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Reduction of palladium onto pyrogallol-derived nano-resin and its mechanism

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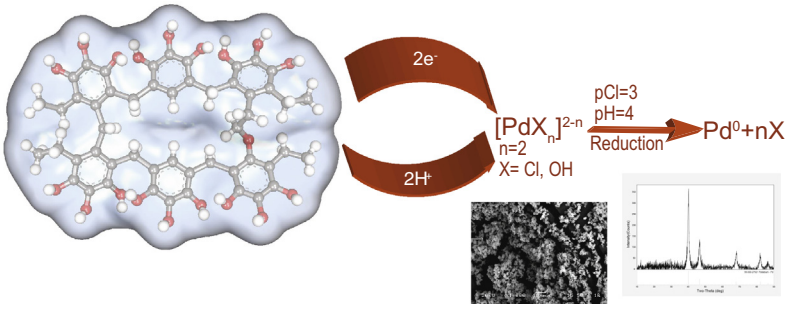
HIGHLIGHTS

- Synthesized PGNR particles interaction with Pd(II) chloro complexes have been characterized.
- Pd(II) reduced to metallic Pd^0 onto PGNR.
- PGNR can be applied to recover PGMs efficiently and simply with low cost.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we designed and synthesized a pyrogallol containing resol nano resin (PGNR) which has the ability to reduce palladium(II) ions to metallic form has been designed and synthesized. The main possible application area of PGNR particles is recycling comparatively dilute e-wastes. According to thermal gravimetric analysis, weight loss of the PGNR particles increased to 87% with changing temperature from 570 K to 712 K. Synthesized polymer was utilized as an adsorbent for recovery of palladium(II) ions from chloride-containing solutions. Then, the effects of pH, chlorine concentration, and temperature on adsorption were investigated and optimized by batch adsorption experiments. As a result, we estimated the palladium particle size as 16 nm. The formation of PGNR and Pd-adsorbed PGNR were characterized by FE-SEM, EDAX, XRD, and FTIR instrumentations. Adsorption of the positively charged and neutral chloropalladium(II) species mostly takes place via redox reduction reaction to Pd(0). The ease of synthesis, having low cost, coupled with the highly efficient and rapid reduction of Pd(II) ions onto surface, make PGNR polymer an attractive adsorbent.

1. Introduction

Recycling noble metals became an important resource since there are limited natural resources but increased demand Automotive catalytic converters use up about 34% of the world's total platinum, 55% of total palladium and 95% of total rhodium [1]. In other areas like dentistry, jewelry, nitric acid, nylon, rubber, fuel cell, coinage, oil refining, polyester, photography, water treatment, hydrogen purification, medicine, electronic are often used in trace amounts. From an economic point of view, recycling of platinum group and precious metals has become very important aspect due to low amount of ores. Industrial cycling techniques such as hydrometallurgical and pyrometallurgical processes have

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been widely used to recover precious metals from electronic wastes [2]. The pyrometallurgical processes are commonly used at the first stage of the recycling but they are not feasible for low grade e-wastes which accounts for almost all waste. Among the hydrometallurgical processes, adsorption seems to be the most suitable method in the case of low concentration recovery of precious metals due to its low cost, safety, and high efficiency. The selectivity of polymeric adsorbent for palladium(II) ion depends on the type of donor atom introduced into the polymeric chain. In addition, catechol moieties of the polymeric chain have the capability of electron donation when transforming into quinone groups [3].

It is extensively known that heavy metals are harmful to the environment and living organisms. Palladium as a heavy metal also has similar effects. To give an example, Shen-Long and Shen-Long are reported the growth inhibitory effect of the catalytic converter originating palladium [4]. In past decades, biosorption of precious metal ions has attracted growing interest because bio-derived materials are inexpensive and environmentally friendly. However, there are very few tannin derived PGM biosorption studies [3,5–10]. Therefore, hydrolysable tannins pyrogallol (PG) is produced with two consecutive transformations [11] as nanoparticles since PG and formaldehyde resol formation reaction takes place extremely fast [9] thus attaining the resin particle's nano diameter.

Like each platinum group metals, high worldwide demand whereas limited supply from ores has made recovery of palladium metal important aspect. Previous studies reported using nano sized polymers, the uptake of some heavy metals and the recovery of PGMs: Ahmedi et al. [12]. published an article about Pb (II) adsorption onto commercial Lewatit FO 36 nano resin. Another study dealing with chromium (VI) removal reported using Lewatit FO 36 nano ion exchange resin [13]. In another study by Li et al. showed wheat straw/acrylic polymer/OMMT nanocomposite adsorbent synthesis [14]. Even though Zeng et al. [15] presented their work on the synthesis of nanoporous hydroquinone/catechol formaldehyde resins and its interaction with gold ions. It should be noted that the particle size of this resin was not in nanoscale. Furthermore, many of these adsorbents are formed in composites with metal oxides [16,17] or other structures [18,19].

In our previous study [9], where we specifically deal with synthesis and characterization of pyrogallol formaldehyde resol resin. Now in this study we are presenting successfully synthesized nano-sized PGNR particles as shown in Fig. 1. In addition, this recent article shows studies with rhodium(III) chloro complexes which have completely different adsorption mechanism. On the other hand, we have not conducted our experiments for neither the recovery chloride containing palladium(II) ions from aqueous solution nor the influence of pH and Cl^- concentration on equilibrium and on kinetics of the adsorption.

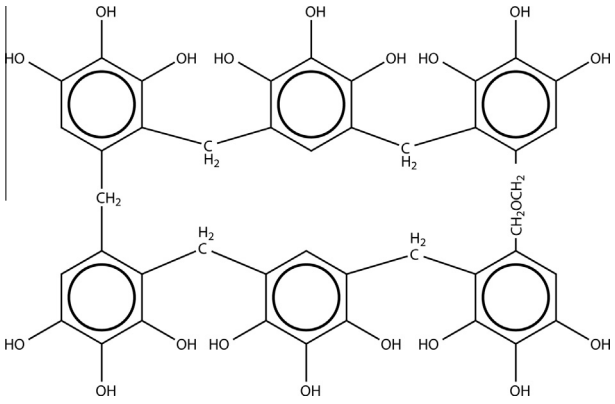

Fig. 1. Estimated chemical structure of PGNR [9].

Although the adsorption of palladium ions onto polyphenol based materials is well known. However, with the exception of our study, none of these studies used nano-sized polyphenolic adsorbents. To understand decomposition behavior or determination, thermo-gravimetric analysis (TGA) of the produced polymer has been conducted. Therefore, in this study, we estimated the sorption mechanism of palladium(II) ions using FTIR and XRD techniques. In an attempt to understand the adsorption conditions (pH, Cl^- concentration, contact time, and temperature), the influence of palladium species was investigated. The equilibrium and thermodynamics of the adsorption were also evaluated.

2. Experimental

The analytical grade pyrogallol and all the other chemicals used were purchased from Merck Turkey. Palladium stock solution containing 1002 ± 5 mg/dm^3 Pd(II) was used from $Pd(NO_3)_2$ in 0.5 M HNO_3 purchased from Merck (Merck KGaA, Darmstadt, Germany).

The synthesis of PGNR was prepared according to our previous research [9]: A solution of PG (90 g) in deionized water (500 mL) and NH_3 solution (20% w/w, 20 mL) was heated to 343 K by magnetic stirring. Then, formaldehyde (P) (37% w/w, 175 mL) was added and the reaction mixture was heated to the same temperature. In order to achieve insolubility under adsorption conditions (1 M HCl) it was continued for 1 h. Then the solution was filtered through a 0.45 μm membrane. The obtained insoluble PGNR was washed with distilled water to make formaldehyde free resin. The filtered precipitate was dried at 353 K in a drying oven over a one-day period.

The Pd(II) solutions were prepared by diluting stock solutions to a concentration of 50 mg/L. 500 mL of Pd(II) solutions with desired pH and pCl (−log[Cl]) were prepared for experiments and stirred with adding 200 mg dry basis PGNR resin. For all experiments a 600 rpm stirring rate was selected for 60 min in a batch-wise system at the desired temperature (from 298 K to 333 K). At the end of the adsorption the solution was centrifuged and filtered with a 0.45 μm membrane. All the experiments were duplicated to verify the reproducibility of the experimental effects. Palladium(II) concentration is calculated by mass balance as follows:

$$q_e = (C_0 - C_e)V/W \quad (1)$$

where q_e is the equilibrium sorption capacity in mg/g, V the volume (L) of the solution, W the weight (g) of the dry PGNR used, C_e the equilibrium and C_0 the initial concentrations (mg/L) of Pd(II). Pd(II) concentrations in the filtered solutions were measured by flame absorption spectroscopy (FAAS). All palladium(II) solution concentrations were measured with a Shimadzu 6701F atomic absorption spectrometer in the emission mode (with a wavelength of 244.8 nm and a slit of 0.5 nm) and using an air-acetylene flame. FAAS was carried out by using standard solutions having 0, 2, 4, 6, 8 and 10 mg/L Pd(II) in 1 M HCl. All samples have been set to measurement limits.

FT-IR spectra (1800–700 cm^{-1}, 25 scans) analysis of resins was measured using a Shimadzu IRPrestige-21. The surface morphology of the PGNR was studied by means of elemental analysis with the SEM-EDS analytical instrument JEOL JSM-6060 LV operating at 20 keV. Local chemical analysis and chemical mapping was carried out in an energy dispersive X-ray spectroscope (EDS) to show the presence of Pd on the PGNR, which was attached to the SEM microscope. For the purpose of clarifying the interaction mechanism, powder X-ray diffraction (XRD) patterns of the samples were obtained using an X-ray diffractometer RIGAKU D_{max} 2200 (voltage 40 kV, current 30 mA) using Cu-Kα radiation (λ = 1.54056 Å).