Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

Synthesis, characterization and experimental assessment of a novel functionalized macroporous acrylic copolymer for gold separation from wastewater

Lavinia Tofan[a], *Ion Bunia*[b], *Carmen Paduraru*[a], *Carmen Teodosiu*[a,*]

[a] *Department of Environmental Engineering and Management, Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University of Iasi, 73, Prof. Dr. D. Mangeron Street, 700050 Iasi, Romania*
[b] *"Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Street, 700487 Iasi, Romania*

ARTICLE INFO

Article history:
Received 30 July 2016
Received in revised form 1 December 2016
Accepted 4 January 2017
Available online 12 January 2017

Keywords:
Gold
Acrylic copolymer
Dimethylaminobenzaldehyde
Wastewater

ABSTRACT

Gold (Au) is one of the precious metals whose availability, use and recovery represent important problems from the economic and environmental point of view. The synthesis of the novel acrylic copolymer bearing dimethylaminobenzaldehyde functional groups (AS–5BA) was carried out in three stages. The structure of the synthesized material was evidenced by infrared spectroscopy (IR) and its morphology by scanning electron microscopy (SEM), while the elemental composition was determined through X-ray photoelectron spectroscopy (XPS). The AS–5BA functionalized copolymer was used for gold sorption from chloride solution by the batch method. The effects of HCl medium acidity, initial Au(III) concentration, and contact time on the Au(III) retention were studied. The maximum Au(III) sorption capacity was evaluated as 87.75 mg/g. The copolymer under study exhibited strong selectivity for the gold in the binary Au(III)–Co(II), Au(III)–Mn(II) and Au(III)–Cd(II) solutions. Gold could be quantitatively desorbed from the loaded sorbent with acidic solution of thiourea at ambient temperature. The developed AS–5BA copolymer was successfully applied to recover gold from a wastewater collected from a gold jewellery manufacturing plant. The AS–5BA functionalized acrylic copolymer with N as donor atoms has good durability as well as good efficiency for its repeated use for gold removal from aqueous solutions.

1. Introduction

Gold (Au) is a noble metal with unique chemical and physical properties that has a wide range of applications in industrial and economic activities (Syed, 2012). Its most common uses are specific for the industry of jewelry, electronics, catalysts, and medical instruments (Goodman, 2002; Ellis, 2004; Harutta, 2004; Navarro, 2009). Gold is internationally recognized as a type of currency under ISO 4217 (Das, 2010).

The growing number of gold uses and its limited availability result in an imperious necessity to recover this precious metal from aqueous and waste solutions. Many methods such as co-precipitation (Yongzhou, 2006; Soylak and Tuzen, 2008), ion exchange (Alguacil et al., 2005; Gomes et al., 2001; Jeffrey et al., 2013), solvent extraction (Kolekar and Anuse, 2001; Khisamutdinov et al., 2007; Vidhate et al., 2015) and sorption have been used to separate and enrich gold. Among these methods, sorption has been considered as the most significant and promising method for gold separation and preconcentration, due to its high efficiency and easy handling (Das, 2010; Syed, 2012). The uptake of gold by sorption is mainly carried out from hydrochloric solutions where this metal exists as sorption-active chloride or aqua-chloride anionic complexes (Myasoedova et al., 2007). A wide range of sorbents have been used (Pyrzynska, 2012; Shaheen et al., 2015), the selectivity for gold being proved by the chelating resins or polymers with

* *Corresponding author.*
E-mail address: cteo@ch.tuiasi.ro (C. Teodosiu).
http://dx.doi.org/10.1016/j.psep.2017.01.002

Table 1 – Chelating polymers with high selectivity for Au(III) ions.

Chelating sorbent	Synthesis method	Remarks	References
Bisthiourea-formaldehyde	Polymerization of bisthiourea with formaldehyde at different molar ratios	The total uptake of Au(III) increases as the content of bisthiourea in the matrix increases	Atia (2005)
Different resins with amine, thio and amine–mercaptan functionalities	Polymerization of glycidyl–methacrylate in the presence of divinylbenzene as cross-linker	The resins showed high stability as well as good performance in acidic media. The amine–mercaptan containing resins were found to be more efficient in the recovery of Au(III)	Donia et al. (2005)
Crosslinked poly(vinylbenzyl chloride) resins bearing diamine and guanidine ligands	A series of 24 resins were synthesised from an expanded gel (A), and porous (B, C) vinylbenzyl chloride copolymers using alkyldiamine (1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane and 1,6-diaminohexane) and cyanamide	The resins contain amine and guanidine functionality of 3.1–5.7 mmol/g. The resins reveal excellent sorption ability towards gold, palladium and platinum anions from hydrochloric acid solutions which is proportional to anion-exchange capacity	Jermakowicz-Bartkowick (2005)
Resins based on polymer vinylbenzyl chloride (VBC)/divinyl-benzene (DVB) with amine groups	The amination processes of VBC/DVB with the following amines: piperidine, hexamethyleneimine, *N*-cyclohexyl-1,3-propanediamine, 1-(2-aminoethyl)piperazine and piperazine	These resins are useful for the sorption of gold as tetrachloroaurate and its separation from multicomponent solutions	Jermakowicz-Bartkowick (2010)
Polystyrene-supported 3-amino-1,2-propanediol	Reaction of chloromethylated polystyrene with 3-amino-1,2-propanediol	The resin possesses best enriching property to Au(III) among the Pb(II), Hg(II), Cu(II), Ni(II) and Au(III) ions. The removal efficiency could reach about 98%	Changmei et al. (2011)
Polystyrene-2-aminothiazole (PS-AT)	One-step reaction by grafting 2-aminothiazole in a chloromethylated polystyrene polymer	The resin exhibits an excellent selectivity for Au(III) ions in the presence of Ni(II), Cu(II), Cd(II), and Co(II) ions. The XPS data, along with IR spectra revealed that gold was adsorbed on the surface of PS-AT in the form of chloride, while nitrogen and sulfur were involved in the chelation of gold chloride	Xiong et al. (2014)
Chitosan derivative	Carboxymethylation and grafting sulfur groups onto crosslinked chitosan backbone	The adsorption capability of the chitosan derivative has no obvious change up to five cycles	Wang et al. (2012)
Thiocarbamoyl chitosans with substitution degrees from 0.4 to 0.9	Reaction in eutectic two-component system ammonium rodanide–thiourea	Gold recovery occurred with reduction of Au(III) to Au(I)/Au(0)	Bratskaya et al. (2011)
N-2-(2-Pyridyl) ethyl chitosan (PE-chitosan) with substitution degrees up to 1.2	The “synthesis in gel” approach for direct addition reaction between 2-vynilpyridine and chitosan	The use of this sorbent for preconcentration of Au(III) with subsequent elution (HCl/thiourea) provides an opportunity to analyze of multi-component solutions with low gold content	Bratskaya et al. (2012)

functional groups. Especially the polymers functionalized with groups containing nitrogen or sulfur donor atoms are preferred in the sorption of gold ions, because of the hard–soft acid–base (HSAB) principle introduced by Pearson (Pearson, 1968; Erim et al., 2013). Some examples of the chelating resins including N and/or S donor atoms for Au(III) ions are presented in Table 1.

Acrylic copolymers represent interesting macromolecular supports due to their higher physicochemical stability and more hydrophilic structure than that of the styrene-based copolymers. The modification of the acrylic matrices conduct to compounds with ionic or ionizable functional groups and high hydrophilic structures (Neagu and Bunia, 2009).

In this context, the present study is focused on the synthesis, characterization and sorption properties of a new acrylic copolymer with dimethylaminobenzaldehyde functional groups (AS–5BA) for Au(III) removal and recovery from aqueous solutions. The synthesis of the chelating resin takes place in three stages: (1) preparation of the etylacrylate/acrylonitrile/divinylbenzene (EA/AN/DVB) copolymer by radical copolymerization; (2) synthesis of the AS-127 acrylic anion exchanger by the aminolysis reaction of EA/AN/DVB copolymer with triethylenetetramine (TETA); (3) synthesis of functionalized copolymer AS–5BA by the aminolysis reaction of AS-127 acrylic anion exchanger with dimethylaminobenzaldehyde (DMABA). The synthesis of this novel resin targeted the introduction in the macromolecular structure of new functional groups with an increased number of electron donors capable of forming complexes with the heavy metals from aqueous solutions. Through the reaction of the amine groups of the ion exchanger with dimethylaminobenzaldehyde, functional groups