Selective Resins, Synthesis and Sorption for Precious Metals

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Summary: Resins based on vinylbenzyl chloride (VBC) and divinylbenzene (DVB) copolymer were synthesised and used for preconcentration and separation of Au, Pt and Pd from hydrochloric acid solutions. Resulted resins show functionality concentration up to 5,8 mmol/g. The acidity and interference of other ions on the resins sorption were discussed. The sorption capacities of gold, platinum and palladium from hydrochloric solutions reaches to 85, 100 and 60 mg/g and distribution coefficients achieve 50 000 value. Recovery of noble metals revealed average of 60-98 % from mulitcomponent solutions.

Keywords: gold; palladium sorption; platinum; selective resins

Introduction

The increase of the price for precious metals over the years and their expanding use in areas such as manufacturing of automobile catalysts, organic catalysts, jewellery, microelectronics and cancer therapy along with lack of availability of these metals has led to development of mining from low grade ores or from secondary raw materials. The recovery of precious metals: platinum, palladium and gold from different souurces require their separation from other metals. A very promising approach to overcome this problem is to use ion exchange and chelating resins for selective recovery of these metals from multicomponent solutions [1-4]. A series of new polymers bearing amino and guanidine functional group were synthesised, characterised and their abilities for noble metals recovery and sorption were determined. Currently, a new class of materials: chelating and ion exchange resins have been developed. They contain aminoguanidine and guanidine functionality with increased basicity (compared with conventional weak base type resin) and therefore capable for gold complexation from alkali (as dicyanoaurate anion) and acidic (as tetrachloroaurate anion) solutions [5-6].

The aim of our work is to present the abilities of resin to recover gold, platinum and palladium from acidic solution.

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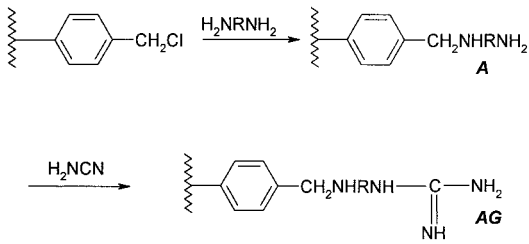
Experimental

An expaned gel copolymer, of vinylbenzyl chloride/divinylbenzene (2%) (VBC/DVB), A, was prepared in the presence of toluene. Polymer was obtained in the suspension polymerisation [5]. Resins were obtained by exchange of chlorine atom by diamines: 1,2-diaminoethane and 1,6-diaminohexane, and subsequent reaction with cyanamide. More details concerning synthesis are present in papers [5-7]. Water regain is measured by centrifugation technique. Nitrogen content is determined by Kiejdahl's method. Anion exchange capacity is determined according to Hecker's method and used to calculate ligand concentration.

Batch method was applied to sorption procedure i.e.: resin in swollen form was contacted for 48 hours with hydrogen tetrachloroaurate (III), hydrogen hexachloroplatinate (IV) and sodium tetrachloropalladate (II) in hydrochloric acid solutions. One-component solution contains 0.24 mM of selected metals i.e. (50 mg Au/L, 50 mg Pt/L and 26 mg Pd/L, while multicomponent solutions contain 0,24 mM of noble metals and 2,4 mM or 20 mM of coexisting metals. Metal sorption was determined using atomic absorption spectrophotometry, type Aanalyst 100.

Results

The synthetic route to A (amino functional resin) and AG (guanidino functional resin) can be described schematically in Figure 1. The first step of the reaction is the exchange of chlorine with diamine resulting in A resin. The next step is modification using cyanamide to AG resin. Characteristic of investigated polymers is shown in Table 1. Obtained resins show higher water content than starting VBC/DVB polymer. The higher ligand content presents AG2 resin up to 2.9 mmol/g.



Where R is $(CH_2)_n$ and n=2 and 6.

Figure 1. Scheme of A and AG resin preparation.

Table 1. Characteristics of investigated polymers

Sample	Water regain g/g	Nitrogen content mmol/g	Ligands conc. mmol/g
Copolymer	0.24	-	-
A2	6.00	6.0	2.8
AG2	3.08	11.6	2.9
A6	2.56	5.2	2.6
AG6	1.90	8.3	2.1

Sorption studies under static conditions were performed with mixture of precious metals and base metals to study the selectivity of resins and thus to judge their application in hydrometallurgical or separation procedures. Multicomponent solutions containing Au(III), Pt(IV), Pd(II) (0,24 mM of each, *S1*) and Fe(III), Cu(II), Ni(II) (2,4 or 20 mM of each, *S2, S3*) were used in sorption experiment. Table 2 and 3 show the influence of each of foreign ions on the noble metals sorption and recovery. It is clear that a large amount of Cu, Fe and Ni (80-fold excess in solution *S3*), caused little interference. The total sorption of Au, Pt and Pd from multicomponent solution *S1, S2* and *S3* are present in Figure 2. The best sorbatibility of investigated noble metals shows AG2 resin, 290 mg/g from *S1* solution and 250 mg/g from *S3* solution with strong fold excess of foreign metals.

Table 2. Precious metals sorption from multicomponent solution *S1*, *S2* and *S3**, (mg/g)

Resin	Foreign ion**	mM	Solution	Au	Pt	Pd	Resin	Au	Pt	Pd
A2	Fe+ Cu+ Ni	0	*S1*	103	93	60	AG2	119	107	66
	Fe+ Cu+ Ni	2.4	*S2*	103	93	60		117	102	67
	Fe+ Cu+ Ni	20	*S3*	90	74	60		100	85	67
A6	Fe+ Cu+ Ni	0	*S1*	82	93	46	AG6	76	77	43
	Fe+ Cu+ Ni	2.4	*S2*	78	78	44		78	70	45
	Fe+ Cu+ Ni	20	*S3*	69	64	34		70	61	41

* Concentration of Au, Pt, Pd is 0.24 mM
**Concentration of each foreign metal

Table 3. Influence of foreign ions on recovery of Au, Pt and Pd*(%)

Resin	Foreign ion**	mM	Solution	Au	Pt	Pd	Resin	Au	Pt	Pd
A2	Fe+ Cu+ Ni	0	S1	92	82	98	AG2	95	89	98
	Fe+ Cu+ Ni	2.4	S2	93	83	99		95	82	99
	Fe+ Cu+ Ni	20	S3	81	66	98		80	67	97
A6	Fe+ Cu+ Ni	0	S1	81	91	84	AG6	93	93	96
	Fe+ Cu+ Ni	2.4	S2	77	76	80		90	80	95
	Fe+ Cu+ Ni	20	S3	69	63	61		81	70	87

* Concentration of Au, Pt, Pd is 0.24 mM
**Concentration of each foreign metal

Figure 3 shows the sorption isotherms for Au(III), Pt(IV) and Pd(II) at 0,1 M HCl obtained from multicomponent solutions (Au+Pt+Pd) in the range of 26-1000 mg/L Au, Pt and Pd concentration. The best sorption reveals AG2 resin. As the Au, Pt and Pd concentration increase maximum sorption of noble metals approach constant values of 300 mg/g; 450 mg/g and 200 mg/g, respectively.

The effect of the HCl concentration on sorption of Au(III) was investigated from gold solution in the range of 50-1000 mg/L on AG2 resin. As presents in Figure 4 resin AG2 shows particularly strong preferences for Au(III) reaches 300 mg Au/g. The sorption from 2-3 M HCl solution is lower and achieves level of 250 mg Au/g.

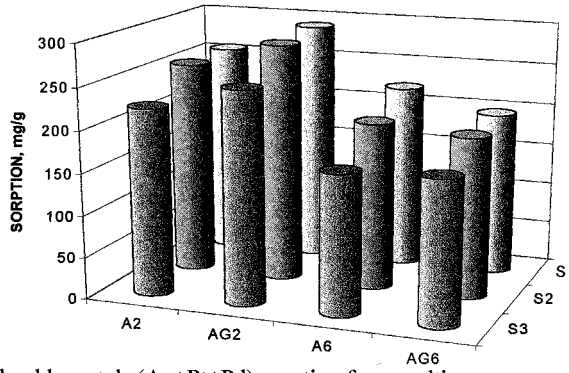


Figure 2. Total noble metals (Au+Pt+Pd) sorption from multicomponent solutions *S1, S2* and *S3.*

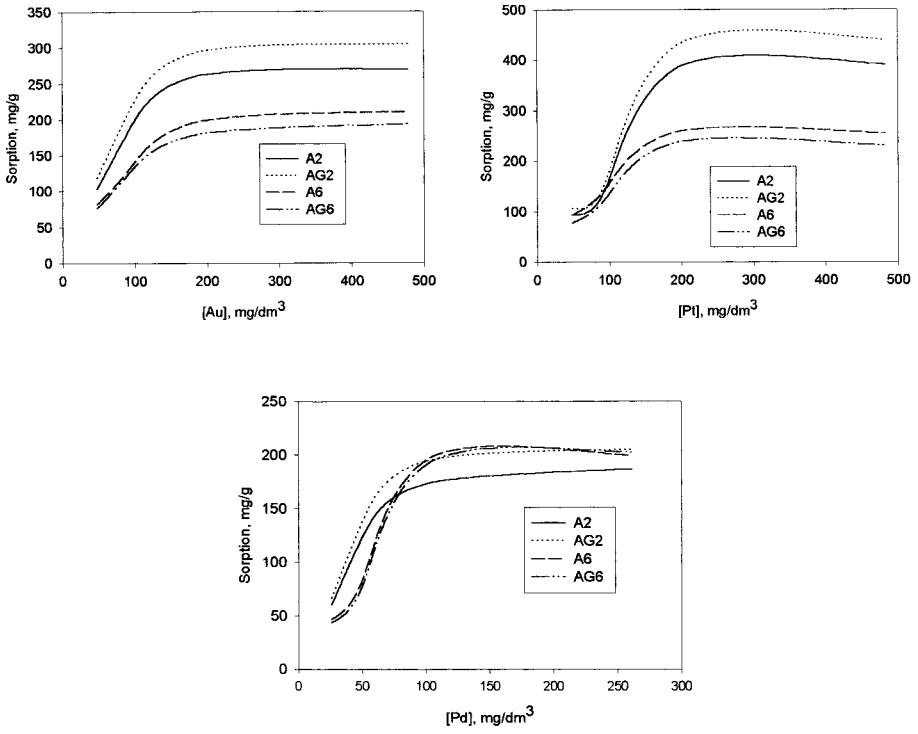


Figure 3. Isotherms of Au(III), Pd(II) and Pt(IV) sorption on resins (0,1 M HCl, 20°C).

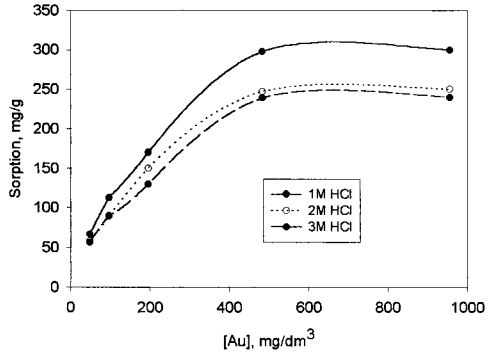


Figure 4. Effect of HCl concentration on the sorption of Au(III) on AG2 resin.

From the results described in this paper, it can be concluded that investigated resins are suitable for the preconcentration and separation of Au, Pt and Pd. The most important characteristics of investigated resins are their high selectivity for these three elements.

Conclusion

1. Incorporation of alkyl diamine ligands to copolymer matrix leads to series of RESINS - A type. The modification of A type RESINS with cyanamide results in the series of resins with guanidyl end groups (AG type).
2. Resins are useful for sorption of tetrachloroaurate, tertachloropalladate and hexachloroplatinate anions from acidic solution. Sorption from single solution of noble metals reaches up to 100 mg/g Au(III) and Pt(IV); sorption of Pd(II) is near 50 mg/g.
3. The best sorption of Au(III) and Pt(IV) from multicomponent solution S3 of (Au+Pt+Pd+Cu+Ni+Fe) reveals RESINS AG2, (100 mg of Au, 85 mg of Pt, for 1 gram of dry resin, respectively.

Acknowledgements

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