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A comparison of ion-exchange resins and activated carbon in recovering gold from cyanide leach solutions with low levels of copper

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Research Article

Keywords:	ABSTRACT
Copper-Rich Gold Ore, Gold Adsorption, Activated Carbon, Resin, Selectivity. <i>Received Date: 05.02.2021</i> <i>Accepted Date: 16.06.2021</i>	This study was conducted to determine the effectiveness of three different adsorbents for the adsorption of gold from a real cyanide leach liquor. An activated carbon (NORIT GAC 1240), strong base (Purogold A194), and weak base (Purogold S992) resins were tested as the adsorbents. The pregnant leach solution (PLS) was derived from cyanide leaching (1.5 g/L NaCN, 25% w/w solids ratio, 1.5 L/min air flow rate, pH 10.5 – 11, 24 h) of the roasted copper-rich refractory gold ore pretreated with H_2SO_4 . Gold and copper concentrations in the PLS were analysed to be 26.1 mg/L Au and 62.4 mg/L Cu, respectively. Activated carbon was found to be the best performing adsorbent as it achieved the highest gold loading. Purogold A194 loaded the highest amount of copper amongst the adsorbents tested. Despite the fact that activated carbon loaded a high amount of gold, it was less selective than Purogold S992. Purogold A194 exhibited the lowest selectivity, which was defined as the distribution ratio of gold to copper, compared with Purogold S992 and activated carbon. Therefore, the order of selectivity of the adsorbents tested was as follows: Purogold S992 > Activated carbon > Purogold A194.
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1. Introduction

Some gold ores can contain high levels of copper, which presents specific difficulties during the extraction of gold via cyanidation. Due to the rapid exhaustion of free milling ores, the world has now turned to refractory ores including Cu-Au ores. This group was formerly deemed economically unappealing. Fleming et al. (2011) pointed out that as of 2009, more than 20% of the global gold production was from copper - gold ores. The process of gold recovery from these ores is often associated with different problems ascribed to the ready dissolution of most copper minerals in cyanide solutions (Sceresini, 2005; Bas et al., 2012; Bas et al., 2015; Msumange et al., 2020). The dissolution of copper minerals essentially leads to high cyanide consumption and low gold recoveries (Marsden and House, 2006).

Several factors can contribute to the refractory character of the ore. These include inorganic / organic carbon present in the ore and gold locked in sulfides such as arsenopyrite and pyrite. The presence of cyanides such as copper is another reason for refractory behavior (Habashi, 1999; Marsden and House, 2006; Adams, 2016; Chryssoulis and McMullen, 2016). Sulfide in gold ores not only consumes cyanide and oxygen but also forms a coating on grains of gold. This

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passive layer interferes with gold leaching (Marsden and House, 2006; Bas et al., 2012). A previous study (Yen and Aghamirian, 2002) suggested that sulfide minerals could affect the leaching of gold. Stibnite, chalcocite, and pyrrhotite have often negative effects. But pyrite, chalcopyrite, arsenopyrite, and sphalerite neither seriously reduce nor greatly improve gold leaching. Galena may enhance gold leaching (Yen and Aghamirian, 2002).

The recovery of gold from cyanide leach solutions is widely carried out by adsorption on activated carbon (Dai et al., 2012; Van Deventer et al., 2014). There are three industrial activated carbon adsorption processes used for gold recovery; namely, carbon in leach (CIL), carbon in pulp (CIP), or carbon in column (CIC). However, copper, if present in the cyanide leach liquor competes with gold during the adsorption process (Van Deventer, 2014; Msumange, 2019; Msumange et al., 2021). High copper concentration may severely affect gold adsorption (Van Deventer et al., 2014). In this respect, the formation of $Cu(CN)_2$ complex should be controlled to minimize copper loading onto the activated carbon since Cu(CN),⁻ competes with $Au(CN)_2^{-}$ directly. This may be achieved by maintaining excess free cyanide or elevating pH (Van Deventer, 2014). Some researchers focused on the removal of copper in alkaline (Bas et al., 2012 and 2015) or acid solutions (Yazıcı et al., 2015; Msumange, 2019) before cyanide leaching to eliminate the copper interference during leaching and adsorption stages.

Various investigators (Kotze et al., 2005, Kotze, 2010; Van Deventer et al., 2012, Van Deventer, 2014) have mooted that ion exchange resins have some advantages over activated carbon for the recovery of gold from leach solutions. These include better selectivity for gold over copper, enhanced gold recoveries from preg-robbing ores, and no requirement for thermal regeneration. The main drawback of ion exchange resins is that they are more expensive than activated carbon (Van Deventer, 2014).

The objective of this study is to compare the effectiveness of activated carbon and different types of resins (Purogold A194 and Purogold S992) in the recovery of gold from a cyanide liquor with low copper concentration (62.4 ppm Cu). Gold selectivity over

copper (Au / Cu), distribution ratio, and the loading capacity of Au and Cu of adsorbents were evaluated.

2. Experimental Studies

A copper-rich refractory gold ore sample (108 g/t Au, 1.6% Cu), mainly composed of quartz (67.3%), cordially supplied by Koza Gold Co. (Gümüşhane/ Mastra, Türkiye), was used to produce the leach solution. The ore can be categorized as refractory due to its low response to direct cyanide leaching (1.5 g/L NaCN, 25% w/w solids ratio, air flow rate: 1.5 L/min, pH 10.5 - 11) under typical cyanidation conditions i.e., 18.4% Au extraction over 24 h. Different pretreatment routes were tested and roasting was found to be an auspicious route for high gold extractions from the ore (Msumange, 2019).

Adsorption tests were carried out using the pregnant leach solution produced from cyanide leaching (1.5 g/L NaCN) of the roasted ore (at 650 °C for 8 h), which was firstly pretreated by acid leaching (1 M H_2SO_4 , Leaching time: 2 h) to remove reactive copper. Cyanide leaching of the roasted ore was carried out under the conditions of 1.5 g/L NaCN, 25% w/w solids ratio, 1.5 L/min air flow rate, pH 10.5-11, and 24 h leaching time. Gold and copper concentrations in PLSs were analysed to be 26.1 mg/L Au and 62.4 mg/L Cu, respectively. The PLSs were used in the adsorption tests.

The effectiveness of strong base (Purogold A194) and weak base (Purogold S992) resins for gold recovery from the cyanide leach solution generated was evaluated in comparison with an activated carbon (NORIT GAC 1240). These resins were claimed to be particularly developed for adsorption of gold - cyanide complexes from cyanide liquors. Gold selectivity over copper and loading capacity of adsorbents were evaluated. The distribution ratio of Au and Cu was also studied. The activated carbon sample used (NORIT GAC 1240) is 0.65 mm in size (NORIT, 2003). The technical properties of the resins, used in the study, are presented in Table 1.

The PLSs were prepared in 50 mL Erlenmeyer flasks, which were then placed onto an orbital shaker (Wiggen Hauser). Prior to the addition of adsorbents,

Name/brand of the resin	Matrix / Type	Functional Group	Ionic Form	Capacity	Moisture retention (%)	Effective Size
Purogold A194	Macroporous / Strong base anion	Quaternary Amines	Cl-	3 eq/kg	44 - 52	710 - 1300 μm
Purogold S992	Macroporous Polystyrene - divinylbenzene / Weak base, Chelating	Mixed Amines	Free Base	4.4 eq/kg	47 - 55	800 - 1300 μm

Table 1- Technical properties of the ion exchange resins used in the tests (PUROLITE, 2015; 2016a, b; 2020).

these flasks with PLSs were aerated at 1.5 L/min, and pH of PLSs was adjusted at 10.5 - 11 by using 1 M NaOH, if required. pH was maintained at 10 - 10.5 where the weak - base resin, Purogold S992, was employed due to its sensitivity to the high alkalinity (>pH 10.5). To avoid evaporation of the leach solution, the top of the flasks was kept covered by a sponge. The adsorption tests were carried out using the adsorbents (5 g/L) under the conditions of 25 °C at 170 rpm agitating speed over the period of 4 h. The sampling of each flask was carried out at 0.5, 1, 2, and 4 hours by removing a 1 - mL solution. Metal concentrations (Au and Cu) in solutions were analysed by atomic absorption spectroscopy (AAS, Perkin Elmer AAnalyst 400).

The weak base resin (Purogold S992) was initially transformed into the form of sulphate before its use in the adsorption tests. It was contacted with two - bed volumes (BVs) of a $0.5 \text{ M Na}_2\text{SO}_4.10\text{H}_2\text{O}$ solution in a column at a flow rate of 2 - bed volumes per hour. Thereafter, the resin was treated with 4 BVs of water to remove the excess reagent from the resin (Van Deventer et al., 2014).

The selectivity (μ) and adsorbent loading capacity (A) were calculated using the equations below:

$$\mu = \frac{D_{Au}}{D_{Cu}} = \frac{[Au]_{adsorbent} x[Cu]_{solution}}{[Au]_{solution} x[Cu]_{adsorbent}}$$
(1)

where D_{Au} and D_{Cu} are the distribution ratio for Au and Cu, respectively.

$$A = (C_0 - C_f) \times V \times m^{-1}$$
 (2)

Where, C_0 : Initial concentration of the adsorbate in solution (mg/L), C_f : Equilibrium concentration of the adsorbate in solution (mg/L), A: Adsorbent loading (mg/g), V: Volume of solution (L), m: Adsorbent mass (g).

3. Findings

The pH - dependent distribution of Cu(I) - cyanide species in the pregnant leach solution (PLS) was plotted using MEDUSA (2009) software (Figure 1a). This plot shows that the dominant Cu(I) - cyanide species in the pregnant leach solution used in the adsorption tests are Cu(CN)₄³⁻ with \approx 70% followed by Cu(CN)₃²⁻ with \approx 30 % over the pH range of 10 -11. Figure 1b also illustrates the speciation of cyanide (CN⁻) as a function of pH in the PLSs produced. At pH 10 - 11, 78 - 88% of cyanide is present in the free cyanide (CN⁻) form.

In the adsorption tests, the selectivity of gold over copper and metal loadings are shown in Table 2.

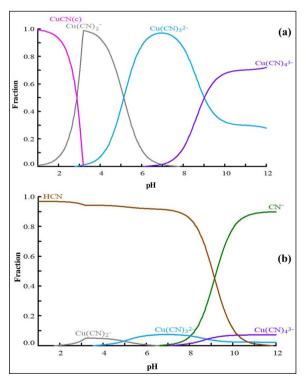


Figure 1- Speciation of ; a) Cu(I) species vs. pH, b) cyanide (CN⁻) species vs. pH (CN_{Total}= 38.8 mM (1.90 g/L NaCN), Cu(I)= 62.4 mg/L, Au(I)= 26.1 mg/L) reflecting the conditions of PLSs produced (MEDUSA, 2009).

Figures 2 - 4 demonstrate the kinetics of gold/copper loading onto adsorbents and the change in the solution metal concentration at pH 10.5 - 11 (for Purogold A194) or 10 - 10.5 (for Purogold S992). It was found that 25 kg of gold was loaded per ton of activated carbon within 4 hours (Figure 3). During the first hour of adsorption, approximately half of the amount of gold initially present in the solution was observed to load onto Purogold S992 resin with 12 kg/ton. At the same time interval, 20 kg of gold were loaded per ton of activated carbon, while the gold loading for Purogold A194 was 16 kg/ton.

At the first hour of adsorption, 80% of the total gold loaded onto the activated carbon was achieved. This suggested the trend of the adsorption process since only 20% of the total loaded gold was attained within the 3 remaining hours of adsorption. For the case of Purogold A194, 70% gold loading was attained during the first hour. These data (Figure 3) show that the activated carbon has fast kinetics and a high capacity for gold adsorption compared with the tested resins. When it comes to copper, Purogold S992 loaded only 5 kg copper per ton of the resin over 4 hours. There was a remarkable change in the amount of copper loaded onto this adsorbent from the second to fourth hour (i.e., only 0.3 kg/ton was loaded). In comparison,

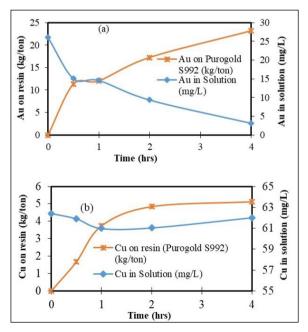


Figure 2- a) Kinetics of gold and b) copper loading onto Purogold S992 and metal concentrations (concentration of adsorbent: 5 g/L, pH 10 - 10.5, 25 °C).

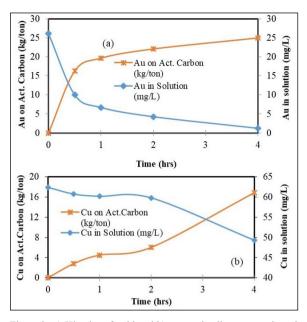


Figure 3- a) Kinetics of gold and b) copper loading onto activated carbon and concentrations (concentration of adsorbent: 5 g/L, pH 10.5 - 11, 24 °C).

17 kg/ton of copper was loaded onto activated carbon over the same time interval. The extent of adsorption onto the strong base anion resin (Purogold A194) was also high as it loaded 23 kg/ton of Cu over a time frame of 4 hours. When compared to the Purogold S992, the activated carbon loaded 11 kg/ton of copper

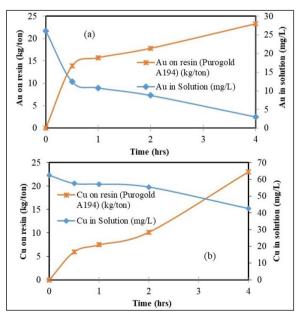


Figure 4- a) Kinetics of gold and b) copper loading onto Purogold A194 and metal concentrations (concentration of adsorbent: 5 g/L, pH 10.5 - 11, 25 °C).

from the second hour to the fourth hour whilst the Purogold A194 loaded 13 kg/ton from the second hour to the fourth hour of adsorption (Figure 4). Despite the fact that the gold loading capacity attained by the activated carbon was high compared to the resin - type adsorbents tested, yet it was less selective for gold over copper compared to the Purogold S992. The amount of copper loaded onto activated carbon was higher by 11.7 kg/ton than that on to Purogold S992. These results indicate that the Purogold S992 is more a selective adsorbent than the activated carbon and the Purogold A194. Figure 5 shows the percent recovery of metals (Au and Cu) from the leach solution by the activated carbon and resins. The results showed that 96% of gold and only 27% of copper were adsorbed onto activated carbon.

The distribution ratios of gold and copper were 20027 and 342, respectively. This gave a selectivity of 59 for the activated carbon. Similar findings (i.e. 89% Au and 37% Cu) were also observed for Purogold A194 for which the distribution ratio for

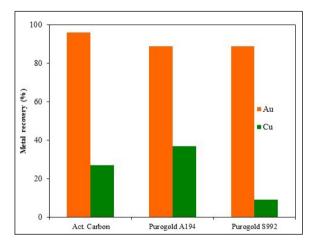


Figure 5- The percentage of metals recovered by adsorbents (concentration of adsorbent: 5 g/L, pH 10.5 – 11, 25 °C, 4 hours).

gold and copper was determined to be 7757 and 540, respectively. The selectivity was 14. For Purogold S992, 89% of gold and 9% of copper were observed to occur (Figure 5). The distribution ratio of gold was found to be substantially larger than that of copper indicating the high selectivity of S992 resin as the most selective adsorbent tested for gold (Table 2). In this respect, the Purogold S992 appeared to be 1.5 and 6 times more selective than the activated carbon and the Purogold A194 as shown in Table 2, respectively. There appears to be a relatively limited number of studies on the recovery of gold from refractory ores by ion exchange resins compared with activated carbon. The current findings seem to be consistent with the previous studies. A previous study conducted by Van Deventer (2014) also showed that Purogold S992 was a selective adsorbent. The investigator employed a synthetic cyanide liquor with 9 mg/L Au, 13.6 mg/L Cu, 1 mg/L Zn, and 10.4 mg/L Ni in solution.

Gold loadings onto carbon and Purogold S992 were 16450 mg/kg and 4183 mg/kg, respectively. The loading of copper onto the activated carbon was 105 mg/kg whilst no copper loading onto Purogold S992 was recorded by the researcher. It was concluded from these findings that Purogold S992 has high selectivity for gold over copper. Other researchers (Fleming and Cromberge, 1984; Van Deventer et al., 2012) also found that the selectivity of weak/medium base resins for gold over copper is higher than strong base resins. Voiloshnikova et al. (2014a) studied the adsorption of metals from cyanide solutions using Purogold S992 and showed that the selectivity for gold is higher than zinc, silver, iron (III), and copper. Ahlatcı et al. (2018) also indicated that the adsorption of copper onto Purogold S992 was low, limited to 2.2% from a waste cyanide solution (1.5 g/L NaCN, pH 10.5) containing 135 mg/L Cu, 196 mg/L Zn and 5.3 mg/L Fe.

Table 2- The comparison of the activated carbon with IX resins used for the adsorption of Au and Cu from a real cyanide leach solution (26.1 mg/L Au, 62.4 mg/L Cu, concentration of adsorbent: 5 g/L, pH 10.5 - 11, 25 °C, 4 hours).

Adsorbent	D (Au)	D (Cu)	μ (Selectivity)	Au on Adsorbent (kg/ton)	Cu on Adsorbent (kg/ton)
Activated Carbon	20.027	342	59	25	17
Purogold A194	7.757	540	14	23	23
Purogold S992*	7.353	83	89	23	5

*pH for Purogold S992 was maintained at 10 - 10.5.

4. Conclusions

Three adsorbents i.e. activated carbon, Purogold S992, and Purogold A194 were employed to compare their efficiency for the recovery of gold and copper from a pregnant evanide leach solution (PLS) with a low level of copper. The PLS had 26.1 ppm of gold and 62.4 ppm of copper. Activated carbon had high loadings of gold (25 kg/ton) compared to other adsorbents tested (23 kg/ton) whilst Purogold S992 had the lowest copper loadings of about 5 kg/ton. This compared to 17 kg/ton for the activated carbon and 23 kg/ton for Purogold A194. The selectivity was found to be 14, 59, and 89 for Purogold A194, activated carbon, and Purogold S992, respectively. The latter seems to have the highest selectivity for gold over copper. These findings suggest that Purogold S99 can be used as the selective adsorbent for the selective recovery of gold from copper - laden cvanide leach solutions.

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