Effect of zinc ion on copper speciation and adsorption on activated carbon

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ABSTRACT

This paper describes the effect of zinc ions on copper speciation and adsorption on activated carbon in solutions with varied cyanide levels and containing calcium. Batch and column adsorption experiments were carried out under atmospheric conditions at different levels of CN/Cu using two types of activated carbon. Raman analysis shows that CN/Cu molar ratio, ionic strength (by adding calcium ions to the solution), and zinc ions can be used to control copper speciation in cyanide solutions. The addition of Zn^{2+} to cyanide solutions causes the conversion of CN^- and $Cu(CN)_4^{3-}$ species to $Cu(CN)_3^{2-}$, and the concomitant formation of $Zn(CN)_4^{2-}$, regardless of cyanide concentration and ionic strength. As $Cu(CN)_3^{2-}$ has a high affinity for the solid surface, copper adsorption was favored. The co-addition of Ca^{2+} to the solutions produces an even larger enhancement of copper adsorption on activated carbon and has no effect on zinc adsorption. Column experiments show a significant reduction in the volume of cyanide solution to be further treated and an important increase in the concentration of copper. These findings may aid in the design of copper and cyanide recovery strategies.

1. Introduction

In nature, gold is usually found in association with other metals, mostly silver, iron, and copper. The occurrence of copper minerals in gold deposits, typically in the form of secondary sulfides, affects the leaching process due to their fast and high dissolution rate in the cyanide media (Marsden and House, 2006). The presence of cyanide-soluble copper minerals in the ore increases cyanide consumption and the concentration of copper cyanocomplexes in the solution to be treated (Estay et al., 2014). In addition, the oxidation of free cyanide to cyanogen by soluble copper species may cause irreversible losses of reagent, about 0.4 kg NaCN/kg of copper available in the solution (Scerescini, 2005).

The environmental restrictions to the disposal of effluents containing cyanide and metal cyanocomplexes in tailings dams, combined with the costs associated with cyanide consumption, make cyanide recovery and recycling a relevant issue to gold industry. Cyanide recovery and recycling is especially relevant where significant concentrations of metal cyanocomplexes, such as copper, are present in cyanidation tailings.

The classic AVR (acidification, volatilization, reneutralization) process and its variations for cyanide recycling are not able to recover copper cyanocomplexes. SART (sulfidization, acidification, recycling and thickening) technology has become one of the main options to treat effluents with a high concentration of copper cyanide. In this process,

sulfide ions and acid are added to cyanidation tailings to precipitate copper sulfide, which is then thickened and filtered. The HCN gas is released and recycled to gold cyanidation. A detailed description of the process can be found elsewhere (Barter et al., 2001; Fleming, 2005; Ford et al., 2008; Estay et al., 2014). Nevertheless, if solutions with low concentrations of cyanide and copper are treated, large thickeners are required, thus increasing capital and operating costs. A previous concentration of the cyanide solution to be treated can thus make cyanide recovery technologies suitable to treat effluents with a broad range of cyanide concentrations and render the precipitation stage more efficient in metal recovery.
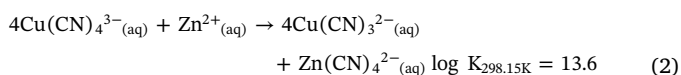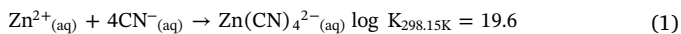
Among the potential alternatives in this regard, the use of ion exchange resins, including its advantages and limitations has been revised (Fleming, 2001; Ciminelli, 2002; Dai et al., 2012). Attempts to introduce cyanide recovery processes using ion exchange resin have not been commercially successful yet. Intrinsic characteristics of the resin, as a fine particle size (hampering further separation from the pulp), and degradation due to osmotic shock effects (*e.g.* volumetric changes caused by alternating alkaline and acid cycles) are some difficulties to be considered. These factors tend to promote resin losses during the cyanide recovery process. Other issues that may have hampered the initial applications of resin are the slow adsorption of free cyanide and the poisoning of the resin by precipitates formed during the acid recovery step.

The concentration of copper cyanide solutions by means of

adsorption on activated carbon, a process well established in the gold industry, appears to be an option that warrants further study. Marsden and House (2006) proposed the following adsorption trend: Au $(CN)_2^-$ > $Hg(CN)_2^-$ > $Ag(CN)_2^-$ > $Cu(CN)_3^{2-}$ > > Zn $(CN)_4^{2-}$ > $Ni(CN)_4^{2-}$ > $Fe(CN)_6^{4-}$, which indicates that the tri-cyanocuprate (I) complex has a high affinity by the sorbent. Nonetheless, it is relevant to mention that the cyanide solution produced by gold cyanidation may have a relatively high concentration of free cyanide, which favors the predominance of the tetracyanocuprate (I) complex, $Cu(CN)_4^{3-}$. It is well established that this change in coordination negatively affects its adsorption on activated carbon (Fleming and Nicol, 1984; Souza et al., 2014a, 2014b).

The addition of reactive ions to the cyanide solution, such as Zn^{2+}, may lead to the formation of stable complexes, such as $Zn(CN)_4^{2-}$, through the consumption of free cyanide available in the solution. According to the spontaneous reactions listed below, this alternative may represent a potential option to enhance copper adsorption on activated carbon in a concentration stage prior to cyanide recovery. All CN^- and $Cu(CN)_4^{3-}$ species are expected to be converted into Zn $(CN)_4^{2-}$ and $Cu(CN)_3^{2-}$ complexes. The thermodynamic parameters are shown in Table 1.

$$Zn^{2+}_{(aq)} + 4CN^-_{(aq)} \rightarrow Zn(CN)_4^{2-}_{(aq)} \quad \log K_{298.15K} = 19.6 \tag{1}$$

$$4Cu(CN)_4^{3-}_{(aq)} + Zn^{2+}_{(aq)} \rightarrow 4Cu(CN)_3^{2-}_{(aq)}$$
$$+ Zn(CN)_4^{2-}_{(aq)} \quad \log K_{298.15K} = 13.6 \tag{2}$$

In this context, the main objective of the present investigation was to evaluate the effect of zinc ions on copper cyanide speciation and adsorption on different types of activated carbon. A reduction in the volume and concentration of copper in a cyanide solution to be treated is expected to favor the subsequent stages of copper and cyanide recoveries.

2. Experimental

2.1. Activated carbon samples

In this work, two types of activated carbon samples were used: one sample produced from coconut shell (sample C) and one from *Eucalyptus* powder (sample E). Sample C is used industrially for gold adsorption from cyanide solutions. Sample E exhibits high copper adsorption capacity (Souza et al., 2014a). Prior to the adsorption experiments, both samples were thoroughly rinsed with 0.1 mol L^{-1} sodium hydroxide (NaOH, Synth 99%) solution in order to withdraw humic acid residues. The solid/liquid ratio used in the procedure was 1/100 g mL^{-1}. After, the samples were thoroughly rinsed with Milli-Q water (resistivity of 18.2 MΩ cm, Millipore®) and then dried in a furnace at 60 °C for 24 h.

2.2. Characterization of activated carbon samples

The activated carbon samples were characterized according to the

Table 1
Selected species and thermodynamic parameters at 298.15 K and ionic strength, I = 0[a].

Species		Ref.
HCN	$pK_a^o = 9.21$	[1]
$Cu(CN)_2^-$	$\log \beta_2 = 24$	[1,2]
$Cu(CN)_3^{2-}$	$\log K_3 = 5.3$[a]	[3]
$Cu(CN)_4^{3-}$	$\log K_4 = 1.5$[a]	[3]
$Zn(CN)_4^{2-}$	$\log \beta_4 = 19.6$	[4]

Kyle and Hefter (2015) [1]; Lu et al. (2002) [2]; Izatt et al. (1967) [3]; Solis et al. (1996) [4].

[a] Values at infinite dilution were obtained by extrapolation or by correction for activity coefficients.

(i) specific surface area; (ii) ash content; (iii) density of surface functional groups; (iv) point of zero charge (PZC) and (v) morphology. The specific surface area was determined by the Brunauer, Emmett, and Teller (BET) method using a Quantachrome (NovaWin2) analyzer. The ash content was determined by the weight loss of each sample, after heating in a porcelain crucible at 900 °C for 1 h using a muffle furnace (Jung, LF0614), according to the standard method (JIS, 2014).

The density of surface functional groups and the identification of the corresponding groups was determined by the Boehm method (Boehm, 1994). Using this titration method, the acid groups available on the solid surface (*i.e.* carboxyl, lactones, and phenols) were quantified by means of neutralization with $NaHCO_3$, Na_2CO_3, and NaOH solutions. Alkaline groups, typically amines, pyrones, and quinones, were determined by neutralization with HCl solution. In the procedure, 0.5 g of solid sample was added to 50 mL of 0.05 N NaOH, sodium bicarbonate ($NaHCO_3$, Synth 99.9%), sodium carbonate (Na_2CO_3, Synth 99.9%) or hydrochloric acid (HCl, FMaia 36%) solutions under a nitrogen (N_2, 99.999%) atmosphere. The heterogeneous mixture was kept under stirring (200 rpm) at 25 ± 1 °C for 24 h using a shaker (New Brunswick Scientific, Innova 44). Next, the mixture was vacuum filtered and an aliquot of each solution was back titrated with standard 0.1 N NaOH or HCl solutions in order to quantify the density of acid and basic groups, respectively.

The PZC value of the activated carbon samples was obtained according to the procedure described by Strelko and Malik (2002). Thus, 0.1 g of solid sample was added to 20 mL of 0.1 N sodium chloride (NaCl, Synth 99%) solutions with initial pH ranging from 2 to 11. The pH was adjusted by adding the required volumes of 0.1 N HCl and 0.1 N NaOH solutions. Next, the heterogeneous mixture was kept under stirring (200 rpm) at 25 ± 1 °C for 24 h using a shaker. The pH was monitored before and after stirring, and the PZC value was determined when the initial and final values of pH coincided.

The morphology of both activated carbon samples was analyzed by scanning electron microscopy (SEM) coupled to energy dispersive spectrometry (EDS), using a JEOL (JSM 6360 LV) microscope equipped with a ThermoNoran (Quest) spectrometer. The micrographs were obtained using a 20 kV accelerating voltage.

2.3. Adsorption experiments

2.3.1. Shaker

Adsorption data were obtained at 25 ± 1 °C from solutions prepared by dissolving copper (I) cyanide (CuCN, Sigma-Aldrich 99%), potassium cyanide (KCN, Sigma-Aldrich 96%), and zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$, Sigma-Aldrich 99%) in Milli-Q water. The amount of KCN added to the solution varied according to the desired CN/Cu molar ratio and concentration of free cyanide. The amount of zinc added to the solution was defined stoichiometrically, according to Eqs. (1) and (2), aiming at converting all CN^- and $Cu(CN)_4^{3-}$ species to $Zn(CN)_4^{2-}$ and $Cu(CN)_3^{2-}$ complexes, respectively. Thus, 128.7, 254.5, and 443.2 mg L^{-1} of Zn^{2+} ions were added to solutions with CN/Cu equal to 4, 5, and 7.5, respectively. The pH was adjusted to 10.5 by adding the required volumes of 0.1 N potassium hydroxide (KOH, Synth 99%) solution. For some tests, ionic strength was controlled around 1 by adding 0.33 mol L^{-1} calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$, Synth 99%).

With regard to the experimental procedure, 1.0 g of solid was added to 100 mL of solution. The heterogeneous mixture was kept under stirring (200 rpm) in a shaker for 24 h. Next, the mixture was vacuum filtered and the concentrations of copper and zinc were analyzed by means of inductively coupled plasma optical emission spectrometry (ICP-OES) using a Perkin Elmer (Optima 7300 DV) spectrophotometer. The amount of metal adsorbed on the activated carbon, A, in mg g^{-1}, was determined through a mass balance, as given by:

$$A = ([M]_i - [M]_f)V/(m_s) \tag{3}$$