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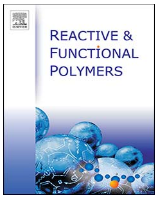

Surface-activated anion exchange resins for synthesis and immobilization of gold and palladium nano- and microstructures

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ABSTRACT

A series of surface-activate anion exchange resins, bearing amino functionalities, were employed in processes of multiple adsorption and desorption of $AuCl_4^-$, $PtCl_6^{2-}$ and $PdCl_4^{2-}$ from solutions in 0.1 and 3 $mol \cdot L^{-1}$ HCl. The resins with ethylenediamine (EDA) and 1-(2-aminoethyl)piperazine (AEP) functionalities efficiently removed up to 100 wt% of the noble metals, however, instead expected total elution, they revealed only up to 50 wt% of desorption. The phenomenon was caused by the fact, that the anion exchange resins revealed an ability to reduce ionic forms of gold and palladium to their nano- and microparticles creating colloids and nanocomposites. For that reason the generated metallic forms were investigated using X-Ray Diffraction (XRD), Dynamic Light Scattering (DLS) and Scanning Electron Microscopy (SEM). The size of the obtained structures was in range of 50–1000 nm, however, because reduction involves the transfer of an electron from a donor nitrogen it is dependent on the number of nitrogen atoms in amino ligands. A very close look at the changes in the resins' chemical structures has been taken using Fourier Transformation Infrared Spectroscopy allowing to determine a possible reason of the reduction.

1. Introduction

Nanotechnology has gained a great deal of attraction from the most developed societies all over the world. Research on production and utilization of various nanoparticles is recognized as the major factor that facilitates improving the quality of life. To date, nanoparticles have been successfully applied in the treatment of various diseases [1,2], targeted drug delivery systems, medical diagnostics [3] as well as treatment of various types of industrial wastes [4–6]. Among them, *nano* forms of noble metals are particularly important. Gold nanoparticles, for instance, have multiple applications in biomedicine [7] and are useful as X-Ray contrasting agents [8] or drug delivery systems for the treatment of cancer [9]. Moreover, gold nanoparticles reveal sensing abilities indicating the presence of multiple species, including heavy metals, proteins, toxic chemicals or drugs [10]. Platinum as well as palladium nanoparticles in turn are proven to be extremely stable and effective catalysts of different reactions, including hydrocarbon conversion [11], oxygen reduction [12] or hydrogenation of alkenes [13,14].

Because nanoparticles of noble metals are very versatile, plenty of methods for their synthesis have been already published. The most recent include bio-inspired procedures [15,16] and dry plasma reduction [17]. However, procedures of nanoparticle obtainment are often complicated and require the use of specific and toxic reducing agents or sophisticated infrastructure. Therefore, in our previous work we reported a novel phenomenon of reduction-coupled adsorption of noble metals on the amino-functionalized Dowex M4195 resin. It resulted in the formation of nanoparticles and microplates of noble metals [18]. The described method is based on the ability of amino functionalities to spontaneously reduce metallic species, unlimitedly generating their nanoparticles [18,19]. Moreover, because of the fact that both, amino-functionalized ion exchange resins and the reduction mechanism itself are proven to be selective towards noble metals [18–20], the method of their nanoparticle synthesis seems to be very attractive. Simplicity of

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the procedure and the possibility of the multiple reuse of a polymer can be seen as the main advantages of such a solution. The worldwide scientific literature lacks of information about application of ion exchange resins for intended reduction of noble metals leading to obtainment of their nanoparticles or development of a new extraction technique.

Following that idea, the purpose of the present studies is to employ new *surface activate* anion exchange resins [21] as unlimited selective generators of gold and palladium nano- and microparticles during the repeated adsorption and desorption of Au(III), Pt(IV) and Pd(II) from their multicomponent solutions in hydrochloric systems. The syntheses of the nano- and microparticles were carried out from solutions in $0.1\ \mathrm{mol\,L^{-1}}$ and $3\ \mathrm{mol\,L^{-1}}$ HCl containing $AuCl_4^-$, $PtCl_6^{2-}$ and $PdCl_4^{2-}$, respectively. As the original idea, was to apply the synthesized resins for the repeated removal and recovery of the noble metals, an eluting agent for desorption step, should had been able to entirely regenerate the so-loaded resins, to make them fully operational in following steps of the procedure. For this reason, the solution of 5 wt% thiourea in 0.1 M HCl was selected. The thiourea reveals high complexation ability [22] that increases desorption effectiveness [23,24]. Moreover, it is proven to be extremely efficient for elution of noble metals [25–29] allowing to entirely regenerate amino-functionalized resins. However, as it turned out, the obtained anion exchange resins did not require the desorption step, as their functionalities were able to unlimitedly reduce metallic species. Nevertheless, the application of thiourea solution as the eluting agent made determination of the possible mechanism of the reduction easier.

The ethylenediamine (EDA) and 1-(2-aminoethyl)piperazine (AEP) functionalized resins were obtained via simple modification of *core-shell* type polymeric supports [30]. These anion exchange resins are characterized by different amounts of amino functionalities acting as reducing agents, as well as the diversified porous structure of a polymeric matrix. The presence of nanoparticles of gold (AuNPs) and palladium (PdNPs), as well as their microstructures, was proven by X-Ray Diffraction (XRD); morphology of their agglomerates was assessed using Scanning Electron Microscopy (SEM) and their size distribution was defined using Dynamic Light Scattering (DLS). In order to determine how various factors influence the properties of the obtained nanoparticles, the syntheses were carried out repeatedly in media characterized by different pH. Changes in the resins' chemical structures were constantly monitored using Fourier Transformation Infrared Spectroscopy (FTIR) that enables the possible mechanism of the phenomenon to be determined.

2. Methods and materials

2.1. Materials

An initial polymeric matrix, Amberlite XAD-4, and poly(vinyl alcohol) (PVA, $M_w = 130{,}000$) were purchased from Fluka. Vinylbenzyl chloride (99%, mixture of 3 and 4 isomers, VBC), divinylbenzene (80%, DVB), ethylenediamine (99%, EDA) and 1-(2-aminoethyl)piperazine (99%, AEP), used for the synthesis of anion exchange resins, were acquired from Sigma-Aldrich Co. The monomers, VBC and DVB were purified before use by distillation under reduced pressure and the rest of the reagents were used as received.

$HAuCl_4{\cdot}4H_2O$, H_2PtCl_6 and H_2PdCl_4 were acquired from Avantor Performance Materials Inc. (gold) or INNOVATOR Ltd. (platinum and palladium) and then dissolved in $0.1\ \mathrm{mol{\cdot}L^{-1}}$ HCl or $3\ \mathrm{mol{\cdot}L^{-1}}$ HCl in order to obtain media for the synthesis of metallic nano- and micro-gold and palladium.

Other reagents, used for preparation and analysis of the products, were purchased from Avantor Performance Materials Inc. and used without any pretreatment.

2.2. Analyses methods

The $0.001\ \mathrm{mol{\cdot}L^{-1}}$ HCl regain was measured using the centrifugation technique [31]. The chlorine content, which defines efficiency of modification, was determined using the Schöniger [32] method. The nitrogen content, which assists in estimating the amount of the introduced amino functionalities acting as reducing agents, was determined in accordance with the Kiejdahl [33,34] procedure. A number of active ion exchange places was determined by analysis of ion exchange capacity determined applying Hecker procedure [35].

The FTIR spectra in KBr pellets were recorded using a Nicolet 6700 spectrophotometer at different stages of the synthesis of nano- and microparticles.

The concentrations of the metals in solutions remaining after reduction-coupled adsorption were determined using the ICP-OES model 38S manufactured by Jobin Yvon (France) at analytical wavelengths 242.795 nm for Au, 340.458 nm for Pt and 214.423 nm for Pd.

Removal and recovery [%] of gold, platinum and palladium, that represents on the one hand, the ability of the resins to concentrate the solutions, and on the other, the amount of the metals reduced to their nano- and microparticles, were calculated from the mass balance.

The N_2 adsorption at 77 K using an Autosorb IQ gas adsorption analyzer (Quantachrome) was used to define the porosity of the *core-shell* type anion exchange resins. Before analysis, the samples were outgassed at 60 °C for 24 h. The BET equation was applied to calculate the specific surface area (S_{BET}).

Presence of the reduced metals was confirmed by the X-ray powder diffraction method (XRD). Measurements were executed in the symmetric $\theta/2\theta$ Bragg-Brentano geometry using a Philips X'PERT system.

The morphology of the obtained nano- and microparticles was assessed using a Scanning Electron Microscope JSM 5800LV (SEM), equipped with a JSIS 300 Oxford X-ray analyzer.

The size distribution of the nano- and sub-microstructures was defined using the Dynamic Light Scattering (DLS) method on a Photocor Complex (Photocor Instruments). The device was equipped with a 657 nm/36 mW laser and measurements were performed in round vials characterized by an internal diameter of 14.8 mm. Samples were submerged in decalin- refractive index-matching liquid; the scattering angle was set at 90°. Results were analysed using DynaLS softwate (Alango Ltd.).

2.3. Synthesis of surface-active anion exchange resins

The procedure presented in previous works cited under numbers [21,30,36] consists of two steps as displayed in the Scheme 1: (1) preparation of the polymeric supports, and (2) their functionalization to the anion exchange resins.

To differentiate the porous structure of the resins, the polymeric supports were prepared in accordance to the methods presented in the reference cited under number [36]. First, (A) the commercial base, Amberlite XAD-4, was swollen overnight in two different solutions which contained toluene and a mixture of the monomers VBC and DVB (10 mol% in respect to VBC), which constituted 90 wt% (support 2C) or 45 wt% (support 6C) of the liquid organic phase. Then, the excess of impregnating solution was removed applying centrifugation, characterized by a speed of 1000 RPM (support 2C) or 500 RPM (support 6C). The impregnated Amberlite XAD-4 beads were then subjected to suspension polymerization for 21 h at 90 °C using a solution of poly (vinyl alcohol) (PVA) as an aqueous phase [30]. (B) When the process was finished the synthesized 2C and 6C core-shell type polymeric supports were extracted, using toluene, in order to remove all the unreacted monomers and oligomers, and then dried and used for the following step of the procedure. As a result of synthesis, two types of matrixes were obtained. The one obtained using the denser impregnating solution (2C) was characterized by a less developed porous structure than its well-developed 6C equivalent.