Thiocarbamoyl derivatives of polyallylamine for gold and silver recovery from ammonia-thiosulfate leachates*

***Y. O. Privar**, Leading Engineer-technologist*[1]
***A. V. Pestov**, Senior researcher*[2]
***Y. A. Azarova**, Researcher*[1]
***S. Y. Bratskaya**, Head of Laboratory*[1]*, Corresponding member of Russian Academy of Sciences,*
e-mail: sbratska@ich.dvo.ru

[1] *Institute of Chemistry, Far East Branch of Russian Academy of Sciences, Vladivostok, Russia.*
[2] *I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of RAS Yekaterinburg, Russia.*

Growing concern about ecological safety promotes the interest to cyanide-free leaching of gold-bearing ores and wastes, particularly to ammonia-thiosulfate leaching. In contrast to toxic cyanides, thiosulfates are applicable in underground and heap leaching, less expensive and more efficient for carbonaceous ores. However, traditional technologies of gold recovery from cyanide leachates are not feasible in case of ammonia-thiosulfate solutions, thus, the search for economically sound alternatives is urgent. Here we report on simple and "green" synthesis of new thiocarbamoyl derivatives of polyallylamine (TCPAA) in ammonium thiocyanate/thiourea eutectic melt yielding products with substitution degree (DS) up to 0.87. The TCPAAs obtained have the sorption capacities above 2.5 mmol/g for gold and silver ions in ammonia-thiosulfate solutions, and provide 95 % efficacy of gold and silver recovery from model solutions containing 40 mg/L of precious metals at least in three consecutive sorption cycles (without regeneration). Comparison of TCPAAs efficiency with that of strong base macroporous resin Lewatit MP 500 showed advantages of TCPAA, particularly for silver recovery. Derivatives with DS 0.5 and 0.8 did not show significant advantages over lower substituted TCPAA with DS 0.3 in terms of gold and silver recovery, however, efficacy of gold elution with H_2SO_4/thiourea solutions was significantly higher for TCPAA with DS 0.5. The potential of TCPAAs for gold and silver recovery from ammonia-thiosulfate leachates has been corroborated using gold-bearing industrial wastes. 86% of gold was eluted from TCPAA of medium DS using 0.5M H_2SO_4/1M thiourea solution.

Key words: gold, wastes, ammonia-thiosufate leaching, sorption, polyallylamine, thicarbamoylation, S-containing sorbents.

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Introduction

Due to the decreasing number of reach placer gold deposits in Russia and in the world, there is growing interest to the recovery of fine gold from wastes of gold industry [1]. Typically, application of gravitation separation to this type of raw materials is of low efficacy, while cyanide leaching is limited by the presence of refractory minerals [2]. Besides, serious concern regarding ecological safety of gold leaching promotes interest to cyanide-free alternatives, first of all, to ammonia-thiosulfate leaching [3–6]. In contrast to cyanides, thiosulfates are biodegradable and low toxic that makes them applicable in-situ underground and heap leaching, moreover, they are cheaper and more efficient in case of carbonaceous ores and ores, containing copper, lead and zinc [4]. Depending on the type of raw material and leaching solution composition efficacy of ammonia-thiosulfate leaching reaches 50–95% [7]. However, optimization of leaching conditions is rather complicated due to the number of side reactions of oxidation and disproportionation involving thiosulfates [5].

Recovery of gold from ammonia-thiosulfate solutions is also not simple. Cementation is not efficient due to co-precipitation of copper and other metals [8]. Electrowinning allows in principle separation of copper and gold due to the difference in deposition potentials [9], but, in most cases, low purity product is obtain, moreover, low current efficiency markedly increases energy consumption [6]. Organic solvents extraction of gold with high efficacy (up to 97%) [10] is an example of expensive and limitedly applicable technology.

Sorption of gold from cyanide leaching solution is the most simple and economically sound method, however,

* Ivannikov S. I., Shamrai E. I., Polyakova N. V., Malakhova I. A., Yudakov A. A. (Institute of Chemistry FEBRAS) have also contributed to this work.

thiosulfate complexes of gold only weakly adsorb on activated carbon [11]. Relatively high efficacy of gold recovery was found on weak and strong base resins, but they have low sorption capacity, which decreases with increase of pH for weak base resins at pH 8–11 [12], where gold leaching is the most efficient. Although S-containing sorbent are often used for noble metals recovery, their application in ammonia-thiosulfate solutions is scarcely investigated, in particular, ANS-80 resin in alkaline media showed low efficacy of gold recovery — 33.0% in comparison with 85% on strong base resins [13]. To the best of our knowledge, other S-containing sorbents have not been tested, moreover, recent review emphasizes that applicability of sorption technologies to gold recovery from ammonia-thiosulfate leachates is still underinvestigated [6].

Here we report on synthesis of new S-containing derivative of polyallylamine and their sorption properties toward silver and gold ions, including recovery of these metals from ammonia-thiosulfate leachates.

Experimental

Synthesis and characterization of thiocarbamoyl derivatives of polyallylamine (TCPAA)

Polyallylamine hydrochloride (AlfaAesar), thiourea, and ammonium thiocyanate (Sigma-Aldrich) were used as received.

Thiocarbamoylation was performed according to the following procedure: the mixture of 0.94 g (0.01 mol) polyallylamine (PAA) hydrochloride, 2.05 g (0.027 mol) ammonium thiocyanate and 1 g (0.013 mol) thiourea was heated up to 130 ^{o}C for 4 h. The obtained product was extracted by water until negative reaction of washing waters on SCN^- ions (color reaction with Fe(III)) and air-dried. The yield was 1.2 g. (86%), degree of substitution (DS) – 0.53. Derivatives with other DS were obtained via varying reagents ratio according to the Table 1. TCPAA with DS 0.27, 0.48 and 0.8 are further referred as TCPAA 0.3, TCPAA 0.5, and TCPAA 0.8.

The elemental compositions of all products were determined on the Elemental Analyzer Perkin Elmer. The degree of substitution (DS) were calculated from the elemental analysis data according to the formula: DS = $= 1/(n_N/n_S - 1)$, where n_S — the molar quantity of sulfur, n_N — the molar quantity of nitrogen. FTIR spectra were recorded on the Spectrum One FTIR spectrometer (Perkin Elmer) using the Diffuse Reflectance Sampling Accessory.

Sorption of Au(III) *and* Ag(I) *on TCPAA from model solutions*

Sorption capacities of TCPAA with DS 0.3–0.8 toward Ag(I) and Au(III) were determined in $AgNO_3/H_2O$ and $H[AuCl_4]$/0.1M HCl solutions, respectively, at solid:liquid ratio 1:500 and sorption time of 18 h. Efficacy of gold and silver recovery with TCPAA 0.3 and Lewatit MP 500 (strong base macroporous resin) in three consecutive cycles without regeneration was studied from model ammonia-thiosulfate solutions (0.2M NH_3, 0.02M $CuSO_4$, 0.02M $Na_2S_2O_3$, pH = 10.4), containing 40 mg/L of gold or silver, at solid:liquid ratio 1:500. The adsorbed amounts were calculated using the difference in initial and equilibrium concentrations of the metal ions in the solutions determined by the atomic absorption spectroscopy (AAS) using a Solaar M6 spectrometer (Thermo, USA). Elution of gold and silver from the sorbent phase using H_2SO_4/1M thiourea solution was estimated at solid:liquid ratio 1:50, metal concentrations in eluents were determined by AAS.

X-ray powder diffraction (XRD) analysis of TCPAA after sorption of gold and silver ions from ammonia-thiosulfate model solutions or water was carried out on a Dron-3 multipurpose diffractometer (Russia).

Recovery of gold and silver from leachates of gold-bearing industrial wastes

Wastes accumulated in the sludge tanks of Chalgan pilot shop (Amur Scientific Center, Far Eastern Branch of Russian Academy of Sciences) were used as a gold-bearing material. Mineralogical analysis did not revealed presence of visible gold or other noble metals in the sample. Matrix of the sludge contains magnetite, ilmenite, hematite, and low quantities of pyrite, chalcopyrite and arsenopyrite. Significant quantity of mercury in sludge (up to 1.3 kg/t, as determined with the energy dispersive *X*-ray fluorescence spectrometer EDX 800 HS, Shimadzu) originates mainly from the previous technological processing – gold recovery using amalgamation. Neutron activation analysis performed with compact installation with ^{252}Cf excitation source [14] showed gold content in the sludge sample in the range 30–120 g/t. Up to 50 g/t of silver were found in samples by AAS analysis performed according to the method № 130-C of Scientific Council on Analytical Methods.

Ammonia-thiosulfate leaching was performed under the constant stirring using solution of the following composition: 0.2M NH_3, 0.02M $CuSO_4$, 0.02M $Na_2S_2O_3$, pH = 10.4. The solid:liquid ratio was set to 1:2. Gold and silver concentrations in the leachates were monitored by AAS. The mercury concentration was determined using a HVG-1 Hydride Vapor Generator and an AA-6200 atomic absorption spectrometer (Shimadzu, Japan). Recovery of gold, silver and mercury from the leachates on TCPAA and Lewatit MP 500 was studied at solid:liquid ratio 1:500 and 1:200 under constant stirring for 18 h. Elution of the metals from the sorbents phase was performed as described above.

Results and Discussion

Synthesis and characterization of TCPAA

We have previously suggested method of chitosan functionalization with thiocarbamoyl groups to increase its affinity toward noble metal ions [15].

Application of this approach to thiocarbamoylation of polyallylamie (PAA) has significant advantages over the method of PAA functionalization with highly toxic reagent CS_2 reported in [16–17]. Usage of the eutectic melt ammonium thiocyanate/thiourea for polyallylamine functionalization is even more efficient compared to chitosan modification, since PAA is highly reactive and completely dissolves in the melt yielding viscous solution.

Reaction of thiocarbamoylation of polyallylamine:

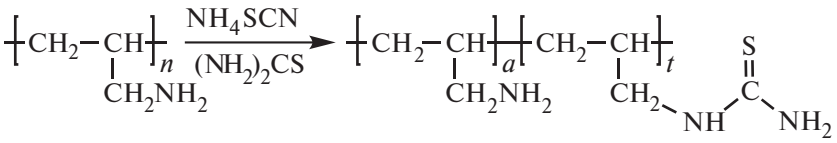

Table 1
Conditions of PAA thiocarbamoylation (T = 130 °C) and products characteristics

Entry	Molar ratio PAA : NH_4SCN : $(NH_2)_2CS$	Time, *h*	Content, %		Degree of substitution (DS) with thiocarbamoyl groups
			N	S	
1	1 : 1.35 : 0.65	4	20.75	15.37	0.48
2	1 : 2.7 : 1.3	4	20.34	16.28	0.53
3	1 : 2.7 : 1.3	8	19.81	14.57	0.47
4	1 : 6.75 : 3.25	4	19.43	19.73	0.80
5*	1 : 6.75 : 3.25	40 min	21.92	10.82	0.27
6	1 : 9.45 : 4.55	4	19.12	20.38	0.87

*Synthesis was performed under ultrasonic irradiation.

As follows from data in Table 1, thiocarbamoylation proceeds efficiently yielding products with DS up to 0.87. Usage of the large molar excess of the reagents (Table 1, entry 6) does not lead to the completely substituted product. Increase of reaction time (Table 1, entries 2 and 3) results in partial dethiocarbamoylation. All synthesized PAA derivatives were insoluble due to the formation of cross-linkages during functionalization that allows direct application of TCPAAs as sorbents.

Composition and structure of TCPAAs were confirmed by elemental analysis (Table 1) and FTIR spectroscopy. On the background of the absorption bands of PAA – 3280 (N – H), 2922 (C – H), and 1161, 1038 (C – N) cm^{-1}, appears new intensive absorption bands at 3183 (N – H), 2053 (S = C = N), 1612, 1522 (N – H), and 1350 (C = S) cm^{-1} corresponding to vibrations of bonds in thiocarbamoyl group.

Sorption properties of TCPAA

Due to the presence of primary amino group and low molecular weight of monomer unit PAA is known as a high-capacity sorbent for metal ions [18–19]. PAA is highly reactive in polymer modification yielding N- and S-derivatives with high affinity toward noble metals and mercury ions [16–17, 20]. One of the advantage

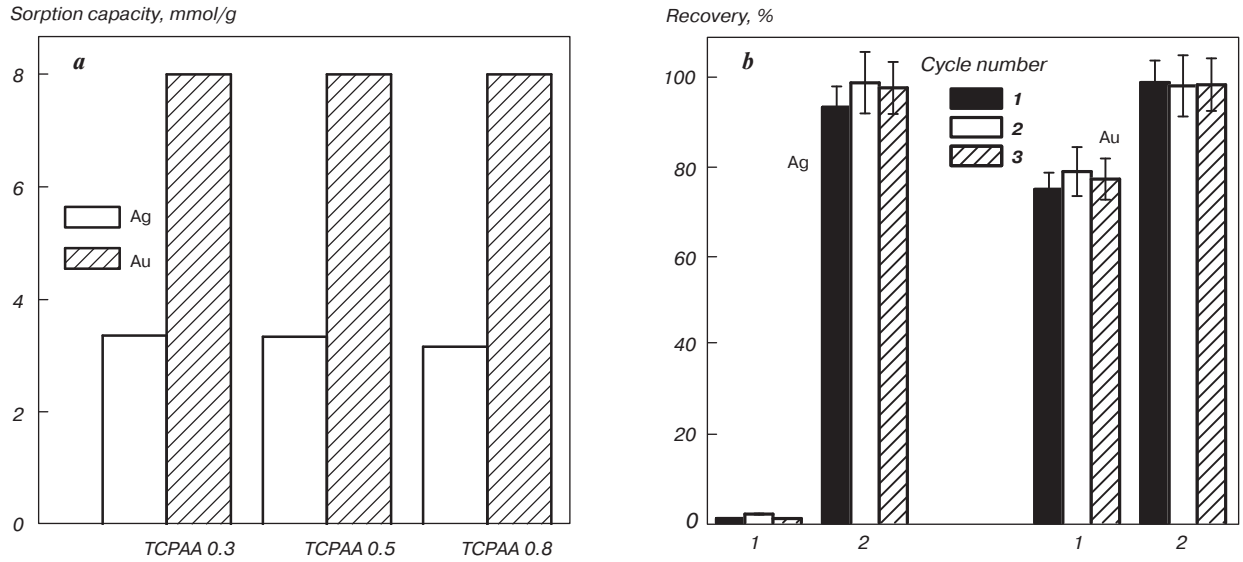

Fig. 1. Sorption capacities of TCPAA for Ag(I) and Au(III) ions in $AgNO_3/H_2O$ and $H[AuCl_4]$/0.1M HCl solutions, respectively (*a*). Recovery of gold and silver with MP 500 Lewatit (*1*) and TCPAA 0.3 (*2*) from model ammonia-thiosulfate solutions (0.2M NH_3, 0.02M $CuSO_4$, 0.02M $Na_2S_2O_3$, 40 mg/l Ag or Au, pH = 10.4), solid:liquid ratio 1:500 (*b*)

of S-containing derivatives is the lower dependence of sorption properties on pH [15–16]. Fig. 1*a* shows that TCPAA with DS 0.3–0.8 had sorption capacities higher than 8 mmol/g and 3 mmol/g for Au(III) and Ag(I), respectively. Despite the presence of anionic complexes $[Cu(S_2O_3)_3]^{5-}$, which are predominant form of copper in thiosulfate solutions and responsible for low selectivity of N-containing sorbents in ammonia-thiosulfate leachates [6], TCPAAs maintain high affinity and sorption capacities above 3 mmol/g and 2.5 mmol/g for gold and silver, respectively. Investigation of sorption capacities at high metals concentrations was not performed due to the poor stability of the solutions or difficulties to maintain pH ~10.5, therefore maximal sorption capacities were not determined. We have earlier shown that sorption of Au(III) from HCl solutions on unmodified PAA is accompanied by complete reduction of Au(III) to Au(0) that determines low efficacy of gold elution [20]. At high concentrations of Au(III) after the sorption on TCPAA we have observed deposition of thin metallic films on the glassware. XRD analysis confirmed presence of the elemental gold in the sorbent phase after the sorption from both – HCl and ammonia-thiosulfate solutions (Fig. 2). Redox sorption of Au(III) is often reported for N- and O-containing polymers [21] but it is often difficult to identify source of the electrons [22]. Although, XRD analysis has not revealed formation of elemental silver, efficacy of silver elution from TCPAA 0.3 with 1M thiourea and 3M $Na_2S_2O_3$,solutions did not exceed 30%, most likely due to the formation of insoluble Ag_2S [6].

Obviously, investigations of TCPAA sorption properties from solutions with very low gold and silver concentrations (below 100 mg/l) have higher industrial relevance for ore and e-wastes leaching [6, 9]. Fig. 1*b* demonstrates that TCPAA 0.3 in three consecutive sorption cycles (without regeneration) provides 95% efficacy of gold and silver recovery from ammonia-thiosulfate solution, while strong base resin Lewatit MP 500 is efficient only for recovery of gold.

Efficacy of TCPAA for gold and silver recovery from ammonia-thiosulfate leachates was tested using gold-bearing sludge from Chalgan pilot shop. Preliminary investigations of the leaching kinetics revealed (Fig. 3) that gold leaching was notably slower compared to silver and mercury, besides leaching efficacy for gold was 60–70% due to the presence of iron compounds catalyzing decomposition of thiosulfate and lowering leaching efficacy [6].

Fig. 4*a* demonstrates higher efficacy of TCPAA compared to Lewatit MP 500 for recovery of mercury, silver, and gold from ammonia-thiosulfate leaching solutions at solid:liquid ratio 1:200. Derivatives with medium and high DS (TCPAA 0.5 and 0.8) did not show significant advantages over lower substituted TCPAA 0.3 in terms of gold and silver recovery, however, efficacy of gold elution with H_2SO_4/thiourea solutions was significantly higher

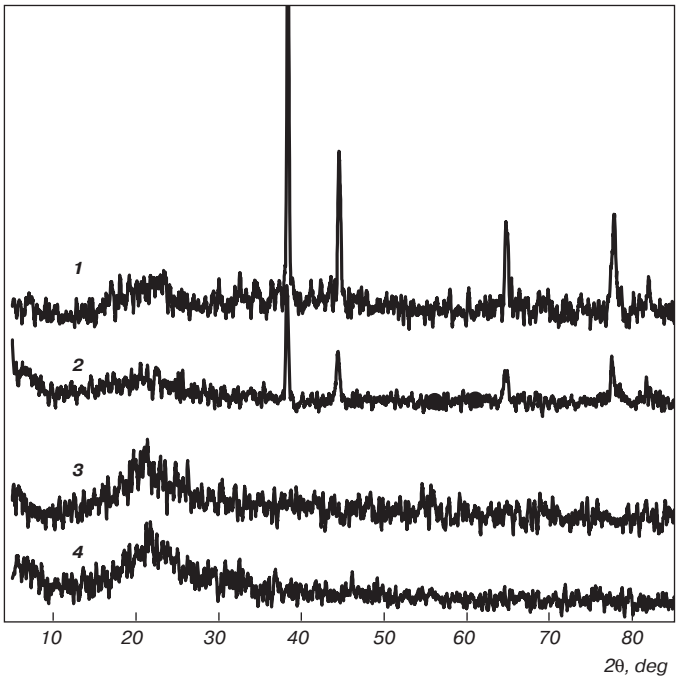

Fig. 2. XRD patterns of TCPAA 0.3 after sorption of gold ions from ammonia-thiosulfate solution (*1*) and 0.1M HCl (*2*) and sorption of silver ions from ammonia-thiosulfate solution (*3*) and water (*4*)

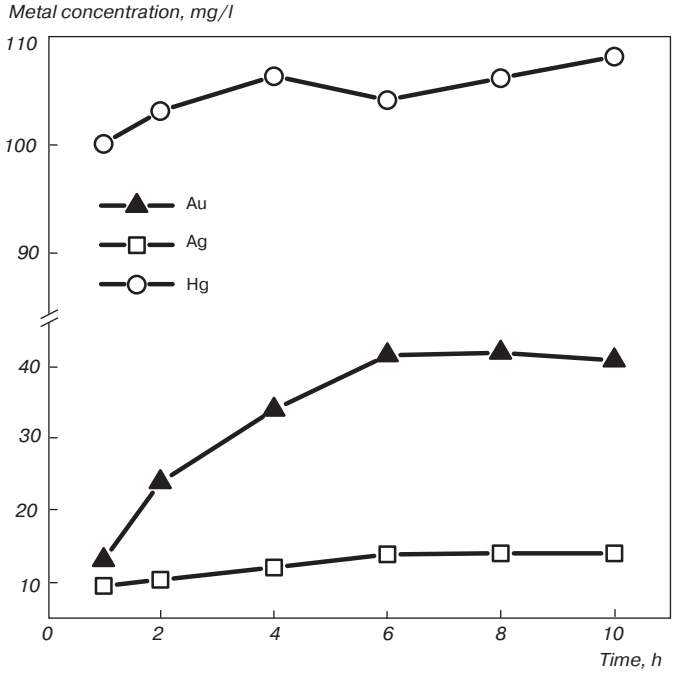

Fig. 3. Kinetics of ammonia-thiosulfate leaching (0.2M NH_3, 0.02M $CuSO_4$, 0.02M $Na_2S_2O_3$, pH=10.4) from Chalgan sludge, solid:liquid ratio 1:2

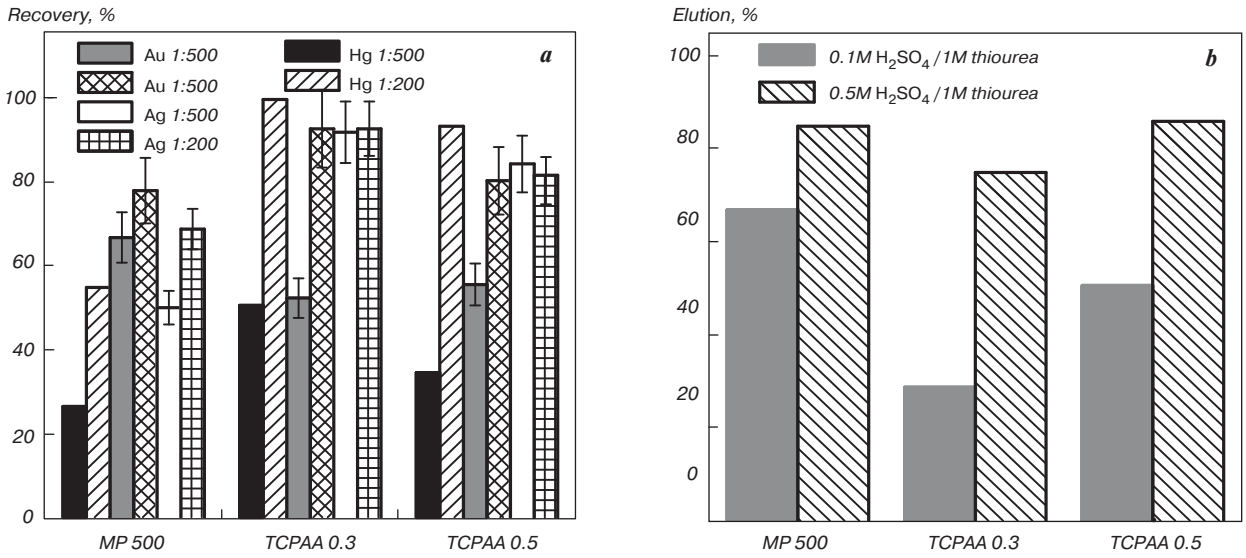

Fig. 4. Efficacy of gold, silver, and mercury recovery from ammonia-thiosulfate leachates of Chalgan sludge (0.2M NH_3, 0.02M $CuSO_4$, 0.02M $Na_2S_2O_3$, pH =10.4, Hg —106 mg/l, Au — 42 mg/l, Ag — 14 mg/l), solid:liquid ratio 1:200 and 1:500 (*a*) and gold elution from the sorbent with H_2SO_4/thiourea solutions (*b*)

for TCPAA 0.5 (Fig. 4*b*). Thus, modification of PAA under mild conditions yields derivatives, which can be considered as promising materials for recovery of silver and gold from ammonia-thiosulfate leachates.

Conclusions

The one-stage method for the synthesis of thiocarbamoyl derivatives of polyallylamine (TCPAA) using ammonium thiocyanate/thiourea eutectic melt has been developed. In comparison with earlier reported in literature synthesis of similar type of derivatives using CS_2 the suggested approach is simpler and safer. Varying ratio of the reagents derivatives with degree of substitution up to 0.87 can be obtained with high yields. We have shown that sorption capacities of TCPAA for silver and gold ions are higher than 8 mmol/g and 3 mmol/g, respectively, moreover, TCPAAs preserves high affinity and capacity in ammonia-thiosulfate solutions in the presence of anionic complexes of copper competing for the sorption cites. TCPAA with medium substitution degree (0.3) provides 95% efficacy of gold and silver recovery from model ammonia-thiosulfate solutions in three consecutive sorption cycles and shows significant advantages of strong base resin Lewatit MP 500 regarding silver recovery. The applicability of TCPAA for gold and silver recovery in industrially relevant systems was demonstrated using leachates of wastes of Chalgan pilot shop. 86% of gold was eluted from TCPAA of medium DS using 0.5M H_2SO_4/1M thiourea solution.

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References

1. Van-Van-E A. P., Litvintzev V. S., Sekisov G. V. State and development of resource potential of goldmining branch of the Far East. *GIAB. Far East—2.* 2009. pp. 32—36.

2. Volkov A. V. Large and super-large gold deposits with "invisible" and refractory gold. *Bulletin of Higher Education Institutions. Geology and Exploring.* 2007. No. 5. pp. 51—54.

3. Grosse A. C., Dicinoski G. W., Shaw M. J., Haddad P. R. Leaching and recovery of gold using ammoniacal thiosulfate leach liquors (a review). *Hydrometallurgy.* 2003. Vol. 69. pp. 1—21.

4. Vinh H. H., Lee J. C. Jeong J., Huynh T. H., Jha M. K. Thiosulfate leaching of gold from waste mobile phones. *Journal of Hazardous Materials.* 2010. Vol. 178. pp. 1115—1119.

5. Wan R. Y., Levier K. M., Solution chemistry factors for gold thiosulfate heap leaching. *Int. J. Miner. Process.* 2003. Vol. 72. pp. 311—322.

6. Xu B., Kong W., Li Q., Yang Y., Jiang T., Liu X. A Review of Thiosulfate Leaching of Gold: Focus on Thiosulfate Consumption and Gold Recovery from Pregnant Solution. *Metals.* 2017. Vol. 7, Iss. 6. 222. DOI: 10.3390/met7060222

7. Aylmore M. G., Muir D. M. Thiosulfate leaching of gold — a review. *Minerals Engineering.* 2001. Vol. 14. pp. 135—174.

8. Awadalla F. T., Ritcey G. M. Recovery of gold from thiourea, thiocynate or thiosulfate solutions by reduction-precipitation with a stabilized from of sodium borohydride. *Randol Gold Forum.* 1990. pp. 295—306.

9. Kasper A. C., Veit H. M., García-Gabaldón M., Herranz V. P. Electrochemical study of gold recovery from ammoniacal thiosulfate, simulating the PCBs leaching of mobile phones. *Electrochim. Acta*. 2018. Vol. 259. pp. 500–509.

10. Zhao, J., Wu, Z., Chen, J. Separation of gold from other metals in thiosulfate solutions by solvent extraction. *Sci. Technol*. 1999. Vol. 34, Iss. 10. pp. 2061–2068.

11. Xu, B., Yang, Y., Li, Q., Jiang, T., Liu, S., Li, G., The development of an environmentally friendly leaching process of a high C, As and Sb bearing sulfide gold concentrate. *Miner. Eng.* 2016. Vol. 89. pp. 138–147.

12. Zhang H., Dreisinger D. B. The adsorption of gold and copper onto ion-exchange resins from ammoniacal thiosulfate solutions. *Hydrometallurgy*. 2002. Vol. 66. pp. 67–76.

13. Kononova O. N. Kholmogorov A. G., Kononov Y. S., Pashkov G. L., Kashin S. V., Zotova S. V. Sorption recovery of gold from thiosulfate system after leaching of products of chemical preparation of hard concentrates. *Hydrometallurgy*. 2001. Vol. 59. pp. 115–123.

14. Ivanenko V. V., Metelev A. Yu., Slavkina T. V., Hiev N. V. Instrumental neutron activation determination of rare earth, noble and other elements in mineral raw materials of the Socialist Republic of Vietnam. *J. Radioanal. Nucl. Chem. A*. 1988. Vol. 122, No. 1. pp. 35–41.

15. Bratskaya S. Y., Ustinov A. Y., Azarova Y. A., Pestov A. V. Thiocarbamoyl chitosan: Synthesis, characterization and sorption of Au(III), Pt(IV), and Pd(II). *Carbohydr. Polym*. 2011. Vol. 85. pp. 854–861.

16. Nagai D., Daimon T., Kawakami S., Inoue K. High-recovery material for mercury ions based on a polyallylamine hydrogel with thiourea groups at cross-linking points. *Ind. Eng. Chem. Res*. 2014. Vol. 53. pp. 3300–3304.

17. Nagai D., Yoshida M., Kishi T., Morinaga H., Hara Y., Mori M. et al. A facile and high-recovery material for rare-metals based on a water-soluble polyallylamine with side-chain thiourea groups. *Chem. Commun*. 2013. Vol. 49. 6852. DOI: 10.1039/C3CC43256D

18. Park J., Won S. W., Mao J., Kwak I. S., Yun Y. S. Recovery of Pd(II) from Hydrochloric Solution Using Polyallylamine Hydrochloride-Modified Escherichia Coli Biomass. *Journal of Hazardous Materials*. 2010. Vol. 181. pp. 794–800.

19. Nesterov D. V., Molochnikov L. S., Korjakova O. V., Kodess M. I., Ezhikova M. A., Pestov A. V. Synthesis of Polyaminostyrene-Based and Polyallylamine-Based Sorbents for Boron Removal. *J. Applied Polymer Sci*. 2016. Vol. 133, Iss. 39. 43939. DOI: 10.1002/app.43939

20. Bratskaya S., Privar Y., Ustinov A., Azarova Y., Pestov A. Recovery of Au(III), Pt(IV), and Pd(II) Using Pyridylethyl-Containing Polymers: Chitosan Derivatives vs Synthetic Polymers. *Ind. Eng. Chem. Res*. 2016. Vol. 55. pp. 10377–10385.

21. Bao Y., Shen G., Liu H., Li Y. Fabrication of Gold Nanoparticles through Autoreduction of Chloroaurate Ions by Thermo- and pH-Responsive Amino Acid-Based Star-Shaped Copolymers. *Polymer*. 2013. Vol. 54. Iss. 2. pp. 652–660.

22. Richardson M. J., Johnston J. H., Borrmann T. Monomeric and polymeric amines as dual reductants/stabilisers for the synthesis of gold nanocrystals: a mechanistic study. *Eur. J. Inorg. Chem*. 2006. Vol. 13. pp. 2618–2623.

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