EFFECT OF SILVER, NICKEL AND COPPER CYANIDES ON GOLD ADSORPTION ON ACTIVATED CARBON IN CYANIDE LEACH SOLUTIONS

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Abstract: The effect of Ag, Ni and Cu cyanides on gold adsorption on activated coconut carbon in cyanide leach solutions was investigated by synthetic cyanide leach solutions containing gold and other metal cyanides. According to the adsorption tests Ag remarkably reduces the gold adsorption on activated carbon by competing with gold to adsorption sites. When the Ag concentration in solution increases up to 200 ppm the carbon adsorption method for gold recovery becomes inapplicable. Ni has an effect on gold adsorption on activated carbon, however even at as high concentrations of Ni as 250 ppm residual Au in solution is still below 1 ppm. Cu addition up to 300 ppm does not affect the gold loading significantly. According to the adsorption test studies, it is concluded that the metal-cyanides diminish the gold adsorption on activated carbon by adsorbing themselves and competing with gold. When the metals are present in the leach solution all together with gold, they also prevent adsorption of themselves as well as gold. Thus, when Au, Ag, Ni and Cu are present in solution simultaneously, the adsorption of all these metals decreases. The adsorption results were modeled by Fleming k,n adsorption kinetic model.

Introduction

Gold is recovered from its ores hydrometallurgically by the cyanide leach process. The gold reacts with cyanide according to reaction (Davidson and Sole, 2007):

$$Au^0 + 2CN^- + \tfrac{1}{2} H_2O + \tfrac{1}{4} O_2 \rightarrow Au(CN)_2^- + OH^- \tag{1}$$

The gold ore after grinding to 80% –5 micrometers, is fed to leaching tanks in the form of slurry including 45% solid. Gold is dissolved from its ore by cyanide, according to reaction 1 in leaching tanks and then the slurry passes through adsorption tanks containing activated granular coconut carbon dispersed in the slurry. The system

where gold is recovered from the leach solution by activated carbon is named the CIP (carbon in pulp) process. In the adsorption unit cyanide leach slurry first goes through the last adsorption tank and the carbon from the last tank through the first adsorption tank due to counter current flow. The dissolved gold-cyanide complex ($Au(CN)_2^-$) is adsorbed on the activated carbon (Ibrado and Fuerstenau, 1995; Rees and Van Deventer, 2001). The barren slurry leaves the process from the last tank and gold loaded carbon is driven from the first adsorption tank. Gold loaded carbon is taken to the elution column in which gold is stripped from carbon and directed to the electrolysis process.

Many other metals, such as Ag, Ni, Cu, Fe, Zn etc., are dissolved with gold from ores as cyanide species. Thus, after cyanide leaching of ores, there are many other metal impurities in the leach solution, competing with gold to be adsorb on activated carbon.

According to the previous studies present in the literature, in cyanide leaching Ag dissolves as $Ag(CN)_2^-$ complex and adsorbs on carbon better than the cyanides of Ni and Cu. When the concentration ratio of [Ag]/[Au] reaches 2:1, Ag starts to inhibit the Au adsorption on activated carbon (Vegter and Sandebergh, 1997; Adams, 1992).

Ni dissolves as a $Ni(CN)_4^{2-}$ complex, adsorbs on activated carbon and at high concentrations deceases the Au adsorption (Xie, 2010). Besides, if the gold ore has significant content of Ni that dissolves and adsorbs on activated carbon, Ni comes with gold up to smelting stage and increases the smelting temperature of the metal mixture, because of the high melting point of Ni at 1455 ^{o}C comparing with Au melting point of 1063 ^{o}C.

Among these metals, Cu has a special place. Cu forms complexes with cyanide as $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$. The $Cu(CN)_2^-$ complex adsorbs on carbon much stronger than the gold complex, that it stripes the previously adsorbed gold from activated carbon placing on carbon itself. However, adsorption of $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ complexes is so much lower that these species exert approximately no effect on gold adsorption (Dai and Breuer, 2009). The Cu-cyanide complexes change accordingly to the free cyanide concentration and the pH of the solution. When pH decreases the formation of $Cu(CN)_2^-$ complex occurs according to reactions:

$$Cu(CN)_4^{3-} + 2H^+ \rightarrow Cu(CN)_2^- + 2HCN \qquad (2)$$

$$Cu(CN)_3^{2-} + \ H^+ \rightarrow Cu(CN)_2^- + \ HCN. \qquad (3)$$
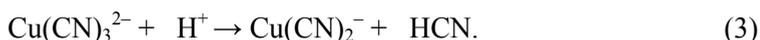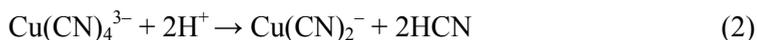
Thus, because pH of the cyanide leach solutions is as high as 10.5 and the leach solution contains as much free cyanide as 200 ppm NaCN, it might be expected that $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ forms are obtained and they have no significant effect on the gold adsorption (Xie, 2010). This phenomenon is confirmed by adsorption tests with synthetic Cu-cyanide presented in this paper.

Iron dissolves from its sulfide minerals as a $Fe(CN)_6^{4-}$ strong complex. However this complex does not either adsorb on the carbon or prevent the adsorption of gold

even at as high concentrations as 1000 ppm (Romero and Sampaio, 1993; Sheya and Palmer, 1989).

Besides, Zn-cyanide has no significant effect on adsorption of gold between pH of 6 and 12 according to the previous studies (Romero and Sampaio, 1993; Sheya and Palmer, 1989).

Also, the SCN^- complex formed by dissolution of sulfide minerals by cyanide at as high concentrations of cyanide as 1000-2000 ppm decreases gold adsorption to some degree but not as much as Ag (Romero and Sampaio, 1993).

Thus, many metal-cyanide species occur in cyanide leaching process, but many of them adsorb weakly on carbon without affecting the gold adsorption. Among these metals, Ag and Ni exert negative effect on gold adsorption and in the case of Cu this effect depends on pH and free cyanide concentrations (Poinern et al., 2011; Fleming et al., 2011; Yin et al., 2011; Petersen et al., 1993). Therefore, in this paper, the effect of Ag, Ni and Cu on the Au adsorption on activated carbon was investigated with synthetic cyanide solutions one by one and all together.

The adsorption of metal-cyanides on activated carbon is selective and the strongest adsorbed complex is $Au(CN)_2^-$. The $Ag(CN)_2^-$ complex adsorbs strongly but not as strong as $Au(CN)_2^-$. The $Cu(CN)_2^-$ and $Cu(CN)_3^{2-}$ complexes shows different adsorption features; $Cu(CN)_2^-$ complex adsorbed strongly while the adsorption of $Cu(CN)_3^{2-}$ complex is insignificant. The $Ni(CN)_4^{2-}$ complex adsorbs weaker than $Au(CN)_2^-$, $Ag(CN)_2^-$, $Cu(CN)_2^-$ complexes but stronger than $Cu(CN)_3^{2-}$, and $Ni(CN)_4^{2-}$ can reduce $Au(CN)_2^-$ adsorption significantly when there is as much as 250 ppm in leach solution. $Fe(CN)_6^{4-}$ and $Zn(CN)_4^{2-}$ adsorption and effects on gold adsorption are insignificant.

The adsorption of metal-cyanide species on activated carbon occurs selectively. First, it was thought that it is because of the difference between ionic diameters of the metal-cyanide complexes. However, although strongest adsorption on activated carbon occurs for the $Au(CN)_2^-$ complex, the ionic diameter is higher than many other cyanide species. Thus, according to the recent studies, the reason for the selective adsorption of metal-cyanide species would be the differences in the levels of hydration of the metal-cyanide molecule. Due to the hydration of the metal-cyanide complex in solution, a water shell occurs around the molecule increasing their diameter at different degrees. The hydration of the molecule relates to the cyanide molecules binding to the metal ion. Thus, increased quantity of CN^- of a metal-cyanide complex will lead to increased hydration level and thus, increased diameter of metal-cyanide molecule. So metal-cyanide could not enter through the micropores of the activated carbon and adsorption of the metal cyanide species will decrease.

On the other hand hydrophobicity increases by decreasing hydration level. Hydrophobic metal-cyanide species tends to form clusters by binding together. Forming clusters is another mechanism of adsorption of the metal-cyanides that they settle down to the activated carbon to increase the adsorption of these metal-cyanide species. Confirming these results of the studies, for example $Fe(CN)_6^{4-}$ and $Zn(CN)_4^{2-}$

complexes are found to adsorb more weakly on activated carbon that these species contain 6 and 4 CN^- molecules, and thus, have increased hydration level and decreased hydrophobicity. As a result they are well dispersed in the solution without forming clusters. The $Ni(CN)_4^{2-}$ complex can serve as a similar example but it has not been studied in the literature as to the hydration levels. Also, $Cu(CN)_3^{2-}$ complex is well dispersed in water and its hydration level is relatively high. Three cyanide bearing complexes, $Au(CN)_2$, $Ag(CN)_2^-$ and $Cu(CN)_2^-$, have the lowest hydration state and form clusters adsorbed on activated carbon. They can be classified from the strongest adsorbed to the least strong: Au>Ag>Cu (Yin et al., 2011).

In this paper, the effect of Ag, Ni and Cu on Au adsorption on activated carbon was investigated, one by one at 10 ppm Au and all together at 10 ppm Au. Because the effect of Ni-cyanide on Au adsorption was less investigated in the literature, detailed investigation of Ni effect would be a beneficial study in concept of this paper.

Materials and methods

Adsorption kinetic tests were performed by bottle rolling using 0.5 dm^3 synthetic solution and 0.6 g/dm^3 granulated activated coconut carbon of 2.36-1.7 mm size range. The bottles were rolled at 30 rpm at 20 ^{o}C for 48 hours. 15 cm^3 solution samples were taken after 1, 3, 5, 7, 22 and 30 hours. The sample solutions were analyzed for Au, Ag, Ni and Cu.

The synthetic solutions were prepared according to the AARL (Anglo American Research Laboratories) procedure. That solution contained: 3.1 g/dm^3 H_3BO_3, 3.2 g/dm^3 $CaCl_2 \cdot 2H_2O$ and 200 ppm NaCN in pure water. pH was maintained at 10.7–11 by NaOH. It is shown that high ionic strength of the solution increases the gold adsorption on activated carbon. As the ionic strength of the process waters of cyanide leaching plants is rather high, the AARL procedure applies a high ionic strength of the test solutions simulating plant process solutions. $Au(CN)_2^-$ in solution was supplied by a 1000 ppm standard $AuCl_3$ solution. NaCN was used as analytical quality reagent. For $Ag(CN)_2^-$, analytical grade $AgNO_3$, for $Cu(CN)_3^{2-}$ analytical grade $CuCl_2 \cdot 2H_2O$, for $Ni(CN)_4^{2-}$ analytical grade $NiCl_2.6H_2O$ reagents were used. The adsorption tests conditions are shown in Table1.

Table 1. Composition of experimental adsorption solutions

Metal content of adsorption solutions, ppm														
Au ppm	5	15	10	10	10	10	10	10	10	10	10	10	10	10	10
Ag ppm	0	0	0	20	50	100	200	0	0	0	0	0	0	0	200
Ni ppm	0	0	0	0	0	0	0	40	80	160	250	0	0	0	200
Cu ppm	0	0	0	0	0	0	0	0	0	0	0	90	180	300	300

To model the adsorption results the Fleming k,n method was used. The k,n model is defined as

$$\Delta Auc = k \cdot Aus \cdot t^n .\qquad(4)$$

In this equation *k* and *n* are model parameters: *k* is a kinetic constant (1/hours), and n is a model parameter, t is adsorption time (hours), *Aus* is gold in solution at time *t*, ppm, and ΔAuc is defined as the gold adsorbed on carbon from *t*=0 up to a certain time *t* (ppm). The equation can be linearized:

$$\ln\left(\frac{\Delta Auc}{Aus}\right) = \ln k + n \ln t .\qquad(5)$$

Results and discussion

Gold adsorption

Adsorption tests for aqueous solutions containing Au at the concentrations of 5, 10 and 15 ppm and 200 ppm NaCN at pH 10.7–11.0 were performed at 20 °C during 48 hours. Granulated activated carbon (0.6 g/dm^3) was used. The adsorption recovery of Au is presented in Fig. 1.
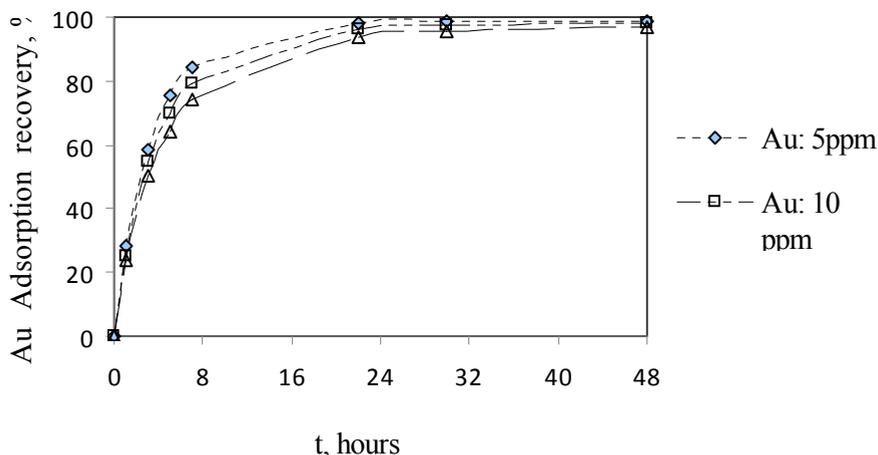
Fig. 1. Adsorption recoveries vs. time at 5, 10 and 15 ppm Au solution concentrations

According to Fig. 1 the adsorption of gold from solution on activated carbon is very fast up to 7 hours and slows down after 7 to 22 hours finally reaching equilibrium between 30 and 48 hours.

Silver effect on gold adsorption

Au adsorption tests at 10 ppm of Au and Ag concentrations of 20, 50, 100 and 200 ppm were performed. The results are presented in Fig.2.
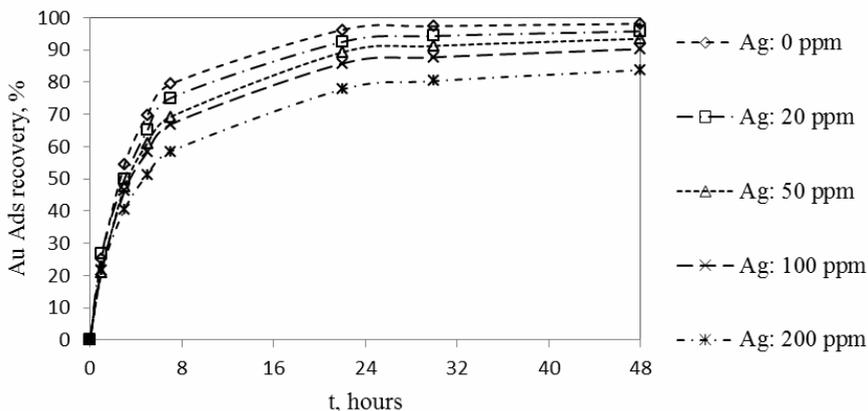
Fig. 2. **G**old adsorption recovery at different Ag concentrations

As presented in Fig. 2, the Au adsorption recoveries decrease according to increasing silver concentration starting with as low as 20 ppm Ag up to 200 ppm. At 200 ppm Ag concentration gold adsorption efficiency decreased by as much as 20% (Fleming and Nicol, 1984; Romero and Sampaio, 1993; Vegter and Sanderbergh, 1997; Yin et al., 2011). Also silver loading to carbon is shown in Table 2.

Table 2. Adsorption of Ag with Au on activated carbon

	Ag: 20 ppm	Ag: 50 ppm	Ag: 100ppm	Ag: 200ppm
Ag on carbon after 48 h.	5915 ppm	10261 ppm	11216 ppm	24986 ppm
Ag adsorption rec. after 48 h.	46.90%	31.69%	17.33%	18.83%

Nickel effect on gold adsorption

Au adsorption tests at the Ni concentrations of 40, 80, 160 and 250 ppm and 10 ppm Au were performed. The results are presented in Table 3 and Fig. 3. As represented in Fig. 3 the inhibition of the Au adsorption is lower than in the case of Ag. $Ni(CN)_4^{2-}$ complex has 4 CN^- ions compared to 2 CN^- in $Ag(CN)_2^-$ which results in higher hydration. Thus, it is better dispersed in the solution without forming clusters which enables the adsorption on activated carbon (Yin et al., 2011).
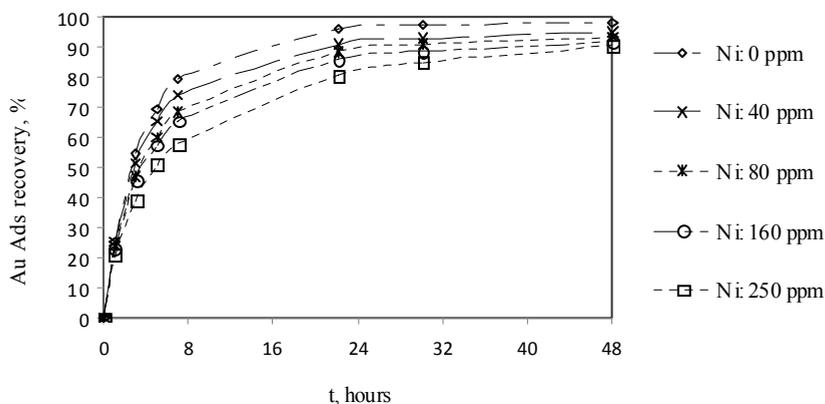
Fig. 3. **G**old adsorption recovery at different Ni concentrations

Table 3. Adsorption of Au with Ni on activated carbon

	Ni: 40 ppm	Ni: 80 ppm	Ni: 160 ppm	Ni: 250 ppm
Ni on carbon in 48 h	2034 ppm	2356 ppm	5561 ppm	4706 ppm
Ni adsorption rec. in 48 h	8.38%	4.77%	5.46%	3.08%

Table 3 confirms that the Ni adsorption is lower than that of Ag and this phenomenon indicates higher hydration of $Ni(CN)_4^{2-}$.

Copper effect on gold adsorption

Cu concentrations of 90, 180 and 300 ppm with 10 ppm Au were used for adsorption tests. The results are presented in Table 5 and Fig. 4.

According to Fig. 4 and Table 4, copper concentration at 90 ppm has no effect on Au adsorption and with 180 ppm Cu the Au adsorption starts decreasing slightly up to 300 ppm Cu. However, Cu effect on Au adsorption is very limited. With 300 ppm Cu in solution the decrease of gold adsorption recovery was as low as 3%. This phenomenon indicates that the Cu-cyanide species are in the forms of $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ of which hydration levels are higher than $Cu(CN)_2^-$ which adsorbs strongly on activated carbon preventing Au adsorption. Besides, the conditions of solution of adsorption tests (pH 10,7–11 with 200 ppm NaCN) represent a typical process solution of Au cyanide leaching at plants where $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ species are formed rather than $Cu(CN)_2^-$.

As presented on Table 4, Cu adsorptions on activated carbon are lower than that of Ag and Ni indicating that Cu shows lower effect on gold adsorption on activated carbon.
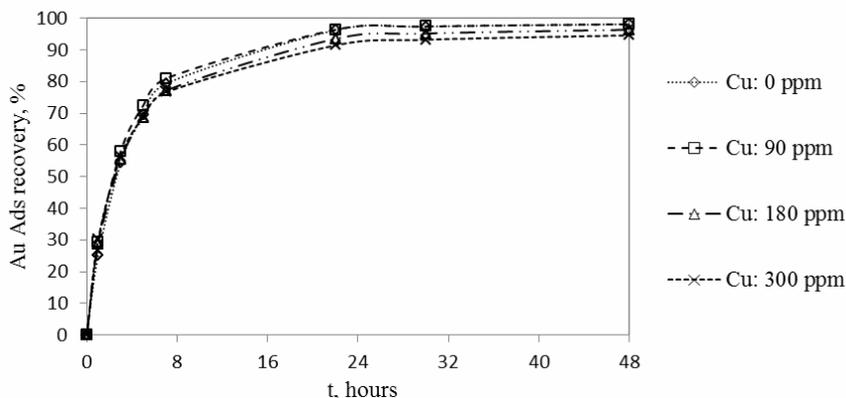
Fig. 4. Gold adsorption recovery at different Cu concentrations

Table 4. Adsorbed Cu with Au on activated carbon

	Cu: 90 ppm	Cu: 180 ppm	Cu: 300 ppm
Cu on carbon in 48 h	3038 ppm	2889 ppm	4135 ppm
Cu adsorption rec. in 48 h	5.40 %	2.59 %	2.26 %

Simultaneous effect of Ag, Ni and Cu on gold adsorption

Ag, Ni and Cu cyanide complexes were added together to the adsorption solution to have 200 ppm of Ag and Ni, and 300 ppm Cu at 10 ppm of Au. The test parameters were: solution temperature, 20 °C, 200 ppm NaCN, pH 10.7–11. Results are shown in Fig. 5.
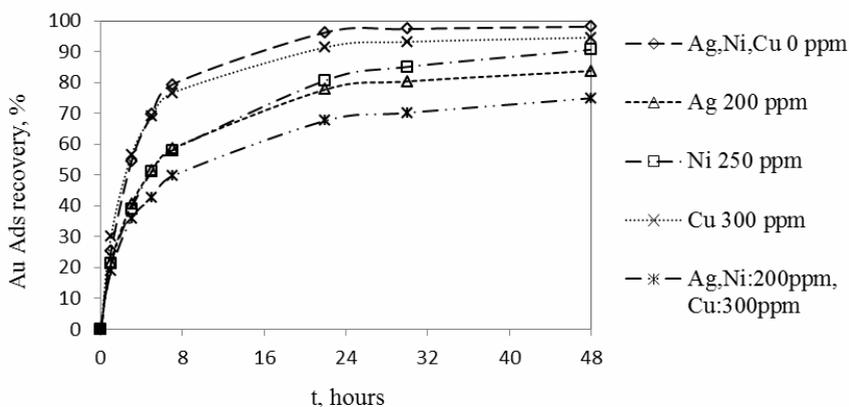
Fig. 5. Comparative results of Ag, Ni: 200 ppm and Cu:300 ppm with metals one by one

As shown in Fig. 5, 200 ppm Ag has more decreasing effect than 250 ppm Ni on Au adsorption while Ag, Ni 200 ppm and Cu:300 ppm has the most significant effect. Besides, when Ag, Ni and Cu placed all together in the same solution with 10 ppm Au, they prevent adsorption of each other. The comparative results are presented in Table 5.

Table 5. Comparative results of adsorption of metals together and separately

Solution metal contents	Adsorption of Ag, Ni and Cu		
	Ag	Ni	Cu
Ag,Ni: 200 ppm; Cu:300 ppm together	11.69%	4.43%	0.66%
Ag:200 ppm separately	18.83%		
Ni: 160 ppm separately		5.46%	
Cu:300 ppm separately			2.26%

As shown in Table 5 the test: Ag, Ni: 200 ppm and Cu, 300 ppm together with 10 ppm Au, presents the results that Ag, Ni and Cu adsorption on activated carbon decreased to a lower level than that of the separate tests with Ag 200 ppm; Ni 160 ppm and Cu 300 ppm. Ni at 160 ppm test shows more Ni adsorption recovery than that of the test with Ni at 200 ppm with Ag and Cu together. These results indicate the metals prevent adsorption of each other when present in the solution together.

Modeling of the Au adsorption data adsorption by the Fleming k,n model

The Fleming k,n modeling is applied to 48 hour adsorption data as shown in Fig. 6 (Fleming and Nicol, 1984).
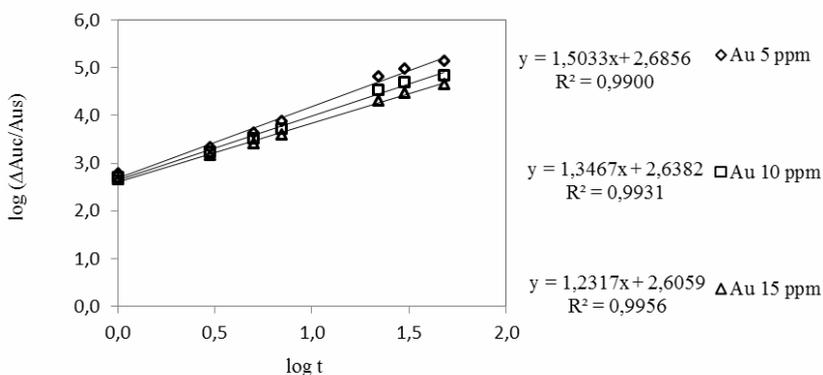
Fig. 6. The Fleming k,n model application graphs for 48 hours gold adsorption data.

As shown in Fig. 6, the Fleming k,n model fits well to the adsorption data giving R^2 values that are very close to 1. Model parameters *k* and *n* were found by an non-

linear regression analysis. According to Fig. 6, increased n values indicate rapid adsorption of Au on activated carbon. Thus, with decreasing concentration of the Au solution the slope of the model graphs increases indicating increased *n* values. Parameter *n* is presented as adsorption strength and *k* is a parameter representing Au adsorption capacity of carbon.

Conclusions

Adsorption tests regarding Au concentrations of 5, 10 and 15 ppm were performed. For 48 hours adsorption tests the Au adsorption recoveries were 99.04%, 98.13% and 97.16% for 5, 10 and 15 ppm Au in solution, respectively.

The test with 200 ppm Ag showed the strongest decreasing effect on Au adsorption recovery decreasing it from 98.13% to 83.77%. 250 ppm Ni decreased the Au adsorption recovery to 90.65% and 300 ppm Cu decreased it to 94.59%.

When metals are added together to the same solution (Ag, Ni 200 ppm and Cu 300 ppm) Au adsorption recovery decreased to 74.92%. When the metals are added together, the adsorption recovery of Au decreased more than that of the metals used separately. Also metals prevent adsorption of themselves as well as that of gold, when they are present in the solution together.

The data of Au adsorption recoveries for 48 hours adsorption time modelled by the Fleming k, n adsorption kinetic, where k and n are the model parameters which could be used to design and optimize an adsorption unit of a gold cyanide leach plant. Knowing *k* and *n* values such variables as adsorption tank quantities and volumes, carbon concentrations (g carbon/dm^{3}slurry) for each tank and weekly carbon stripping quantities can be determined.

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