



# Rice straw modified by click reaction for selective extraction of noble metal ions



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## HIGHLIGHTS

- Rice straw was used as sorbents to remove noble metal ions.
- Rice straw was modified by azide–alkyne click reaction.
- The modified straw showed excellent selectivity for noble metal ions.
- The modified straw exhibited excellent reusability.

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## ABSTRACT

Rice straw was modified by azide–alkyne click reaction in order to realize selective extraction of noble metal ions. The ability of the modified straw to adsorb Pd<sup>2+</sup> and Pt<sup>4+</sup> was assessed using a batch adsorption technique. It was found that the sorption equilibrium could be reached within 1 h and the adsorption capacity increased with temperature for both Pd<sup>2+</sup> and Pt<sup>4+</sup>. The maximum sorption capacities for Pd<sup>2+</sup> and Pt<sup>4+</sup> were respectively attained in 1.0 and 0.1 mol/L HCl. The modified straw showed excellent selectivity for noble metal ions in comparison to the pristine straw. In addition, the modified straw was examined as a column packing material for extraction of noble metal ions. It was indicated that 1.0 mL/min was the best flow rate for Pd<sup>2+</sup> and Pt<sup>4+</sup>. The modified straw could be repeatedly used for 10 times without any significant loss in the initial binding affinity.

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## 1. Introduction

The increase of the price for precious metals over the years and their expanding use in areas such as organic catalysts, jewellery, microelectronics and cancer therapy along with lack of availability of these metals have led to development of mining from low grade ores or from secondary raw materials. Therefore, the recovery of noble metal ions from waste solutions is an important economical and ecological problem that is attracting the ever-increasing attention of researchers (Gurung et al., 2013; Ran et al., 2012; Wołowicz and Hubicki, 2011; Renuka and Balasubramanian, 2012; Jermakowicz-Bartkowiak, 2007; Bratskaya et al., 2011).

In recent decades, several processes have been developed in order to recover and separate noble metal ions from synthetic or industrial effluents, including sorption, ion exchange, liquid–liquid extraction, and membrane processes (Herincs et al., 2013; Kagaya

et al., 2000). Although liquid–liquid extraction and related processes, including impregnated resins or liquid membranes are powerful techniques, they may involve environmental drawbacks such as release of solvents or extractants. Furthermore, these techniques are efficient only in the treatment of dilute effluents. For these reasons, sorption and ion-exchange processes based on sorbents are well recognized as the simplest and most efficient method (Jermakowicz-Bartkowiak et al., 2005; Won et al., 2014; Ramesh et al., 2008; Kwak et al., 2013).

Sorbents play a very important role in sorption treatment process. Ion exchange resins are commonly used as sorbents to remove noble metal ions from aqueous solution. According to Pearson's hard and soft acid–base concept, chelating resins containing sulfur and nitrogen atoms possess excellent adsorption and selectivity properties for noble metal ions. Therefore, the classical approach to the synthesis of sorption materials for selective recovery of precious metals ions is based on the introduction of nitrogen and sulfur-containing functional groups to polymer backbones (Guibal et al., 2002; Ji et al., 2010; Bratskaya et al., 2012).

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However, ion exchange resins are usually too expensive to treat large volumes of wastewater, resulting limitations for application in developing countries or rural areas. There is still a need for the development of inexpensive and effective sorbents. Biopolymers such as agricultural by-products have recently received a great deal of attention due to the fact that they represent renewable resources and are more environmental friendly than conventional materials (Pan et al., 2010; Kim and Han, 2012; Park et al., 2014). In addition, agricultural by-products also exhibit particular properties such as its chemical stability and high reactivity, resulting from the presence of reactive hydroxyl groups in cellulose/ hemicellulose chains (Chen et al., 2011). In China, about 200 billion kilograms of rice straw are produced annually as a byproduct of rice production. The disposal of rice straw by open-field burning frequently causes serious air pollution. Therefore exploring new applications of straw residues are helpful for protecting the environment and contribute to sustainable development (Zhang et al., 2011; Zhao et al., 2011).

Generally, the sorption capacity of native rice straw is low. In order to improve the sorption capacity and selectivity of the sorbent, the rice straw was chemically modified in the current research by click reaction, which describes pairs of functional groups that rapidly and selectively react with each other. Click chemistry has continuously received huge attention owing to its ease of implementation and high efficiency. The Huisgen 1,3-dipolar cycloaddition of azides and alkynes is one of the most popular click reactions as it can be performed under mild reaction conditions and has a good tolerance of functional groups. The utility of the azide-alkyne cycloaddition has been amply demonstrated effective for the synthesis and modification of polymers with a wide range of functionality, architecture and intended purpose (Brotherton et al., 2009; Arado et al., 2013; Kislukhin et al., 2013). The modified straw was then used to adsorb Pd<sup>2+</sup> and Pt<sup>4+</sup> using a batch adsorption technique. The effects of various experimental parameters such as acidity of solutions, temperature and contact time were examined. Finally the modified straw was examined as a column packing material for solid phase extraction of noble metal ions from aqueous solutions.

## 2. Methods

### 2.1. Materials

Rice straw was collected from a suburb near Yancheng, China. Sodium azide, propargylamine, palladium(II) chloride (PdCl<sub>2</sub>) and platinum(IV) chloride (PtCl<sub>4</sub>) were purchased from Sigma–Aldrich Chemical Co. and used as received. All other reagents and solvents were used without further purification.

### 2.2. Preparation of the modified rice straw

About 5 g of crushed rice straw was dispersed in 50 mL of dry pyridine. Then 1 g of methanesulfonyl chloride in 10 mL of dry dichloromethane was dropwise added over 30 min, and the reaction mixture was allowed to stir for another 12 h. The mixture was filtrated and the solid was dried under reduced pressure for 24 h (Yao et al., 2010). After that, a mixture of 5.0 g of the above prepared product and 1.0 g of sodium azide in 50 mL dry dimethylformamide (DMF) was reacted at 80 °C for 24 h. Again the mixture was filtrated and the solid was dried at 50 °C under reduced pressure. Finally the azide-functionalized straw was exposed to an aqueous solution containing propargylamine (15 mg/mL), copper(II) sulfate (0.30 mg/mL), and sodium ascorbate (0.8 mg/mL) for 8 h in order to prepare the amino-functionalized straw

(Kislukhin et al., 2013). The procedure for the modification of rice straw by click reaction was shown in [Scheme S1](#).

### 2.3. Batch studies for sorption and desorption of noble metal ions

Stock solutions of Pd<sup>2+</sup> and Pt<sup>4+</sup> were prepared by dissolving a weighted amount of PdCl<sub>2</sub> and PtCl<sub>4</sub> in concentrated HCl. Both of the initial concentrations of Pd<sup>2+</sup> and Pt<sup>4+</sup> were 100 mg/L. To study the sorption properties, the modified rice straw was shaken with solutions of PdCl<sub>2</sub> and PtCl<sub>4</sub> in HCl solution during 24 h. The sorption capacity was calculated using the difference in initial concentration and equilibrium concentration of the metal ions determined by the atom absorption spectroscopy (AES).

For desorption experiments, the loaded straw was shaken with eluent solution (HCl or thiourea/HCl) for 24 h. Afterwards the concentration of precious metals was determined by AES.

### 2.4. Adsorption kinetics

Batch tests were performed to determine the adsorption kinetics. In a typical procedure, the desired amounts of noble metal ion solutions (100 mL) were added to glass tubes, which were placed in a thermostated shaking bath. When the desired temperature was reached, a known amount of the modified rice straw (0.01 g) was added to each tube, and the mixed solutions were mechanically shaken. At regular intervals, the solutions in the specified tubes were separated from the adsorbent, and the concentration of metal ions was determined by AES.

### 2.5. Fourier transform infrared spectroscopy (FTIR)

The rice straws before and after modification were dried, crushed and made into potassium bromide pellets. FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer in the range 4000–400 cm<sup>-1</sup>.

### 2.6. Surface morphology study

SEM/EDX was used to investigate the surface morphology and element of the rice straw. Measurements were taken on the FEI QUANTA 200 scanning electron microscope. The samples were coated with carbon before examination.

### 2.7. Selective sorption study

Selective sorption ability was studied using two kinds of solutions containing noble and base metal ions. To be specific, in one kind of the solutions, both of the concentrations of noble and base metal ions were 100 mg/L. While in the other solution, the concentrations of noble and base metal ions were respectively 100 and 300 mg/L. The pristine and modified rice straws were shaken with the above solution respectively for 24 h in order to achieve the sorption equilibrium. Subsequently the concentration of the each ions in the solution was determined by AES.

### 2.8. Dynamic extraction of noble metal ions

The modified straw was used as a column filling material for solid phase extraction of noble metal ions. The modified straw was poured into a glass column, and a small amount of glass wool was placed at both ends to prevent the loss of straw during sample loading. Solutions of Pd<sup>2+</sup> and Pt<sup>4+</sup> with the concentration of 100 mg/L were passed through the column respectively. Then the metal ions retained on the column were eluted with thiourea/HCl solutions. The concentration of the eluted metal ions was determined by AES.

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