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GOLD RECOVERY FROM GUANIDINE RESINS

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ABSTRACT

This article describes some studies of dicyanoaurate anion elution from vinylbenzyl chloride resins containing guanidine ligands. The elution of gold (I) cyanide anions from loaded guanidine resin (resin with guanidine ligands) using sodium hydroxide eluent and modified caustic eluent: mixture of sodium hydroxide and sodium benzoate were studied. Full elution of gold cyanide using dynamic method of elution was achieved.

Key Words: Gold recovery; Guanidine resin; Dicyanoaurate

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INTRODUCTION

It has now been discovered that an ion-exchange resin carrying guanidyl functionality (containing different guanidine ligands) and which has a pK_a about 12 may be employed in the process of precious metals extraction such as gold and silver from aqueous alkaline, cyanide solutions.[1–5] In our previous papers, extraction of dicyanoaurate anions, $Au(CN)_2^-$, on vinylbenzyl chloride (VBC) copolymers from alkaline solution has been studied.[4–6]

The gold-loaded resins were stripped using many reagents and methods. The effects of such variables as eluent concentration and contact time were examined.[2,3,7–10] Attempts to modify the caustic sodium hydroxide eluent to improve elution included the use of alcoholic (ethanol or methanol) sodium hydroxide solutions. While such addition of alcohol provided some improvement in the elution of gold, it also caused potential fire hazard in the electrowinning cells employed in the subsequent recovery of the gold. Virnig[3] preferred a modified eluent: a mixture of sodium hydroxide and sodium benzoate, preferably mixture of 0.5 *M* sodium hydroxide and sodium benzoate.[3] He[11] stripped gold (I) cyanide complexes from newly developed AuRIX® resin produced by Cognis Corporation. This resin (volume capacity 0.25–0.35 eq/L) is made from styrene and divinylbenzene (DVB) macroreticular resin bead functionalized with trialkylguanidine. Virnig used this mixture along with 100 ppm of free cyanide, at a temperature of 60°C. Lin, Mattison, and Virnig[1,2] used aqueous solutions containing 10% NaOH and solution of 1% NaOH with 0.5% NaCN at different guanidine resin/aqueous ratios. Gold recovery was successful and 98–100% was achieved. The gold sorption from cyanide solution may occur by different mechanisms according to the basicity, pK_a, of the ion-exchange resin.[12] Gold may be loaded on a weak base resin as a result of sorption mechanism of dicyanoaurate anions $Au(CN)_2^-$ (reactions 1 and 2), sorption of ion pairs,[8,10,13] and sorption of AuCN or metallic gold Au(0).[14] All of these mechanisms were proved by x-ray photoelectron spectroscopy (XPS) in Vernon's study on polydiallylamine weak base resin (PDAA).[12,14]

The sorption processes of dicyanoaurate anions on a weak base resin require the primary, secondary, and tertiary amino groups to be first protonated:[9]

$$\mathbf{P}{-}NR_2 + HX \Leftrightarrow \mathbf{P}{-}N^+R_2HX^- \tag{1}$$

where **P** is a matrix of polymer, R any alkyl group, and X, an anion electrostatically bound to the resin. Gold cyanide is extracted to the resin phase by ion-exchange reaction, shown below:

$$\mathbf{P}{-}N^+R_2HX^- + Au(CN)_2^- \Leftrightarrow \mathbf{P}{-}N^+R_2HAu(CN)_2^- + X^- \tag{2}$$

Gold can be desorbed (eluted) from weak base resin by simple base hydrolysis. The elution of gold cyanide from a weak base resin by increasing the solution pH is illustrated in reaction (3):[8,9]

$$\mathbf{P}\text{—}N^{+}R_2HAu(CN)_2^- + OH^- \Leftrightarrow \mathbf{P}\text{—}NR_2 + Au(CN)_2^- + H_2O \tag{3}$$

The aim of this work is to develop the conditions of dicyanoaurate anions removal from loaded expanded gel guanidine resins. Sodium hydroxide and its mixture with sodium benzoate were used as eluents.

EXPERIMENTAL

Materials

The starting expanded gel copolymers of VBC, methyl methacrylate (MM), DVB (2%), and VBC, DVB (2%) were obtained by suspension polymerization in the presence of toluene and synthesis details are presented elsewhere.[15,16]

Guanidylation with aminoguanidine bicarbonate, resulting in Resins 1 and 2 bearing aminoguanidine ligands were carried out using aminoguanidine bicarbonate solutions in dioxane.[15] Resin 3 having longer guanidyl ligands was obtained in a different way. First, polymer has been modified with ethylenediamine in order to introduce primary and secondary amino groups into its structure. Next, amino groups attached to polymeric matrix were transformed in the reaction with dimethylcyanamide resulting in a long-arm guanidine ligand.[5]

Methods

Water regain is measured using a centrifugation technique. Nitrogen content is measured using Kjeldahl's method. Anion exchange capacity is determined according to Hecker's method[17] and used to calculate ligand concentration. Approximately 1 g of swollen polymer was placed in an ion-exchange column and washed in 250 mL of 1 *M* HCl, about 200 mL of 0.001 *M* HCl until the final filtrate concentration reaches 0.001 *M* HCl. Then, 500 mL of 4% sodium sulfate in 0.05 *M* NH_4OH was passed through the ion-exchange column and the eluate was collected in a 500 mL volumetric flask and analyzed for its chloride concentration.

Affinity of Resins 1 and 2 towards $Au(CN)_2^-$ anions was determined by contacting the resins in swollen form with 50 ppm solutions formulated with 0.05 *N* KCN (pH of this solution has been adjusted to 9.6), whereas Resin 3 was loaded using 500 ppm solution of gold cyanide at pH 9.6. After 48 hr, the polymers were separated by filtration and Au concentration was determined by atomic absorption spectrophotometry (AAS) method with wavelength set at 242.8 nm. Gold concentration in eluents was also determined by AAS method.

Mixed Method of Gold Recovery from Resin 1

Resin 1 in swollen form (0.543 g) loaded with 9.39 mg of gold was placed in an Erlenmeyer flask together with 50 cm^3 0.1 *M* NaOH. During 11 days, the flask was shaken at room temperature. Later, the solution was removed and Au concentration was determined. The same sample of Resin 1 was quantitatively placed in an ion-exchange column and the next portion of 0.1 *M* NaOH eluent was passed through the column. The eluent was collected in a measuring flask and its Au concentration was determined. This procedure was repeated for 5 days and subsequently 0.5 *M* NaOH was used in the same way. The process of elution was carried out for 21 days.

Batch Method of Gold Recovery from Resin 2

The appropriate portions of Resin 2, called Resin U BIS in Ref. [18], (188 mg wet resin, each sample loaded with 2.36 mg of gold) was placed in six Erlenmeyer flasks and stripped with 50 cm^3 of aqueous solution containing 0.5 *M* NaOH. The flasks were shaken for 1–49 hr. After 1, 2, 5, 10, 24, and 49 hr loaded resin was filtered and gold concentration was determined in aqueous solution.

Batch Method of Gold Recovery from Resin 3

Swollen Resin 3 (3.47 g) was contacted with 200 cm^3 of solution containing 500 mg/cm^3 gold and 50 mg/cm^3 cyanide at 9.6 pH. Gold sorption was 44.1 mg/g. Next, the samples of Resin 3 were divided and stripped with given portions of 1 *M* NaOH solution and with a mixture of 0.5 *M* solution (NaOH and sodium benzoate) at room temperature and at 60°C.

Dynamic Method of Gold Recovery from Resin 3

A polypropylene (PP) small calibrated syringe with an internal diameter of 4 and 70 mm length was adapted for column experiment at ambient temperature. The outlet of the column was blocked with a small piece of glass wool. Then 153 mg of water-swollen Resin 3 (after centrifugation) loaded with 4.32 mg of Au was placed into the column. The top of the column was again blocked with a small piece of glass wool. The bottom of the column was connected via pump tubing to a liquid-processor working as a peristaltic pump and simulating continuous flow of liquid. The eluent was quantitatively collected in glass vessels and the gathered fractions were analyzed for gold concentrations. Afterwards, 0.5 *M* solution of NaOH and sodium benzoate was used as an eluent. They were pumped through the column with 5 μL/min speed.

RESULTS AND DISCUSSION

Characteristics of three guanidine resins investigated in this article are presented in Table 1. These resins were developed in the cause of our previous work and studied for possible applications in the sorption of gold. Resins 1 and 2 are the same as the resin mentioned as Resin U BIS in Ref. [18]. They differ in ligand concentration only. Resin 3 is the same as presented in Ref. [5]. All of them are gel-expanded resins with 2% content of DVB. Resin 3, having long guanidine ligand was modified in a two-stage process: first, with ethylenediamine and subsequently by dimethylcyanamide. Such modification gave 2 mmol/g ligand concentrations and 0.56 g/g of water regain. Resins were gold loaded using batch method by contacting wet resins for 48 hr with gold cyanide solution at pH 9.6. After sorption, each portion of loaded resin was separated from the solution and the equilibrium gold concentration was measured. Gold sorption was calculated from differences between initial and final gold concentration in solution. Sorption was 23, 19, and 44.1 mg of gold per 1 g of dry Resins 1, 2, and 3, respectively.

The effects of different extractants and methods of gold elution from Au-loaded guanidine resins are presented. Batch desorption studies were carried out by loading samples of the resins with dicyanoaurate anions $Au(CN)_2^-$ at pH 9.6 followed by a treatment with excess of the eluent reagent.

Two kinds of extractants were used: (1) sodium hydroxide of various concentrations and (2) equimolar mixture of sodium hydroxide and sodium benzoate. Table 2 shows the effects of stripping reagents (eluents) and their concentrations, the effect of temperature on elution efficiency, and the amount of used sodium hydroxide (presented as ratio to gold loaded on resin). Figures 1–4 present the influence of these factors for gold desorption.

The gold-loaded Resin 1 was eluted using mixed method: batch and dynamic. In the first stage of the experiment when the excess of NaOH over gold loaded on Resin 1 was only 100 mmol/mmol, desorption was low and reached only 22%. Figure 1 shows the correlation between time, NaOH/Au ratio, and gold desorption. During elution tests, desorption of gold was 78% after 21 days and the total amount of used sodium hydroxide was about 160 mmol. These results agree with those obtained previously.[2,3]

The results of gold desorption from Resin 2 are shown in Fig. 2. The elution efficiency of gold was plotted as a function of time. Elution was only 70% in this experiment and extension of elution time was not necessary. The maximum desorption was achieved in 6 hr. The rates of sorption and desorption are similar

Table 1. Characteristics of the Investigated Resins with Aminoguanidyl and Guanidyl Ligands

Resin	Matrix	Ligand	Z_H (mmol/g)	Water Regain (g/g)	N (%)	Gold Sorption (mg/g)
1	VBC/MM/DVB	$-NHNH(C{=}NH)NH_2$	1.20	0.33	7.7	23.0
2	VBC/MM/DVB	$-NHNH(C{=}NH)NH_2$	1.09	0.34	7.4	19.0
3	VBC/DVB	$-NHCH_2CH_2NH(C{=}NH)N(CH_3)_2$	3.81	0.56	11.6	44.1

Z_H—group concentration based on Hecker's method,[17] mmol/g.

Table 2. Desorption of Gold from Loaded Resin

Resin	Eluent	Temperature (°C)	NaOH/Au (mmol/mmol)	Desorption (%)
1	$(0.1\,M + 0.5\,M)$ NaOH	20	3260	78
2	$0.5\,M$ NaOH	20	1900	70
3	$1\,M$ NaOH	20	2286	34
3	$1\,M$ NaOH	60	2313	40
3	$0.5\,M$ (NaOH + SB)	20	3453	73
3	$0.5\,M$ (NaOH + SB)	60	3433	79
3	$0.5\,M$ (NaOH + SB)	20	9600	100

SB—sodium benzoate.

when the maximum of gold sorption was achieved in 6 hr.[4] This result supports the assumptions that incomplete desorption of $Au(CN)_2^-$ anions is caused by insufficient amount of sodium hydroxide. In Table 2, it can be seen that molar NaOH/Au ratio was 1900. Lin et al. achieved the similar effect on different substituted guanidine resin.[2] Desorption achieved was 30–60% only. In addition, elution of gold from Aurix Resin was 60%.[11]

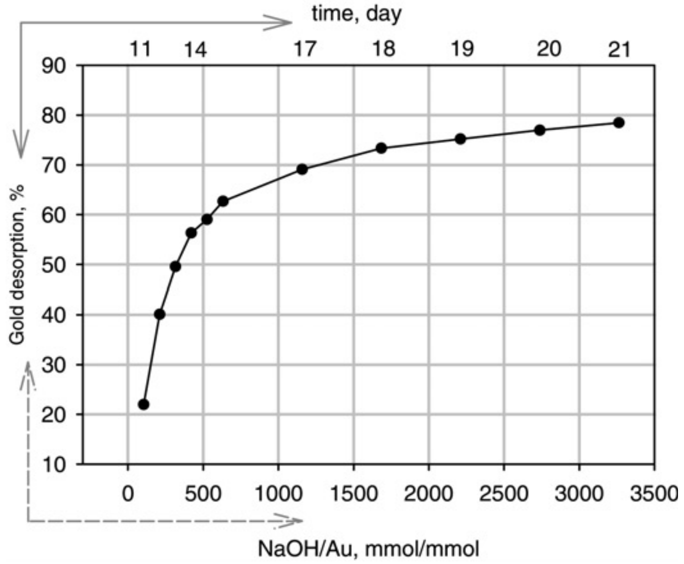

Figure 1. The influence of time and NaOH/Au ratio, (mmol/mmol), on gold desorption from Resin 1.

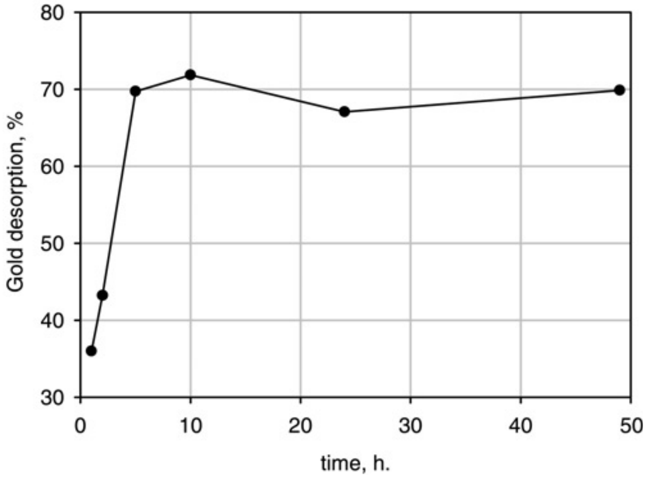

Figure 2. Time effect on gold desorption from Resin 2.

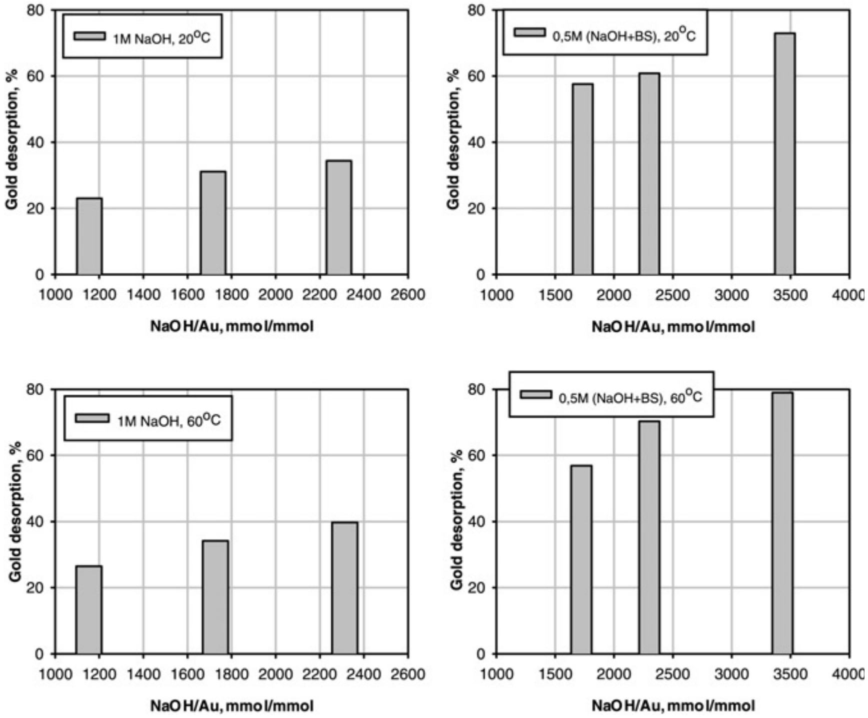

Figure 3. The NaOH/Au ratio effect on gold desorption from Resin 3.

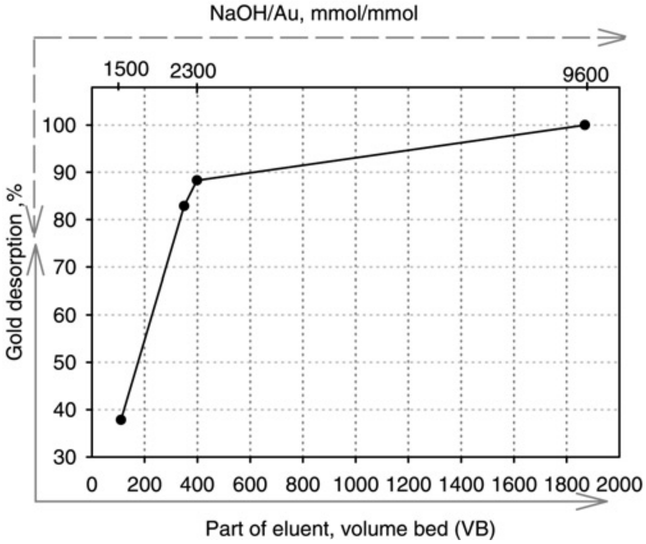

Figure 4. Dynamic method of gold desorption from Resin 3.

As shown earlier, the crucial factor that may affect gold desorption from guanidine resins is the significant excess of eluent over loaded gold. Increasing the ratio of NaOH/Au to 1900 for Resin 1, to 3200 for Resin 2, and to 2300 for Resin 3 caused partial, about 70%, gold desorption.

It has been observed that an increase in desorption temperature to 60°C, for Resin 3 eluted with 1 *M* NaOH was unsuccessful and did not cause an increase in elution efficiency (see Fig. 3 and Table 2).

The yield of elution increased significantly when 0.5 *M* mixture of sodium hydroxide and sodium benzoate solutions were used. As shown in Fig. 3, an application of this eluent makes it possible to elute 70% of gold at room temperature and 80% at 60°C. Complete desorption was possible (Fig. 4). It indicates that dicyanoaurate anions were sorbed on guanidine resin via ion-exchange mechanism according to the reaction 2. The mass balance of the gold desorbed from Resin 3 is shown in Table 3. The data shows that average concentration of gold in first three fractions reaches the level of 42.4 mg/dm^3. This concentration is a dozen times higher than common gold concentration in rough solution. Due to incomplete data available in literature, mostly presented in patents or conference proceedings,[1–3,19,20] it is difficult to compare the efficiency of our resins in gold recovery. We believe that the presentation of our preliminary studies in the synthesis of resins with guanidine ligands will show the way to obtain an effective sorbent for gold hydrometallurgy.

Table 3. Mass Balance of Gold Eluted from Resin 3

Fraction Number	0.5 *M* (NaOH + SB) Volume (cm^3)	Gold Concentration (mg/dm^3)	Total Amount of Gold Desorbed (mg)	Fraction of Gold Eluted (%)
1	25	65.40	1.64	37.8
2	54	36.06	3.58	45.0
3	11	21.24	3.82	5.4
4	330.5	1.54	4.32	11.8

SB—sodium benzoate.
Bead volume, 0.23 cm^3; 153 mg of swollen Resin 3.

CONCLUSIONS

This article discloses some information about resins with guanidine ligands and possibilities of gold desorption as aurocyanide anions. Using mixed sodium hydroxide and sodium benzoate solutions of gold elution resulted in 100% of gold desorption. Higher temperature does not increase gold desorption significantly. The most important factor influencing the efficiency of gold elution is NaOH/Au ratio. An excess of sodium hydroxide was needed in order to achieve full gold recovery.

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