Water Washing of Fungal-treated Carbonaceous Ores: Effect on Aurocyanide Adsorption by Activated Carbon in CIL Circuit*

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Abstract

A typical challenge encountered on most gold processing plants during leaching of refractory ores is the reduction in recovery due to the presence of carbonaceous matter which preg-robs dissolved gold. To reduce preg-robbing during cyanidation, carbonaceous matter has to undergo pretreatment to passivate the active surface. The fungus, *Phanerochaete chrysosporium* has been shown to biotransform carbonaceous matter, thus reducing its ability to preg-rob gold. However, the possible transfer of entrained fungal biomass into Carbon-In-Leach (CIL) circuits has been reported to decrease the activity of activated carbon, and a proposed solution to this was to wash the fungal-treated material thoroughly with water before CIL operation. This paper therefore set out to assess the effect of water-washing on aurocyanide adsorption by activated carbon in CIL following fungal pretreatment of carbonaceous ores. To realise the objective, activated carbon was contacted with cell-free extract of *P. chrysosporium* under varying conditions of pH and time, after which it was washed with different volumes of water, and its gold-adsorption ability assessed. The results revealed a decrease in the activity of activated carbon as a function of increasing contact time with the cell-free extract. The percentage decrease was higher after treatment in the acidic medium (13%) than the basic medium (9%). After washing the carbon (treated in acidic medium), gold adsorption was found to increase directly with the volume of water used from 64% at 0 mL to 84% at 500 mL and 91% at 1000 mL. Correspondingly, the carbon treated in basic medium recorded 69% at 0 mL to 87% at 500 mL and 93% at 1000 mL. This paper thus concludes that, sufficient water washing should be employed after fungal-biotransformation of refractory ores before CIL operation to decrease the effect of entrained biomass on the adsorption capacity of activated carbon.

Keywords: Carbonaceous Gold Ore, Activated Carbon, Carbon-In-Leach, Cell-Free Extracts

1 Introduction

Gold ores can be categorised based on metallurgical processes as refractory and non-refractory. Refractory gold ores are ore types that are insusceptible to direct leaching by cyanide or simple gravity concentration. They can either be sulphidic, carbonaceous or double-refractory in nature. Gold associated with carbonaceous materials are preg-robbing. Carbonaceous material (CM) in gold ores have been known to include charcoal, carbon, coal, shale, decaying wood, wood ashes and other vegetable matter. Natural CM in refractory carbonaceous gold ores behaves like activated carbon and adsorbs dissolved gold from solution (Adams *et al.*, 1996; Rees and van Deventer 2000; Schmitz *et al*., 2001; Tan *et al.*, 2003).

Refractory gold ores must necessarily undergo pretreatment processes so as to improve upon overall gold recovery. Mineralogy and other specific characteristics of refractory gold ores play a vital role when considering an appropriate technique for processing these gold ores. Bacterial oxidation of sulphide minerals is a familiar and commercially available process to enhance gold recovery with problem ores. Microbial pre-treatment of refractory carbonaceous gold ores are gaining more attention presently as a potential replacement for other processes of pretreating methods such as roasting and surface blinding (Adams and Burger, 1998; Marsden and House, 2006). This is due to lower cost, less environmental issues, lower operating temperatures and the self-rejuvenating ability of the microorganisms employed (Marsden and House, 2006; Ofori-Sarpong *et al.*, 2010; 2017). The commercial bacterial oxidation process (BIOX), which has been used for about three decades now, however, encounters possible recovery challenges such as gold losses due to the presence of carbonaceous matter. This is because the bacteria used in the BIOX system are not able to deactivate the carbonaceous matter present in the gold ore (Amankwah *et al.*, 2005; Madigan and Martinko, 2006; Ofori-Sarpong and Osseo-Asare, 2013; Ofori-Sarpong *et al.*, 2013b; Adam *et al.*, 2017).

Studies on different grades of carbonaceous matter in gold ores are normally done using different ranks of coal as surrogate due to the geological, structural and chemical similarities (Amankwah and Yen, 2006; Ofori-Sarpong *et al*., 2010; Ofori-Sarpong and Osseo-Asare, 2013). Biotreatment of different grades of carbonaceous matter have been reported using various bacteria (*Streptomyces setonii, Pseudomonas spp., Achcromobacter spp., Arthrobacter spp.* and *Rhodococcus spp*) and fungi (*Trametes versicolor, Aspergillus bruneio-uniseriatus* and *Penicillium citrimum*) (Brierley and

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Kulpa, 1993; Amankwah and Yen, 2006; Yen *et al.*, 2008). Most of these researchers observed the highest degradation with bituminous-grade carbonaceous matter relative to the others.

Studies conducted on different ranks of coal have revealed that, anthracite has the highest capacity to preg-rob dissolved gold (Ibrado and Fuerstenau, 1992; Ofori-Sarpong *et al*., 2010), and anthracite-grade carbonaceous matter accounts for more than 50% of preg-robbing in gold processing (Stenebraten *et al.*, 2000).

Ofori-Sarpong and Osseo-Asare (2013) therefore undertook a study that targeted on deactivating carbonaceous matter, and after treating lignite, bituminous and anthracite coals with the fungus, *Phanerochaete chrysosporium*, it was observed that, gold adsorption by anthracite decreased the most. Decrease in the ability of carbonaceous matter to preg-rob gold after fungal-treatment could be due to complete loss of carbon through the formation of carbon dioxide or the introduction of oxygen groups on the carbon leading to a disruption in the continuous nature of the graphitic planes required for adsorption. Other reasons assigned include coating of the carbon surface with fungal biomass, leading to deactivation by passivation (Helm *et al.*, 2009; Ofori-Sarpong *et al*., 2013a; Qian *et al*., 2014).

Activated carbon is a carbonaceous material with a high degree of porosity and extended high surface area. Elemental carbon makes up more than 90% of activated carbon (Cecen, 2014). A major development in gold hydrometallurgy has been the industrial use of activated carbon for gold adsorption from alkaline cyanide leach solutions. Activated carbon is used to selectively concentrate dilute gold-bearing solutions to produce higher grade solution from which gold can be effectively extracted (Marsden and House, 2006). The gold is dissolved as $Au(CN)_2^-$ complex and is recovered from the solution by Carbon-In-Pulp (CIP) or Carbon-In-Leach (CIL) processes (Bhattacharyya *et al*., 2014). In CIL operations, 25 g/L of AC is currently applied on most free-milling gold processing plants (Marsden and House, 2006).

Activated carbon, intentionally introduced in CIL circuit to be used in recovery of dissolved gold from cyanide solution, is itself a carbonaceous matter in nature. When it is contacted with *P. chrysosporium,* there could be the possibility of surface deactivation of the carbon due to oxidation and/or coating by fungal biomass which serves as organic foulant (Helm *et al.*, 2009; Ofori-Sarpong *et al*., 2013a; Qian *et al.*, 2014; Bonnah *et al*., 2016). Carbonaceous gold ore biotreated with *P. chrysosporium* could carry along entrained fungal biomass into the CIL circuit, and this organic matter could have deactivating effect on the activated carbon. A study conducted by Bonnah *et al*., (2016) on the effect of fungal biomass on the adsorption of gold by activated carbon revealed that entrained biomass could reduce activated carbon adsorption by 18% - 21% depending on pH and contact time.

These authors therefore recommended that feed from pretreatment process be washed thoroughly with water before entering the CIL circuit. Hence, the objective of this paper was to assess the effect of sufficient water washing on aurocyanide adsorption by activated carbon in CIL following fungal pretreatment of carbonaceous ores.

2 Resources and Methods Used

2.1 Materials Used

Materials used for the experimental work include fungal spores of *Phanerochaete chrysosporium* which was obtained from the Minerals Engineering Laboratory of the University of Mines and Technology, Tarkwa, pH modifiers (sodium hydroxide and sulphuric acid), activated carbon and gold solution, all from the Minerals Laboratory. Corn bran used as the growth media was obtained from a nearby Corn Mill Shop.

2.2 Methods Employed

The entire experiment was carried out in the Minerals Engineering Laboratory of the University of Mines and Technology, Tarkwa. The step by step procedures by which this work was done successfully include culturing of fungus, harvesting of cell-free extract after growth, conditioning of activated carbon, and contacting of cell-free extract with conditioned activated carbon. Gold solution of concentration 5 ppm was used to conduct adsorption test on the various carbons. A control adsorption experiment was undertaken using as-received, conditioned and unwashed treated carbons.

2.2.1 Growth Medium Preparation, Culturing of Fungi and Harvesting of Cell-Free Extract

Corn bran weighing 100 g each was transferred into five different PYREX Narrow Mouth Erlenmeyer Flasks, and 30 ml of distilled water, added. Each flask was covered with aluminium foil and autoclaved at 121 ºC for 30 mins to get rid of residual microorganisms. Upon cooling, fungi spores were introduced into the media at about 0.1 g per 100 g of corn bran. The cultures were allowed to grow at a temperature of 30 ºC for 10 days in an

MRC Orbital Shaker Incubator. Oxygen was introduced into the culture by partially covering the flasks with a piece of foam as shown in Fig. 1. Fungal growth was assessed to be efficient after the incubation period by visual inspection.

Fig. 1 A 10-day culture of *P. chrysosporium*

The biomass was removed from the culture after the incubation period, and the cell-free liquor extracted. This was done by pulping the entire media with 1.5 L of distilled water and sieving through quadruple-layered cheesecloth (Ofori-Sarpong *et al*., 2013c) in order to separate the fungal biomass from the growth media. The pH of the cell-free extract was checked and recorded as 3.46.

2.2.2 Conditioning of Activated Carbon and Contacting with Cell-Free Extract

Twelve beakers were set up to receive 1.25 g each of activated carbon and 30 ml of distilled water, and the mixture left to soak for 10 mins to open up the pores of the activated carbon. The carbons were rinsed after the 10 mins conditioning period. The cell-free liquor extracted after the incubation period was divided into two and the initial pH increased from 3.46 to 4 on one hand, and 3.46 to 10.5 on the other hand using NaOH and H_2SO_4 as pH modifiers. The conditioned activated carbons were contacted with the cell-free extracts for varying time intervals (2, 4, 8, 12, 24 hrs). They were then left in the incubator for the extract to interact with the activated carbon. At the end of each resident time, the activated carbon was rinsed with water.

2.2.3 Rinsing of Treated Samples

Samples treated with cell-free extract for 2, 4, 8 and 12 hours were rinsed with a constant volume of water (200 ml) only to check the effect of treatment time on subsequent processes, whereas those treated for 24 hrs were rinsed with various volumes of water ranging from 50 ml to 1000 ml to ascertain the effect of post-treatment washing on subsequent gold adsorption by activated carbon. The rinsing was done by putting the bottles on rollers to agitate. Table 1 shows the rinsing format for various contact times at pH of 4.0 and 10.5.

Table 1 Rinsing Format for Various Fungal Treatment Times (at pH of 4.0 and 10.5)

Fungal Treatment Time (hrs)	Volume of water used (ml)
2	200
4	200
8	200
12	200
24	200
24	50
24	150
24	300
24	500
24	750
24	1000

2.2.4 Control Experiment

The control experiment was set-up as follows:

(i) 1.25 g of the activated carbon (unconditioned) was contacted directly with 50 ml of 5 ppm gold solution to determine the adsorption rate of the carbon. This was labelled “as-received”;

(ii) 1.25 g of the activated carbon was conditioned with water and contacted with 50 ml of 5 ppm gold solution to determine the adsorption rate of the carbon. This was labelled “as-received (conditioned)”;

(iii) 1.25 g of the activated carbon was contacted with 50 ml of cell-free liquor at pH of 4.0 for 24 hrs but was not washed before contacting with the gold solution. This was labelled as “treated unwashed (pH 4.0)”; and

(iv) 1.25 g of the activated carbon was contacted with 50 ml of cell-free liquor at pH of 10.5 for 24 hrs but was not washed before contacting with the gold solution. This was labelled as “treated unwashed (pH 10.5)”.

2.2.5 Contacting of Various Activated Carbons with Gold Solution

A gold solution of concentration 5 ppm was prepared of which 50 ml each was contacted with the various carbons for 24 hrs. After the 24 hr resident time, loaded activated carbon was separated from the solution by filtration. The concentration of the residual gold solution was analysed using a Varian AA240FS Atomic Absorption Spectrometer (AAS). Results from AAS was analysed using Equations 1 and 2 respectively to determine the amount and

percentage of aurocyanide adsorbed from solution. The adsorption capacities of the fungal-treated carbon were compared with the controls.

$$\text{Adsorption} = \text{Initial conc.} - \text{final conc.} \quad (1)$$

$$\%\ \text{Adsorption} = \frac{\text{Adsorption}}{\text{Initial conc.}} \times 100\% \quad (2)$$

3 Results and Discussion

This paper aimed at ascertaining the effect of sufficient water washing of feed from pretreatment section to CIL, on aurocyanide adsorption by activated carbon. The effect of entrained biomass of *P. chrysosporium* on the adsorption capacity of activated carbon was analysed at pH of 4.0 and 10.5. Pretreatment times were varied as 2, 4, 8, 12 and 24 hours, and 200 ml of fresh water was used to wash the fungal-treated carbons. In addition, samples treated for 24 hours were washed with various volumes of water ranging from 50 ml to 1000 ml. The results obtained are presented and discussed in the ensuing sections.

3.1 Gold Adsorption as a Function of Fungal Treatment Time at pH of 4.0 and 10.5

Conditioned activated carbons treated with the cell-free extracts for 2, 4, 8, 12, 24 hrs were washed with constant volumes of water (200 mL). The washed treated carbon was contacted with 50 ml of gold solution. The amount of gold left in solution was read using an AAS. Fig. 2 illustrates the results of percentage adsorption with respect to bio-treatment time at pH of 4 and 10.5.

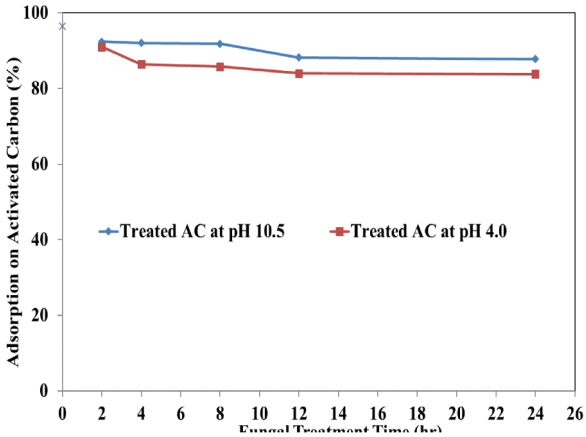

Fig. 2 Percentage Au Adsorption against Fungal Treatment Time at pH 4.0 and 10.5

From Fig. 2, it was observed that, the percentage adsorption of aurocyanide complex onto activated carbon was generally low irrespective of the treatment pH, though the values appeared to be lower after treatment in the acidic medium (pH 4.0) as compared with that of the basic medium (pH 10.5). This can be attributed to the fact that, *P. chrysosporium* grows better under conditions of relatively lower pH (2.0 - 6.5) (Ofori-Sarpong *et al.*, 2010; 2011), even though the fungus can survive over a wider range of pH (Andrawis *et al.,* 1988; Ofori-Sarpong *et al.*, 2017). The decrease in adsorption in both cases over the 24 hours confirms that entrained biomass of the fungi can cause significant damage to carbon activity in the CIL circuit (Bonnah *et al*., 2016).

In acidic medium (pH 4.0), percentage adsorption decreased from 91% at 2 hrs through 84% at 12 hrs and finally to 83.8% at the end of the 24-hour period of contacting the conditioned activated carbon with the cell-free extract. General decrease in adsorption from the 2nd hour of fungal treatment to the end of the 24th hour treatment time was 7.91% for carbon treated with cell-free extract at pH of 4.0 and 4.98% for that treated at pH 10.5. For the overall decrease in carbon activity at the end of the experiment, time 0 to 24, a whopping 13% was recorded for AC treated at pH 4.0 and 8.92% at pH 10.5. It was concluded that biomass of *P. chrysosporium* in CIL circuit can cause significant decrease in carbon activity hence reducing overall gold recovery.

3.2 Gold Adsorption as a Function of Volume of Water Used for Washing after Fungi Treatment at pH of 4 and 10.5

Activated carbons treated at the same contact time (24 hrs) were washed with different volumes of water to analyse the effect of various volumes of water on its adsorption capacity. This was done for pH 4 and 10.5. Activated carbon which was unwashed after contacting with cell-free extract and as-received (both unwashed and washed) activated carbon served as controls. These carbons were contacted with 50 ml of gold solution. The amount of gold left in solution was read using AAS. Table 2 shows the initial condition and the percentage adsoption of the various carbons used as controls.

Table 2 Initial Condition and Percentage Adsoption of Control Carbons

Carbon	Adsorption on Activated Carbon (%)	Volume of Water Used (ml)
As-received (conditioned)	96.4	0
Treated but unwashed, pH 4.0	64.4	0
Treated but unwashed, pH 10.5	68.6	0
As-received	72.8	0

Fig. 3 illustrates results of percentage adsorption with respect to volume of water used after treating the carbons at pH of 4.0 and 10.5.

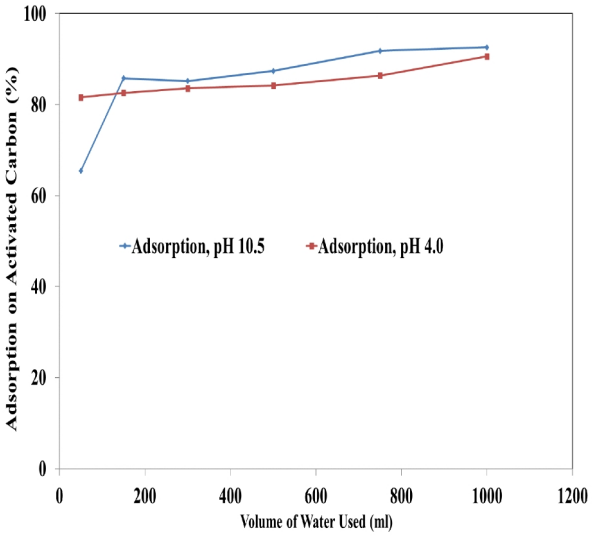

Fig. 3 Gold Adsorption against Volume of Water Used at pH 4.0 and 10.5

Considering gold adsorption at a pH of 4.0, after treating 1.25 g of activated carbon with *P. chrysosporium* for a straight 24 hr period, gold adsorption increased gradually from 81.6% to 90.6% as the volume of water increased from 50 ml to 1000 ml as shown in Fig. 3. This is so because, sufficient water washing effectively removed entrained biomass which may have passivated the carbon and reduced its active site for adsorption (Ofori-Sarpong *et al.*, 2013a). Referring from Fig. 3, percentage adsorption was 81.6% when washed with 50 ml of water; 83.6% when washed with 300 ml of water; and 90.6% when washed with 1000 ml of water.

Comparing the percentage adsorption of 50 ml - 500 ml, an increment of 3% was realised, whereas 7% and 10% were realised for 500 ml – 1000 ml and 50 ml – 1000 ml respectively. Comparing the percentage adsorption of the treated but unwashed carbon to that washed with 50 ml of water, 17.2% increase in adsorption was recorded. This implies that, washing the fungal-treated carbon with enough water can increase the adsorption capacity.

It was also observed that, the fungal-treated but unwashed carbon recorded a percentage adsorption of 64.4%. Comparing this with the as-received (conditioned), percentage difference of 33.2% was observed. However, 11.5% increase in adsorption was recorded when the values of the fungal-treated but unwashed carbon was compared to the unconditioned as-received. This can be attributed to the fact that, as-received (conditioned) was rinsed before contacting with the gold solution which may have removed residual micro-organisms and dust particles present on the surface of the activated carbon (Marsden and House, 2006). Other reasons pertaining to this are subject to further investigation.

Making reference from Table 1 and Fig. 3, an increase in percentage adsorption from 68.6% (at 0 ml) to 92.6% (at 1000 ml) resulted in the case of gold adsorption after treatment at a pH of 10.5. A 25.2% increase in adsorption was observed when the values of carbon washed with 50 ml and 500 ml of water were compared whereas 6% and 42% were observed for 500 ml – 1000 ml and 50 ml – 1000 ml respectively, meaning, washing the fungal-treated carbon with enough water can increase the adsorption capacity of the carbon as also established in the acidic medium.

An adsorption percentage of 72.8% was recorded for the as-received activated carbon and this is relatively low as compared with as-received (conditioned). This may be associated with the fact that the as-received carbon was not conditioned, and hence may have dust particles and residual micro-organisms settling on the carbon surface and blocking the active sites of the activated carbon. This suggests even as-received activated carbon should be washed before introduced into CIL for gold adsorption.

In general cases (both pH 4.0 and pH 10.5), sufficient water washing improved on the recovery of aurocyanide from solution onto the activated carbon.

4 Conclusions and Recommendations

The main objective of this research was to assess the effect of sufficient water washing on aurocyanide adsorption by activated carbon in CIL following fungal pretreatment of carbonaceous ores. In relation to this, activated carbon treated for

2, 4, 8, 12 were washed with 200 ml of water, whereas those treated for 24 hrs were contacted with various volumes of water ranging from 50 ml to 1000 ml. In assessing the effect of activated carbon contact time with cell-free extract, overall decrease in the carbon's activity from time 0 to 24 hrs was a whopping 13% recorded at pH 4.0 and 9% at pH 10.5. In relation to this, it can be deduced that, the presence of the fungal biomass in the CIL circuit has deactivating effect on activated carbon, and this increases with increasing fungal-treatment time. The effect of *P. chrysosporium* appeared to be more pronounced in acidic medium than basic medium since the fungi is more active in lower pH range.

After washing the carbons with various volumes of water, the percentage adsorption gradually increased from 62% to 91% for the acidic medium and 64% to 93% for the basic medium. This represents about 29% increase in both cases. It was therefore concluded that, sufficient water washing decreases the effect of entrained biomass on the adsorption capacity of activated carbon. Further research is being done using real carbonaceous materials treated with *P. chrysosporium*, and assessing the impact of entrained biomass on activated carbon adsorption. In the meantime, it is recommended that pretreated materials should be washed with sufficient water before CIL operations.

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