The Precious metals (Au, Ag, Pt, Pd, Rh) adsorption on the Silicon – organic sorbents

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Abstract: Sorption activity of two types of Silicon-organic sorbents for the previous metals has been studied. A polymer – poly (3- silsesquioxanilpropylthiocarbamate) - 3- silsesquioxanilpropyl-ammonium which was obtained by the hydrolytic poly-condensation reaction and has been determined its physical, chemical characteristics and its sorption activity for the Ag(I), Au(III), Pt(IV), Pd(II), Rh(III). It has been found out that the sorbent shows high static sorption of Gold (III), Mercury (II) at acidic condition. The second a net structured silicon-organic copolymer $\{SiO_2 * 2[O_{1.5}Si(CH_2)_3NHC_5H_4N]\}_n$ was synthesized by hydrolytic co-poly-condensation reaction. It likely to react as an anionit that adsorbs chloro-complex anion of the Au (III), Pt(IV), Pd(II), Rh(III).

Introduction

Initial systemic research about the complexity and silicon-organic ionite which contain complex forming or ion exchange groups started since 1977, when discovered the poly-mercaptomethylsilsesquioxane's xerogel [1,2]. It was taken from hydrolytic poly-condensation of the mercaptomethyltrialcosisilan $HSCH_2Si(RO)_3$ (R =CH_3, C_2H_5). Poly-mercapto-methylsilsesquioxane's xerogel is an adsorbent that has ability to adsorb Mercury (II) from the extremely diluted solution (0.01-2mg/l Hg) in the high diapason of the pH, fully [3]. This adsorbent showed high selective adsorption of Mercury(II) from solution which contains over concentrated ions of the Zn(II), Fe(II), Co(II), Ni(II) at pH 0.3-3. Now days this adsorbent is using for removal of Mercury from waste water of chlorine industry [3]. Also this sorbent has

shown high activity (1.1mg-equa/g) in case of Ag(I) [4]. Then, adsorbed silver was fully desorbed by 0.25M ammonium hydroxide. When solution pH > 3, this sorbent has full sorption capacity for Pb(II) and Sn(II) and developed a spectrometer speedy method that used to determine these elements in spa water [4].

Therefore, silicon-organic sorbent (PTCA-3A) with dithiocarbamate group has been synthesized [5-7]. We are performing research evaluating of adsorption capacity of Hg(II), Au(III), Ag(I), Pt(IV), Rh(III) from aqueous solution .

Organic derivatives of the dithiocarbamate have been used widely in practice. Most of them have an unique biological activity and therefore, it is become raw material of the pharmacy [8]. There is a special trend of the practical usage of organic compounds with dithiocarbamate group for determination of heavy metals in the

industrial waste water and its purification [9.10]. Also, there are different types of adsorbent materials which contain dithiocarbamate group and parts [11.12].

Silicon-organic complexities and ionits [13.14] have stability to high temperature (till 250^0C). But study of their ion exchange property is scarce and never been studied its practical usage.

Silicon-organic compounds with hetero-cycle ion has unique biological activeness. But poly-orginalsilsesquioxanes containing hetero-cycle in their organic radical are effective adsorbents which could form complex [7.17]. Therefore, we did research for eluvidation of precious metals (Au, Ag, Pt, Pd, Rh) adsorption ability of the silicon-organic copolymer (PAPS-2) or $\{SiO_2*2[O_{1.5}Si(CH_2)_3NHC_5H_4N\}_n$ that contains 2-aminopyridin which was synthesized by the co-poly-condensation reaction [18].

Experimental

Materials. Poly(3-silsesquioxanil propylthiocarbamate) 3-silsesquioxanilpropyl ammonia (PTCA-3A) is a net constructed polymer with yellow color, finely dispersed powder. Silicon- organic copolymer PAPS-2 is brown colored and coarse sized powder. Table 1 shows physical and IR spectrum data of used polymers.

Table 1. Polymer (PTCA-3A) and PAPS-2

Formula	Physical data						T^0C	IR spectrum (ν, cm⁻¹)
	P_6 (g/cm³)	P_n (g/cm³)	$P_т$ (g/cm³)	P_A (%)	V(cm³/g)	S (m²/g)		
Si₂C₇H₁₆N₂S₂O₃ (PCKA-3A)	1.24	0.58	0.55	56.0	1.01	-	220	3400, 2930, 1540,1020 (NH), 2570(S-H), 1340 (C=S), 1100(Si-O-Si)
C₁₆H₂₂N₄O₅Si₃ (PAPS-2)	-	-	-	-	1.39	515	280	3400, 3300 (NH), 1615, 1595, 1480, 1440 (circle of the Pyridine C=C, C=N), 1120-1000(Si-O-Si), 1560 [δ(NH)]

P_6 – density, P_n – pour density, $P_т$ – apparent density, P_A – porosity , V – total pore volume, S – surface area

IR spectrum of polymers before and after sorption of the precious and rare metal ions were obtained by using high purity KBr with Specord IR 75 and Specord M 80. Physical data were determined according to previous method [19].

Colour of polymer (PTCA-3A) is changing to yellow after adsorption of Hg(II) while with Au(III) – orange, Pt(IV) – yellowish, Pd(II) – brown, Rh(III) – pink, Ag(I) – amber.

Sorption method of the precious metals

Sorption of Hg(II), Au(III), Pt(IV), Pd(II), Rh(III) was studied in hydrochloric acid with concentration of 0.1-5.0 mol/l while Ag(I) sorption was studied in nitric acid with same concentration.

Polymers (PTCA-3A, PAPS-2) were taken 0.05g of and mixed and shaked with solution of precious metal's chloro-complex in 0.1-5.0mol/l concentrated hydrochloric and nitric acids by shaker HY-4. Content of the metals in the solution was 0.05-0.8mg/ml. After a certain time polymer was separated from solution and washed thoroughly and concentration of metal ions left in the solution was determined by spectrophotometer method (HITACHI U-1000 and KFK-2) with tin chloride [20,21].

Precious metals absorption capacity of the of polymers was calculated by maximum content of the metal per gram of polymers at the equilibrium condition. .

Standard solutions of precious metals were prepared by dissolving of $AgNO_3$; $H[AuCl]4H_2O$; $H_2[PtCl_6]6H_2O$; $PdCl_2$ and $RhCl_34H_2O$ in distilled water.
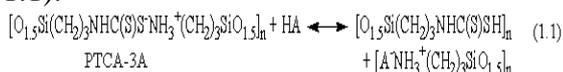
Result and Discussion

Sorption study of PTCA-3A polymer

Adsorption Ag(I) and Pd(II) is correlated with acid concentration, while other ions have no direct correlation. However, Ag(I) and Pd(II) correlation shows reverse behaviour (Figs 1 and 2). Figures 1 and 2 indicate when Ag(I) is adsorbed from nitric acid, proton concentration is increased because of H^+ is interacting with sulfur atom of the thiolyate that caused decreasing Ag(I) adsorption. Sorption of $[PdCl_4]^2$ and $[RhCl_6]$ improved in

result of increasing of chloride ions concentration in solution. Influence hydrochloric acid concentration on the Au(III) and Hg(II) sorption was much weaker than other ions.

It can be suggested that in acid solution thiocarbamate group of polymer (PTCA-3A) is interacting with acid molecule (HA) and reaching to equilibrium condition (equation 1.1).

$$[O_{1,5}Si(CH_2)_3NHC(S)S^-NH_3^+(CH_2)_3SiO_{1,5}]_n + HA \rightleftharpoons [O_{1,5}Si(CH_2)_3NHC(S)SH]_n \quad (1.1)$$
$$PTCA\text{-}3A \qquad\qquad\qquad\qquad + [A^-NH_3^+(CH_2)_3SiO_{1,5}]_n$$

IR spectroscopy result indicated (not shown) peak at $1500 cm^{-1}$ is related in asymmetric fluctuation of NH_3^+ group of the polymer (PTCA-3A) which showed in the equation 1.1. After sorption in nitric acid there appeared a new peak at $1380 cm^{-1}$. It proves that nitrate ion was entered into structure of the polymer.
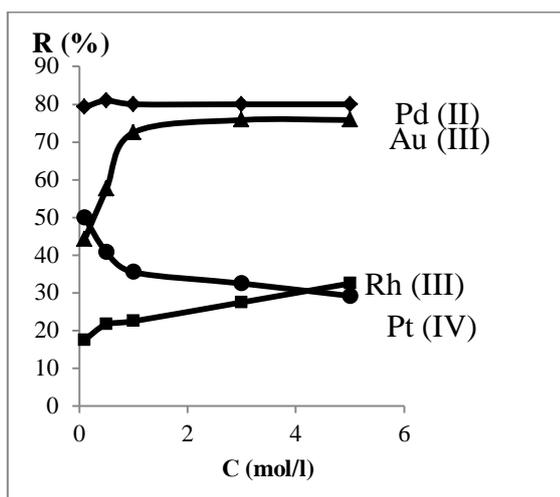

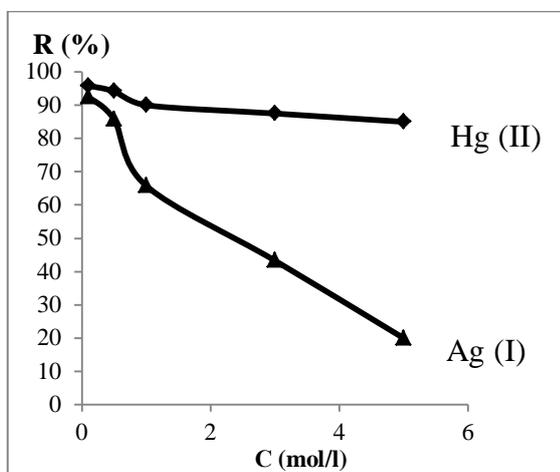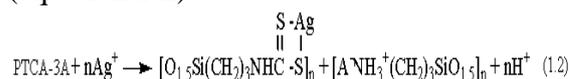Figure 1. Influence of the acid concentration on sorption of Au(III), Pt(IV) and Rh(III)

Figure 2. Influence of the acid concentration on sorption Ag(I), Hg(II)

A solution pH increased a little due to protonation of functional group of polymer (PTCA-3A). This behaviour of the polymer (PTCA-3A) in acid solution shows its functional group has ion-coordination property. Also determines influence of acid concentration on metal ions sorption (Figure1 and 2). In the matter sorption of the Hg(II) and Ag(I) ions occurred by ion-coordination mechanism and possibly was interacted with both 2 atoms of the sulfur (equation 1.2):

$$PTCA\text{-}3A + nAg^+ \rightarrow [O_{1,5}Si(CH_2)_3NHC\overset{\overset{\displaystyle S \cdot Ag}{||\;\;|}}{\cdot}S]_n + [A^-NH_3^+(CH_2)_3SiO_{1,5}]_n + nH^+ \quad (1.2)$$

In the IR spectra of polymer (PTCA -3A) saturated by Hg(II) and Ag(I) ions, disappeared peaks at 1340 (C=S) and 2570 (S-H) cm^{-1} an indication of mechanism shown in equation 1.2 takes place. There weren't shown any changes in amine $(1540 cm^{-1})$ and amino $(1500 cm^{-1})$ groups fluctation.

Desorption of the Hg^{2+} and Ag^{1+} cations by 6M solution of nitric acid indicates that they were adsorbed by ion exchange mechanism.

Functional groups of the polymers could be interacted with $AuCl_4^-$, $PtCl_6^{2-}$, $PdCl_4^{2-}$ and $RhCl_6^{2-}$ via atoms of the nitrogen and sulfur. In the IR spectra of polymers saturated with these ions disappeared peak at $1500 cm^{-1}$ (NH_3^{2+}). Also there were not appeared any peaks associated with the other forms of precious metals in the polymer matrix. Elemental analysis indicated that polymer (PTCA-3A) in acid solution contains Au and Pd as AuCl and $PdCl_{0.5}$. This shows these element atoms are connected with no less than 3 atoms of functional groups (coordination number 4). In the spectrum of polymer saturated with ions Au(III), Pt(IV), Pd(II) and Rh(III) disappeared peak at $1340 cm^{-1}$ (C=S) and peaks of the amine group at 3400 and $1540 cm^{-1}$ were shifted to high wave numbers region. These results and low desorption values (not more than 5-10%) of gold, platinum, palladium, rhodium by hydrochloric and nitric acid solutions (6-9

mol/l) showed that acido-complexes of these metals interacting via ion-coordination mechanism with sulfur atom of thion group and nitrogen atoms of ammonium and amine group. There is chance of ammonium group participation decrease in adsorption of precious metals with increase of hydrochloric acid concentration. Gold and palladium in hydrochloric acid with concentration of 5 mol/l exist as $AuCl_2$ and $PdCl_2$.

Static sorption capacity (SSC) was determined in 3 mol/l acid solution. Connection degree of active group of the polymer (PTCA-3A) was determined by comparison of static sorption capacity value with theoretical sorption capacity value (SSC·100/TSC) and showed in Table 2.

Table 2. SSC, TSC and ratio to connect with chemical active group of PTCA-3A sorbent

Volume	Rh(III)	Pt(IV)	Pd(II)	Au(III)	Ag(I)	Hg(II)
SSC, mg/g	26	86	122	300	160	400
TSC, mg/g	340	660	350	650	370	658
SSC·100/TSC (%)	9.0	14.0	33.0	45.0	46.0	59.0

Connection degree of active group of polymer was increased as: Rh(III)<Pt(IV)<Pd(II)<Au(III)<Ag(I)<Hg(II). This result is in agreement with the previous published reference [22]. It also shows direct dependence with the metal sulfides solubility. Adsorption equilibrium time in hydrochloric and nitric acids with 3 mol/l were for Pd(II)-1.5h, Au(III)-2h, Hg(II)-2h, Ag(I)- 3h, Pt(IV)-3h and Rh(III)-3h, respectively. Poly (3-silsesquioxanilpropylthiocarbamate)3-silsesquioxanilpropylammonium has high adsorption capacity to gold and mercury from acid solution and its static sorption capacity SSC is not less than silicon-organic and organic sorbents which studied previously [5-7,22].

Sorption study of copolymer(PAPS-2)

This silicon-organic copolymer's Au(III), Pt(IV), Pd(II), Rh(III) sorption activity was determined in the hydrochloric acid solution

with concentration of 0.1-0.5 mol/l. Their sorption activity was the highest in hydrochloric acid solution with concentration of less than 1mol/l. When acid concentration is more than 1mol/l, the precious metals sorption (R%) was decreased considerably (Figure 3a,b). When temperature of solution increased from 20^oC to 40^oC there wasn't any change in sorption behaviour of metals (Figure 3a,b) as well as in equilibrium time. Equilibrium time in 0.5M HC at 20^oC and 40^oC was similar i.e 20-40 min. Static sorption capacity and coefficient of interphase distribution (D, cm^3/g) were calculated based on isotherm curves of sorption and showed in Table 3.
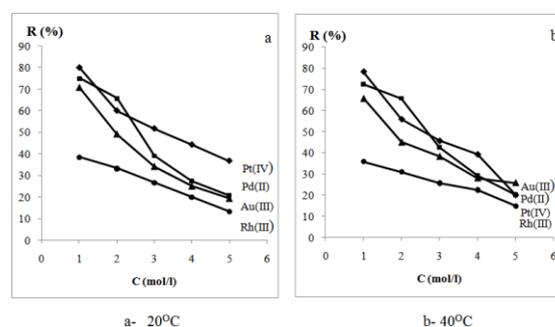

a- 20^oC b- 40^oC

Figure 3. Influence of the hydrochloric acid concentration on metal sorption.
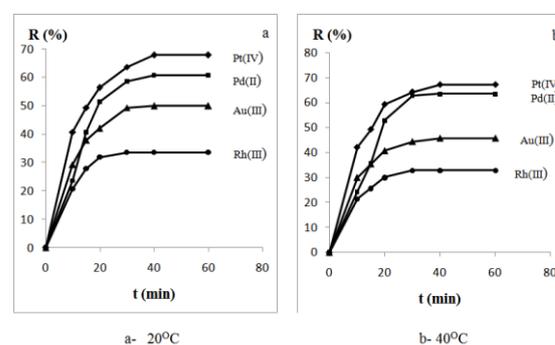

a- 20^oC b- 40^oC

Figure 4. Influence of equilibrium time on the metals sorption.

Table 3. Static sorption capacity (SSC, mg/g) and coefficient of interphase distribution (D,cm^3/g) of the copolymer (PAPS-2)

| Data	Au(III)	Pt(IV)	Pd(II)	Rh(III)
SSC, mg/g	134.0	141.0	124.0	110.0
D·$10^3$$cm^3$/g	4.3	5.4	2.8	1.3

The result shown in Table 3 indicated that it's possible to separate precious metals with a micro content in solution by polymer (PAPS-

2). Metals adsorbed on the polymer (PAPS-2) can be desorbed by 6 mol/l hydrochloric acid solution. When desorption is done at room temperature, 1ml desorbent was capable to desorb 120 ppm Au, 190 ppm Pt, 90 ppm Pd and 35 ppm Rh, respectively.

Sorption mechanism

Precious metals are adsorbed on the polymer (PAPS-2) according to the anion exchange mechanism. Elemental analysis of the polymer saturated with the precious metals showed adsorption occurs in form of $[MCl_n]^{n-k}$ where M-metal, n-4,6, k- oxidation degree of metal. Adsorption occurred according to ion exchange mechanism and it has been supported by decrease of adsorption activity with increasing of acid concentration. This polymer didn't show any capacity to adsorb silver and copper in acid solution. In acid solution Ag(I) and Cu(II) are presented in cation type and it's one more evidence that PAPS-2 acts as an anionit in acid solution. Sorption activity of the PAPS-2 is similar with pyridine based organic sorbents [23].

In order to find out either nitrogen atom of pyridine circle or amine group is participating in anion exchange process were taken comparative IR spectrums of the pure and saturated with precious metals polymer. In the pure polymer (PAPS-2) IR spectrum were found peaks at 1615, 1600, 1485, 1440 cm^{-1} due to –C=C- and –C=N- groups of pyridine and also peak at $1560 cm^{-1}$ due to deformation fluctuation of the NH group. In the spectrum of polymer (PAPS-2) saturated with metal ions was disappeared NH group peak and a clear change in –C=C- and –C=N- groups (peaks at 1600 and $1495 cm^{-1}$ were widened). Such clear changes in IR spectrum indicated in anion exchange were participated both nitrogen atom of pyridine and amine group and it can be showed according to equation 1.3.

$$(SiO_2) \cdot O_{1.5}Si(CH_2)_3NH \underset{\underset{Cl}{\overset{|}{Pd}}{\diagdown Cl}}{\diagup} N \quad (1.3)$$
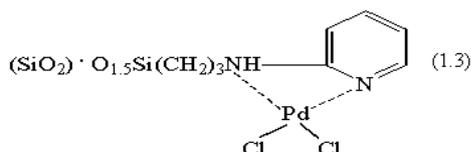
Simultaneously with anion exchange occurred substitution of 2 chlorine atoms with the polymer functional group and formation of the coordination bond with nitrogen atoms

(example: Palladium acido-complex $[PdCl_4]^{2-}$).

Conclusions

The application of PTCA-3A and PAPS-2 polymers for sorption of precious metals was studied. Based on the experimental results following conclusion can be drawn:

* Sorption of Au(III), Ag(I), Pt(IV), Pd(II) and Rh(III) by silicon-organic polymers depend on the concentration of acids. The best result was obtained for concentration of 0.1 and 1 mol/l. Sorption efficiency decreases with the increase of acid concentration.

* Silicon-organic polymers can be used efficiently for removal of a large amount of precious metals from aqueous solutions.

References

1. A.s. SSSR № 585187. Prostranstvenno-sshitii polymer dlya cationoobmennikov i redoxitov / L.P. Phenn, E.B. Slenyakova, M.G. Voronkov, N.N. Vlasova, Ph.P. Kletsko // B.E. 1977. № 47. p. 85.

2. Phenn L.P., Slenyakova E.B., Voronkov M.G., Vlasova N.N., Kletsko Ph.P. Kirrilov A.E., Shklyar T.V. DAN SSSR. 1977. T. 236. № 6. p. 1426-1429.

3. Kirrilov A.E., Zemlyanushnova O.V., Vlasov N.N., Voronkov M.G., Slenyakova E.B., Phenn L.P. JACh. 1982. T. 37. № 7. p. 1201-1204.

4. Zemlyanushnova O.V., Kirrilov A.E., Golentovskaya E.P., Vlasova N.N. Chem. and Chem. Techn.. № 5. p. 568-571.

5. Burmaa G., Vlasova N.N., Pestunovich A.E., Pojedaiv Yu.N., Voronkov M.G. " SO RAN, ser. chem. science". 1992. Edi. 4. p. 89-94.

6. Burmaa G., Pojedaiv Yu.N., Pestunovich A.E., Vlasova N.N., Voronkov G.M. Thesis docladov 8-th soveshaniya. Sankt-peterburg. 1992. p.51.

7. Voronkov M.G., Vlasova N.N., Pozhidaev Yu.N. "Appl. Organomet. Chem. 2000. V. 14. p. 287-303.

8. Yilmgaz V.T., Yazicilar T.K., Cesur H. et al. "Synth. and React. Inorg. And

Metal-Org. Chem. 2003. V.33. N 4. p.589-605.

9. Mehmet Ya. "JACh". 2003. T.58. № 5. p. 513-516.

10. Erven C.A. "Metal Finish". 2001. V. 99. N1. p. 8-19.

11. Denizli A., Kesenci K., Arica Y., Piskin E. "React. and Funct. Polym". 2000. V. 44. N 3. p. 235-243.

12. Venkatesan K.A., Srinivasan T.G., Vasudeva R.P.R. "Separ. Sci. and Technol. 2002. V. 37. N 6. p. 1417-1429.

13. A.s. SSSR № 429074. Sposob polucheniya kationitov / S.E. Vasyukov, K.P. Grinevich, M.V. Sobolevskii, A.Ya. Tagirov, E.A. Chernishov, E.Ph. Bugrenko, T.L. Krasnova, G.P. Matveicheva, E.A. Rogachevskii // V.E. 1974. № 19. S. 80.

14. A.s. SSSR № 523911. Sposob polucheniya kationitov / S.E. Vasyukov, A.E. Demchenko, E.Ph. Bugrenko, A.s. Ananieva, E.A. Chernikov // V.E. 1976. № 28. p. 69.

15. Triphomavo O.M., Chernov N.Ph., Voronkov M.G. "Suc. chem. 1999. T. 68. Edi. 4. s. 318-330.

16. Voronkov M.G., Chernov N.F., Baigozhin A. "J. Coated Fabrics. 1999. Vol. 29. N 1. P. 75-88.

17. Voronkov M.G., Vlasova N.N., Pojidaev Yu.N. "JPH. T. 69. № 5. p. 705-718.

18. G Burmaa, N.N.Vlasova, Yu.N.Pojidaev, M.G.Voronkov, S. Alen, Yu.Ganchimeg "Erdem shinjilgeenii byteeliin emkhetgel" SHUTIS, 2011, № 3/115, p.

19. Iyvazov B.V. Praktikum po khimii poberkhnostnikh yavlenii i adsorbtsii. M.: High school. 1973. 208 s.

20. Marchenko Z. Photometricheskoe opredelenie elementov. M.: Mir, 1971. 540p.

21. Probootbiranie i analiz blagorodnikh metallov: Spravochnik /In red. E.Ph. Barishnekova. M.: Metallurgy, 1978. 430p.

22. Murinov Yu.E., Maistrenko V.A., Afzaletdinova N.G. "Extraktsiya metallov S,N-organicheskimi soedineniyami". M.: science, 1993. 192p.

23. Saldaze K.M., Kopilova-Valova V.D. Komplexoobrazyushie ioniti.M.: Chemistry, 1980. 336p.