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Extraction of precious metals from industrial solutions by the pine (*Pinus sylvestris*) sawdust-based biosorbent modified with thiourea groups

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ABSTRACT

A novel biosorbent based on pine (*Pinus sylvestris*) sawdust with chemical grafted thiourea groups was proposed for preconcentration of precious metals. A simple procedure was proposed for the synthesis of biosorbent by treating of sawdust with ammonium thiocyanate solution and a subsequent heat treatment at 160 °C. The biosorbent has been studied by thermogravimetry/differential scanning calorimetry (**TGA/DSC**), scanning electron microscopy (**SEM**), and Fourier transform infrared spectroscopy (**FT-IR**). The adsorption properties for precious metals ions (Au^{3+}, Pd^{2+}, Pt^{2+}, Pt^{4+}, Ir^{4+}, Rh^{3+}, Ru^{4+}) extraction have been studied. Biosorbent quantitatively extracted precious metals from dilute solutions of hydrochloric acid (0.5–4.0 M). Iron and non-ferrous metals were not extracted in these conditions. The adsorbent showed high adsorption capacity for precious metals: 0.4 (Au^{3+}), 1.7 (Pd^{2+}), 1.0 (Pt^{2+}), 0.8 (Pt^{4+}), 0.45 (Ru^{4+}), 0.55 (Rh^{3+}), 0.4 (Ir^{4+}) mmol/g.

Biosorbent was used for extraction and preconcentration of precious metals from industrial solutions of refinery. Enriched for precious metals desorbing solution was obtained as a result. It is possible to obtain precious metals powder by combustion of biosorbent after adsorption of precious metals.

1. Introduction

The industry produces many types of waste waters containing trace amounts of precious metals. The most effective method for extraction of precious metals and returning them to the process is adsorption method.

A lot of adsorbents, differing both in matrix and functional groups, have been proposed for precious metals preconcentration (Myasoedova et al., 2007; Mokhodoeva et al., 2007; Mladenova et al., 2012; Hubicki et al., 2008). Organopolymer adsorbents with various functional groups allowing extracting precious metals via ion exchange and/or complexation are the most widely used (Sanchez et al., 2001; Gong and Wang, 2002; Kavakli et al., 2006; Myasoedova et al., 1997). Adsorbents with amine groups extracting anionic complexes of precious metals and complexing adsorbents with donor nitrogen and sulfur atoms have relatively high adsorption capacity, but heir significant drawback is the swelling.

Equilibration time of precious metals adsorption is significantly less for organopolymer adsorbents with fibrous structure (Vlašánková and Sommer, 1999; Jermakowicz-Bartkowiak, 2005; Zeytuncu et al., 2015; Cyganowski and Jermakowicz-Bartkowiak, 2016; Zhong et al., 2017). These adsorbents have much lower adsorption capacities compared to organopolymer adsorbents with granulose structure, so, they are not always suitable for application in technology.

Selectivity of the adsorption using complexing adsorbents is determined by the nature of functional groups, able to form stable complexes with a single element or with a group of elements. For preconcentration of precious metals the adsorbents with sulfur-containing complexing groups, for example thiourea or its derivatives, are the most suitable. The advantage of these sorbents is the possibility to separate precious metals from other non-ferrous metals by the adsorption from acidic media.

The most famous industrially available sulfur-containing adsorbents for precious metals preconcentration are Lewatit TP-214 and Purolite S-940 with thiourea derivatives groups (Hubicki and Wolowicz, 2009; Aktas and Morcali, 2011; Won et al., 2011; Won and Yun, 2013; Morcali et al., 2013, 2014). These adsorbents have relatively high adsorption capacity for precious metals (30–80 mg/g), but their limitation is a bad kinetics. The adsorbents synthesized via polycondensation of formaldehyde and thiourea are characterized by relatively high values of adsorption capacity for palladium (0.14–0.30 mmol/g), and good kinetics (Birinci et al., 2009; Muslu and Gülfen, 2011).

There is a significant progress in selective extraction of precious metals and their separation from predominant amounts of nonferrous

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metals and iron by mesoporous organosilica, magnetic nanoparticles (magnetic nanoparticles coated with silica, and modified with chelating groups), silicas chemically modified with thiourea derivatives groups (CMS) (Schilling et al., 1994; Liu et al., 2000, 2002; Zhang et al., 2002; Jal et al., 2004; Walcarius and Mercier, 2010; Lin and Lien, 2013; Sharma et al., 2017). The complexing groups of thiourea derivatives are located on the surface of the CMS, mesoporous organosilica or magnetic nanoparticles, which allows high rates of adsorption and easy elution of the adsorbed elements. However, rather low adsorption capacity of the CMS, mesoporous organosilica, magnetic nanoparticles and their high cost limits their application by the analytical chemistry only (Jal et al., 2004).

Developing of the selective adsorbents for extraction of precious metals from complex industrial solutions is an actual task. The novel adsorbent should be cost-effective and synthesized from available raw materials.

Adsorbents based on organic natural materials, the biosorbents (Das, 2010; Mudhoo et al., 2012; Xue et al., 2016), are of special interest. Most of biosorbents are wastes of agriculture, various kinds of husk (rice, barley, oat, wheat, and rye), sawdust – waste of wood industry (Jain et al., 2016; de Melo et al., 2016).

Sawdust is waste of wood industry. It consists of various organic compounds (cellulose, lignin, hemicellulose) with polyphenol groups that are able to bind heavy metal ions via various mechanisms (Sciban et al., 2006).

To improve the adsorption properties of plant-based materials for metal ions extraction, it is common to modify them with various functional groups (phosphate, sulphate, citrate, amine, etc). (Wang et al., 2015; Jain et al., 2016; de Melo et al., 2016).

Chitosan is used as a basis for biosorbents with thiourea groups for precious metals pre-concentration (Guibal et al., 2002; Ruiz et al., 2003; Dodson et al., 2015).

Development of synthesis of sawdust-based biosorbent with thiourea groups covalently bound to the surface and investigation of its adsorption properties for precious metals extraction were the purpose of the present work. Biosorbent was used for removal of precious metals from complex industrial solutions, for subsequent returning them into the process.

2. Materials and methods

2.1. Reagents

HCl, HNO_3, NaOH, thiourea of analytical grade purchased from Reakhim (Russia) were used.

The stock solutions (1 g/L) of Au^{3+}, Pd^{2+}, Pt^{2+}, Pt^{4+}, Ir^{4+}, Rh^{3+}, Ru^{4+} were prepared by dissolving the $H[AuCl_4]·4H_2O$, $PdCl_2$, $H_2[PtCl_6]·6H_2O$,$H_2[PtCl_4]·2H_2O$, $Na_3[IrCl_6]$, $H_3[RhCl_6]$, $RuCl_3$ of reagent grade in 2 M HCl. The reagents were purchased from JSC «Aurat» (Russia).

Stock solutions of alkaline, alkaline earth elements, and Fe^{3+}, Al^{3+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+} were prepared by dissolving the corresponding salts (Reakhim, Russia) in 0.1 M.

The ICP Multielement Standard USP-III, 100 mg/L: Ir, Os, Pd, Pt, Rh, Ru purchased from Merck KGaA (Darmstadt, Germany) was used as multielement calibration standard for ICP-OES determination of precious metals.

The ICP Multielement Calibration Standard 1 (As, Be, B, Cd, Pb, Mn, Se, Zn), ICP Multielement Calibration Standard 8 (Al, Ca, Cr, Li, Ni, K, Na, Sr), ICP Multielement Calibration Standard 10 (Al, Ba, Be, Co, Cu, Fe, V) purchased from High-purity standards (USA) were used as multielement calibration standards for ICP-OES determination of accompanying elements.

A solution of $AgNO_3$ (0.02 M) for titration was prepared by dissolving of weighted portion of the reagent.

The pH of solutions was adjusted by adding NaOH or HCl solutions.

Table 1
Operational conditions used for the determination of elements.

Parameter	Value
RF power	1150 W
Nebulizer gas flow	0.7 L/min
Auxiliary gas flow	0.5 L/min
Coolant gas flow	12 L/min
Analysis pump rate	60 rpm
Flush pump rate	100 rpm
Sample flush time	30 s
Pump stabilization time	5 s
Integration time	15 s
Observation view	Axial
Number of repeats	3
Element	Emission line[a], nm
Ag	328.068 (I)
Al	396.152(I)
Au	242.179 (I)
Cd	228.802 (I)
Co	228.616 (II)
Cu	327.396 (I)
Fe	238.204 (II)
Ir	212.681 (II)
Mn	293,930 (II)
Ni	231.604 (II)
Pb	220.353 (II)
Pd	324.270 (I)
Pt	265.945 (I)
Rh	343.489 (I)
Ru	266,161 (II)
Zn	206,200 (II)

[a] (I) atomic and (II) ionic emission lines.

A 10% (w/w) thiourea solution in 1 M HCl was usedas a desorbing solution for precious metals.

2.2. Apparatus

The metals distribution between the biosorbent and the solution was controlled by inductively coupled plasma optical emission spectrometry (**ICP-OES**) analysis of the aqueous phase using iCAP 6500 DUO spectrometer (Thermo Scientific, USA) with dual plasma viewing. The operating conditions are represented in Table 1.

The pH of the solutions was measured using SevenMulti ionometer (Mettler-Toledo, Switzerland).

Thermal analyses were performed by the simultaneous STA 449 C Jupiter thermal analyzer (Netzsch, Germany) combined with FT-IR spectrometer Nicolet 380 (Thermo Scientific, USA) and with the TGA/FT-IR interface. This setup allows one to receive the differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data simultaneously, and the released gas phase composition. The temporal dependence of the optical density for each of the released gasses was obtained from IR spectra. The sample was placed into a platinum crucible and heated within the temperature range of 30–760 °C with a rate of 10 °C/min, the air blow of 50 mL/min.

Scanning Electron Microscopy (**SEM**) and Energy Despersive X-ray Spectrometry (**EDS**) of the free and loaded biosorbents were perfomed in back-scattered electron on TM-3000 (Hitachi, Japan) equipped with Energy Dispersive X-ray Spectrometer Qantax-70 (Bruker, Germany) at an electron beam voltage 15 kV.

The EPR spectra were recorded with an Alexsys 580 instrument (Bruker, Germany).

Bioadsorbents were analyzed by Fourier Transform Infrared Spectroscopy (**FT-IR**) using spectrometer Nicolet 380 with Smart Orbit accessories (Thermo scientific, USA) in wavelength range of 4000–400 cm^{-1} with 4 cm^{-1} spectral resolution.

Drying cabinet SNOL 58/350 and a muffle furnace SNOL 7.2/1100 (Utenos Electrotechnika, Lithuania) were used for drying and roasting.