sea water was collected from Mediterranean sea from Ras Elbar (Egypt). The domestic wastewater was provided from Ras El-Bar Sewage Wastewater Treatment Plant (Egypt).

2.6. Geological Samples
The road dust and rock samples were collected from different area in Sakaka city, Saudi Arabia. The samples were dried at 90 °C for 2 hr, ground, passed through a sieve of 120 meshes and homogenized. 2.0 g of each sample was accurately weighed into a 100 mL of beaker. In order to decompose it, 10 mL of aqua regia was added to the beaker and the mixture was heated almost to dryness. Then, 5 mL of aqua regia and 2 mL H₂O₂ were added again to the residue and the mixture was evaporated to dryness. Finally, double distilled water was added to beaker and then the insoluble part was filtered through a filter paper and washed with double distilled water. The pH was adjusted to about 3 using 1 mol L⁻¹ NaOH and the total volume was made up to 50 mL with double distilled water in volumetric flasks.

2.6. Batch Method

In a 250 mL glass-stoppered bottle, 100 mL solution containing 10 µg L⁻¹ Pt (II) and 50 mL of 2x10⁻⁵ mol L⁻¹ ATSC were taken. After adjusting the pH to 4, 50 mg of KLC was added. The mixture was shaken for 10 min, filtered, washed with deionized water and the sorbed metal ion was eluted with 1.0 mL of DMF and the desorbed ion was determined by aspiration the solution into the ETAAS.

2.7. Column Method

KLC (100 mg) was swollen for 24 hr, packed in a glass column (40 mm length and 6 mm diameter) the column high (adsorption bed) was about 2.5 cm, preconditioned with 5 mL (0.2 mol L⁻¹ HCl) at flow rate of 3 mL min⁻¹, controlled by peristaltic pump and washed with deionized water to become acid free. To 100 ml sample solution was added 50 ml of 2x10⁻⁵ mol L⁻¹ ATSC. The pH was adjusted to 4 with addition of acetate buffer. This solution was passed through the column at flow rate of 3 mL min⁻¹. 5 mL bidistilled water was passed through the column to remove any uncomplexing metal ions. Passing 1.0 mL of DMF at 2.0 mL min⁻¹ eluted the Pt(II) complex retained on column. The eluate was collected and the Pt(II) concentration was determined by ETAAS.

3. Results and Discussion

3.1. Surface Area and Porosity of KLC

Fig. 1 (A) shows the adsorption isotherm of nitrogen at -196 °C which is a mixture of type I and type II of the Brunauer, Deming, and Teller (BDDT) classification [21]. The hysteresis loop exhibited by KLC may be due to capillary condensation in the micropores [21]. Applying Brunauer-Emmett-Teller (BET) equation (in the relative pressure range 0.05-0.30)

$$\frac{P/P_0}{V(1-P/P_0)} = \frac{1}{V_m} + \frac{C - 1}{V_m}(P/P_0)$$

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Where, \( V \) is the volume of nitrogen (cm\(^3\)/g) adsorbed at equilibrium pressure, \( P^0 \) is the saturation vapor pressure, \( V_m \) is the monolayer capacity (cm\(^3\)/g), and \( C \) is called BET-constant. Fig. 1 (B) shows the linear plot of \( \frac{P/P^0}{V(1-P/P^0)} \) against \( P/P^0 \) giving a slope and intercept enable us to calculate specific surface area \( S_{BET} \) (m\(^2\)/g), total pore volume \( V_p \) (mL/g) at \( P/P^0 = 0.95 \), and the average pore radius in nm can be calculated from the following equation:

\[
r = \frac{2V_p (\text{mL/g})}{S_{BET} (\text{m}^2/\text{g})} \times 10^3
\]

From the last calculations we obtained a specific surface area 1654 m\(^2\)/g, total pore volume 1.372 mL/g, and average pore radius 1.66 nm. The obtained data indicate that the higher specific surface area may be related to the microporosity on sample surface.

![Fig. 1](image-url)

**Fig. 1.** Adsorption Isotherm (A) and Linear BET-plot (B) for Nitrogen Adsorption at -196 °C on KLC.

### 3.2. Scanning Electron Microscopy

SEM-image (Fig. 2) shows the microporosity on the surface of KLC which explains the direct effect of KOH on the surface, producing microspores on the surface after removal of CO\(_2\) gas.

### 3.3. Chemistry of the Surface

To identify the surface chemistry of AC, FTIR, and pHpzc were used. pHpzc value was found to be 7.8 indicating a slight basic surface due to the effect of KOH activating agent and reduction of surface
acidic groups during activation. FTIR spectra of activated carbon KLC is shown in (Fig.3). The band around 3430 cm\(^{-1}\) can be assigned to the OH stretching vibration mode of hydroxyl functional groups [21]. The band around 2921 cm\(^{-1}\) could be related to C-H stretching for aliphatic groups [22]. The peak at 1628 cm\(^{-1}\) related to C=C stretching for unsaturated aliphatic structures [23]. The complex week bands in the range 1054-1464 cm\(^{-1}\) could be related to ethers, lactones, carboxyl, aromatics and nitrate groups [24].

Fig. 2. SEM for KLC Sample with magnification power of 5000X.

Fig. 3. FTIR of the investigated sample (KLC)
3.4. Effect of Variables

3.4.1. Influence of initial pH

The effect of pH values on Pt(II) uptake was tested using the batch procedure by equilibrating 50 mg of KLC with 100 mL aqueous solution containing 10 µg L\(^{-1}\) of Pt(II) and 2\times10^{-5} \text{ mol L}^{-1}\ ATSC. HCl or NaOH (0.1 mol L^{-1}) and the acetate buffers were used to control pH (1–6). The mixture was shaken for 10 min and the amount of Pt(II) remains in aqueous medium was determined by ETAAS. The results presented in Fig. 4 showed a quantitative extraction (>98%) at pH 2–4. At low pH (<2), the hydrazone nitrogens are protonated which hindering the formation of Pt(II)-ATSC complex; hence pH 2–4 was preferable. The adsorption of Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pd(II), Ag(I) and Pb(II) were studied at the chosen pH. The results showed no interferences for these metal ions, except Co(II). pH 4 is selected as optimal acidity for subsequent experiments. The optimum pH range was found the same for the column packed with KLC.

![Fig. 4](image_url). The recovery of 100 ml solution containing 10 µg L\(^{-1}\) of Pt(II) and 2\times10^{-5} \text{ mol L}^{-1}\ ATSC on 50 mg KLC at pH 1-6

3.4.2. Effect of contact time

The time required for Pt(II) extraction was investigated. The extraction rate of Pt(II) was found rapid at the initial stage. The extraction % of Pt(II) reached equilibrium at 5 min. One min is required for 50% adsorption (t\(_{1/2}\)). It was clear that the solid-phase extraction process is fast using the present sorbent. The functional groups are hydrophilic, the Pt(II) could easily contact with the adsorption sites and trapped by the solid sorbent.
3.4.3. Effect of the ligand concentration

In order to study the effect of ATSC concentration, 100 ml of solution containing 10 µg L⁻¹ Pt(II) and variable concentrations of ATSC (2.0x10⁻⁶ - 1x10⁻⁴ mol L⁻¹) were buffered to pH 4 and were subjected to preconcentration by batch procedure as described in the experimental part. As Fig. 5 shows the % recovery of Pt(II) increases by increasing ATSC concentration up to 2x10⁻⁵ mol L⁻¹, then remain constant. Therefore, a concentration of 2x10⁻⁵ mol L⁻¹ of ATSC was selected as optimum.

![Graph showing the effect of ATSC concentration on the recovery of Pt(II)](image)

**Fig. 5.** The effect of ATSC concentration on the recovery of 100 ml solution containing 10 µg L⁻¹ Pt(II) on 50 mg KLC at pH 4

3.4.4. Effect of flow rate

The flow rate of solution through the packed bed column is a very important parameter for controlling the time of adsorption and analysis. Using the column procedure, the effect of flow rate on adsorption of Pt(II) was investigated at pH 4. The data showed that the flow rate influences the adsorption and desorption of Pt(II)-ATSC complex. For adsorption, a flow rate (<1.0 mL min⁻¹) was not studied to avoid a long time of analysis. Pt(II)-ATSC was adsorbed quantitatively at a flow rate of 2–4 mL min⁻¹. At a flow rate (>4.0 mL min⁻¹), a decrease in percentage adsorption due to the Pt(II) could not equilibrate properly with the KLC beds. So, 3 mL min⁻¹ flow rate was used for further study.

3.4.5. Effect of Sample Volume

The effect of the sample volume on the adsorption of Pt(II) on 100 mg of KLC was studied by passing sample volumes of 10-1000 ml containing the same amount of Pt(II) (10 µg L⁻¹) through the column. The sample volume did not affect on the adsorption of Pt(II). However, in order to determine
low concentrations of Pt(II) and to obtain high speed all the experiments were carried out with 100 ml of sample solution. As the amount of Pt(II) in 100 ml is measured after elution of adsorbed Pt(II) by 1.0 mL DMF, the solution is concentrated by a factor of 100.

3.4.6. Effect of amount of KLC

A 100 ml solution containing 10 µg L\(^{-1}\) Pt(II) and 2x10\(^{-5}\) mol L\(^{-1}\) ATSC was passed through the column containing a known weight of KLC. After elution with 1.0 ml of DMF, the Pt(II) in eluate solution was measured by ETAAS. The results are shown in Fig. 6. The results showed the % recovery of Pt(II) increased by increasing KLC up to 100 mg and remained nearly constant at higher values. Therefore, 100 mg activated carbon was used for routine works.

![Figure 6](image-url)

**Fig. 6.** Effect of the amount of KLC on the adsorption of Pt(II). Conditions; Pt(II), 10 µg L\(^{-1}\); ATSC, 2x10\(^{-5}\) mol L\(^{-1}\); pH 4.

3.4.7. Choice of eluent and the effect of its volume and flow rate

In order to choose a proper eluent for the retained Pt(II)-ATSC complex, various organic solvents were studied. Their effectiveness was evaluated and the following sequence was obtained: DMF > acetonitrile > acetone > ethanol > methanol. So DMF was selected as eluent. The effect of the volume of eluant solution was also studied. The results show that the optimum volume of the eluant was 1.0 mL. There is a decrease in the % recovery of Pt(II) with volumes >3.0 mL. This is due to the dilution of the solutions by increasing their volumes. The influence of the flow rate of elution on the sensitivity and precision (triplicate determinations) of 10 µg L\(^{-1}\) Pt(II) was investigated at 0.5-4.0 mL min\(^{-1}\). Maximum
sensitivity and high precision were obtained in the range 0.5–2.0 mL min\(^{-1}\). Therefore, a flow rate of 2.0 mL min\(^{-1}\) was selected.

### 3.4.8. Effect of ionic strength

The influence of ionic strength on the extraction of Pt(II) in batch method was studied using sodium/or potassium chloride, bromide, sulphate, nitrate, chlorate with concentrations (0.1 mol L\(^{-1}\) to saturation). The results showed no effect on the extraction efficiency. These observations showed the specificity of the procedure and the possibility of using this method for separation of Pt(II) from highly saline solutions.

### 3.5. Interferences

The effect of different cations and anions on the determination of 10 µg L\(^{-1}\) of Pt(II) by the proposed method was studied. An ion was considered to be an interferent when it caused a variation greater than ±5% in the absorbance of the sample. For the determination of 10 µg L\(^{-1}\) Pt(II) by this method, the foreign ions can be tolerated at the levels given in Table 1. Most of the cations and anions examined do not interfere with the extraction and determination of Pt(II). However, Co(II) interfered in the separation and selective evident of Pt(II). These interferences can be eliminated using 0.01 mol L\(^{-1}\) EDTA masking agent.

### Table 1. Tolerance of foreign ions in the determination of 10 µg L\(^{-1}\) of Pt(II)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Tolerance ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+), K(^+), Mg(^{2+}), Ni(^{2+}), SO(_4^{2-}), Cl(^-), Br(^-), ClO(_4^{-}), PO(_4^{3-})</td>
<td>&gt;4000</td>
</tr>
<tr>
<td>Pb(^{2+}), Mn(^{2+}), Al(^{3+}), Ba(^{2+})</td>
<td>2000</td>
</tr>
<tr>
<td>Cr(^{3+})</td>
<td>1000</td>
</tr>
<tr>
<td>Ca(^{2+}), Cd(^{2+}), SCN(^-)</td>
<td>700</td>
</tr>
<tr>
<td>Cu(^{2+}), Zn(^{2+}), Fe(^{2+}), Fe(^{3+})</td>
<td>500</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>200</td>
</tr>
<tr>
<td>Sn(^{2+})</td>
<td>100</td>
</tr>
<tr>
<td>Pd(^{2+})</td>
<td>50</td>
</tr>
</tbody>
</table>

### 3.6. Analytical Accuracy and Precision
Under the selected conditions, 10 portions (100 mL) of 10 µg L\(^{-1}\) Pt(II) were treated and analyzed followed the column procedure. The relative standard deviations (RSD) were 1.82%, indicating a good precision for the method of analysis. The detection limit (3σ, n=7) is 0.11 µg L\(^{-1}\). The calibration graph for determination of Pt(II) was prepared by applying the suggested separation procedure to Pt(II) standard solutions. The equation of the calibration curve is A=0.416 C+0.0204 (r=0.9993) where A is the peak area absorbance and C is the concentration of the Pt(II) in µg mL\(^{-1}\) with a linearity range of 0.15–120 µg L\(^{-1}\). For the assessment of the accuracy of the proposed methodology, it was applied for determination of Pt(II) in spiked water samples from different sources. The recoveries of known amounts of Pt(II) added to the samples were examined by the described method, and the results are shown in Table 2. The results indicated that the recoveries are quantitative at reasonable levels for trace Pt analysis, ranging from 97–102%.

Table 2: Determination of Pt(II) in spiked water samples by the proposed method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of Pt(II) (µg L(^{-1}))</th>
<th>% Recovery</th>
<th>RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Added</td>
<td>Found±S.D.</td>
<td></td>
</tr>
<tr>
<td>Tap water</td>
<td>-</td>
<td>BDL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.02±0.05</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.02±0.08</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5.00±0.11</td>
<td>100</td>
</tr>
<tr>
<td>River Nile water</td>
<td>-</td>
<td>BDL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.99±0.03</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.00±0.06</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5.05±0.08</td>
<td>101</td>
</tr>
<tr>
<td>Brackish water</td>
<td>-</td>
<td>BDL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.02±0.02</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.96±0.07</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.90±0.10</td>
<td>99</td>
</tr>
<tr>
<td>Sea water</td>
<td>-</td>
<td>BDL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.97±0.04</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.98±0.09</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.95±0.14</td>
<td>99</td>
</tr>
<tr>
<td>Wastewater</td>
<td>-</td>
<td>BDL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.03±0.03</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.96±0.07</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5.10±0.09</td>
<td>102</td>
</tr>
</tbody>
</table>

BDL: below detection limit.
The results are mean of five measurements ± standard deviation.
3.7. **Comparison with other Methods**

Comparative information from some studies on preconcentration of Pt(II) by various methods for the figure of merits is given in Table 3. Generally, the limit of detection by the present method is superior or comparable to the other methods. The short time of Pt(II) removal and the easily preparation of KLC are other advantages of the proposed method.

3.8. **Applications**

In order to evaluate the analytical applicability of the proposed method, it was applied to the determination of Pt(II) in road dust and rock samples. The results obtained were compared with the direct analysis by ICP-MS (Table 4). As shown, there is no significant difference between the results obtained by the proposed method and with those obtained by ICP-MS. This indicated that the proposed method is validated for the determination of Pt(II) in real samples.

4. **Conclusion**

A synthetic route for activated carbon based rice husk has been described. It has an alternative and efficient route for separation/preconcentration purpose in the determination of Pt(II) in various spiked natural water, rocks and road dust with a recovery >97%. The concentration of Pt (II) on the sorbent surface can be determined by ETAAS. This sorbent has high selectivity. High preconcentration factor was obtained easily by this method. The proposed method can be applied for environmental and other samples. The method is found accurate and precise and it has relatively lower LOD compared to other methods.
### Table 3. Comparison of the proposed method with some preconcentration methods

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Retention condition: sample pH and flow rate</th>
<th>Elution conditions: volume of eluent and flow rate</th>
<th>LOD, µg L⁻¹</th>
<th>Detection technique</th>
<th>Sample</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified silica gel C₁₈</td>
<td>ion associate complex of Pt with onium salt</td>
<td>2 mL of ethanol</td>
<td>5</td>
<td>ICP-OES</td>
<td>engine soot NIES 8, airborne particulate matter</td>
<td>25</td>
</tr>
<tr>
<td>Dowex 1-X8</td>
<td>sample after digestion in aqua regia</td>
<td>total digestion of resin</td>
<td>4.2</td>
<td>ETAAS</td>
<td>copper ores, concentrates spiked tap water</td>
<td>26</td>
</tr>
<tr>
<td>Activated alumina (acidic form)</td>
<td>pH 2.5, 3 mL min⁻¹</td>
<td>500 µL of 2 mol L⁻¹ NH₃aq; 1 mL min⁻¹</td>
<td>0.33</td>
<td>ETAAS</td>
<td>spiked tap water</td>
<td>27</td>
</tr>
<tr>
<td>Cellex-T</td>
<td>pH&gt;2.5; 3 mL min⁻¹</td>
<td>3 mL of 0.01 mol L⁻¹ glycine (pH&gt;12) or 75 µL of 1.2 mol L⁻¹</td>
<td>0.22</td>
<td>ETAAS</td>
<td>spiked tap water</td>
<td>28</td>
</tr>
<tr>
<td>Silica gel modified</td>
<td>pH 3.6–5.6 (acetate buffer); 2.4 mL min⁻¹</td>
<td>40 µL of 2 mol L⁻¹ HNO₃; 2.4 mL min⁻¹</td>
<td>1</td>
<td>ETAAS</td>
<td>catalyst SRM 2557, spiked soil, pine leaves, water</td>
<td>29</td>
</tr>
<tr>
<td>Dowex 1-X8 modified with PSTH</td>
<td>pH 9.4 (glycine-NaOH buffer); 2.4 mL min⁻¹</td>
<td>40 µL of 2 mol L⁻¹ HNO₃; 2.4 mL min⁻¹</td>
<td>1</td>
<td>ETAAS</td>
<td>catalyst SRM 2557, spiked soil, pine leaves, water</td>
<td>30</td>
</tr>
<tr>
<td>Pt-AcTSn—IIP</td>
<td>pH 0.5 and 3.5–9.5; 0.5 mL min⁻¹</td>
<td>2 mL of 0.3 mol L⁻¹ TU in 0.3 mol L⁻¹ HCl; 0.5 mL min⁻¹</td>
<td>0.16</td>
<td>ETAAS</td>
<td>anode slime spiked tap water and tunnel dust</td>
<td>31</td>
</tr>
<tr>
<td>KLC</td>
<td>pH 4; 3 mL min⁻¹</td>
<td>1.0 mL of DMF; 2.0 mL min⁻¹</td>
<td>0.11</td>
<td>ETAAS</td>
<td>Spiked water and geological samples</td>
<td>The present work</td>
</tr>
</tbody>
</table>

Onium salt=N (1-carbaethoxypentadecyl)trimethyl ammonium bromide (Septonex); DPTH=1,5-bis-(di-2-pyridyl)methylene thiocarbohydrazide; PSTH=1,5-bis[(2-pyridyl)-3-sulphophenyl methylene] thiocarbonohydrazide; Pt-AcTSn—IIP- ion imprinted polymer based on Pt-acetaldehyde thiosemicarbazone chelate; TU=thiourea
Table 4. Determination of Pt(II) in geological samples by the recommended procedure in comparison with those obtained by direct ICP-MS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt(II) concentration $^a$</th>
<th>The present work</th>
<th>ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Road dust samples (ng g$^{-1}$)</td>
<td>17.83±3.91</td>
<td>16.55±4.13</td>
<td></td>
</tr>
<tr>
<td>Rock samples (ng g$^{-1}$)</td>
<td>30.42±5.23</td>
<td>31.33±4.82</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Mean±S.D. (n=10)

References


