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Fungal degradation of elemental carbon in Carbonaceous gold ore

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ABSTRACT

Phanerochaete chrysosporium was used to decompose elemental carbon in Carbonaceous gold ore and enhance cyanide recovery of gold. The degradation of elemental carbon amounted to 34% due to fungal treatment for 14 days. A positive correlation between the fungal degradation of elemental carbon and the activity of degradation enzymes was noted. Organic acids and nitrogenous bases, which are generated by the fungi, caused the degradation of elemental carbon indirectly. *P. chrysosporium* caused a surface exfoliation of elemental carbon in the form of layers and the destruction of the microcrystalline and pore structure. The amount of oxygen-containing groups and of aliphatic groups was increased. The amount of aromatic rings, the specific surface area, the pore volume and the condensation index of aromatic rings were decreased. Also the thermal properties of elemental carbon changed significantly, whereas the amount of the low-stability compounds was increased. *P. chrysosporium* can reduce the interference of elemental carbon with the cyanide recovery of gold. The amount of gold recovery increased from 44% to 62%. This improvement is ascribed to the combined effect of degradation and passivation of elemental carbon by *P. chrysosporium*.

1. Introduction

Carbonaceous gold ore is a kind of refractory gold ore resources. Its processing has complicated by "preg-robbing" and the inhibition of the dissolution of gold by carbonaceous matter (Rees and Van Deventer, 2000; Tan et al., 2005). Biooxidation is considered as an economic processing technique for Carbonaceous gold ore. There are many advantages associated with biooxidation, such as mild conditions, low energy consumption and selective oxidation. Consequently, many studies have been performed to decompose and passivate carbonaceous matter by microorganisms. As an example, a heterotrophic bacterial flora, which is comprised of *Pseudomonas maltophilia*, *Pseudomonas oryzihabitans*, *Achromobacter* sp. and *Arthrobacter* sp., can passivate carbonaceous matter, and thus, increase the gold recovery (Brierley and Kulpa, 1992). However, the addition of required hydrocarbons for bacterial growth could result in problems with the solid–liquid separation and interfere with gold recovery. Additionally, some leaching bacteria, such as *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans*, were used to oxidize sulfides and deactivate carbonaceous matter (Wang et al., 2000; Yang et al., 2003). At present, a consensus has not been derived about the effect of these leaching bacteria on carbonaceous matter. Some reports state that these bacteria cannot oxidize and destroy carbonaceous matter (Amankwah et al., 2005; Pyke et al., 1999; Yen et al., 2009). Furthermore, the acidic environment, needed for the growth of these bacteria, could activate carbonaceous matter (Amankwah et al., 2005; Pyke et al., 1999). A further study using fungi suggested that *Trametes versicolor* causes a passivation of carbonaceous matter (Yen et al., 2009), and *Streptomyces setonii* can even destroy it (Amankwah et al., 2005).

Carbonaceous matter is mainly composed of elemental carbon, organic carbon and hydrocarbons. Among these constituents, elemental carbon, as the "preg-robbing" component, has been discovered in almost all Carbonaceous gold ore. Elemental carbon is a mixture of crystalline graphite and amorphous activated carbon, and its capacity to adsorb gold is similar to activated carbon (Tan et al., 2005; Stenebraten et al., 1999; Ofori-Sarpong et al., 2013a). Humic acids are the important components of organic carbon, which can "rob gold" by adsorption and/or chelation through their functional groups (Katsumata et al., 2008; Uyguner and Bekbolet, 2005). Hydrocarbons are not involved in the "preg-robbing". However, they can coat the surface of other carbonaceous matter and even reduce their "preg-robbing" potential (Schmitz et al., 2001). Carbonaceous matter cannot be easily separated from the gold ore because of its low amount (1.0%–3.6%), fineness (0.002 μm–2 μm), coexistence of crystal and amorphous carbon types and the interference with metallic minerals and gangue minerals (Yang et al., 2013). Consequently, lignite, sub-bituminous coal, bituminous coal, anthracite, wood chips and activated carbon were chosen as substitutes to study the ability of *S. setonii* and *Phanerochaete chrysosporium* to decompose carbonaceous matter and decrease its "preg-robbing" capacity. The results indicate that both of these microorganisms can effectively degrade the carbonaceous substitutes and reduce their "preg-robbing" capacity (Ofori-Sarpong et al., 2010; Martin and Petersen, 2001; Liu et al., 2014).

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P. chrysosporium, as the model strain of white-rot fungi, is a filamentous fungus belonging to the Basidiomycetes. *P. chrysosporium* has many advantages for use in biotechnology, such as an extracellular lignin degradation system, constituous enzyme production, diversity of substrates and the inhibition to other microorganisms. The degradation of recalcitrant compounds by *P. chrysosporium* requires the participation of cytochrome P450, besides extracellular enzymes like laccase (Lac), lignin peroxidase (LiP) or manganese peroxidase (MnP) (Sato et al., 2007; Teramoto et al., 2004). *P. chrysosporium* cannot only degrade and passivate carbonaceous materials, but also decompose metallic sulfide minerals through surface modification and catalytic oxidation. This allows a synchronized treatment of carbonaceous matter and sulfides in refractory gold ores (Ofori-Sarpong et al., 2013b; Yang et al., 2006; Liu et al., 2013). Nevertheless, most of the previous studies have focused on tests with carbonaceous substitutes. The fungal treatment of carbonaceous matter associated with Carbonaceous gold ore has been studied insufficiently. Therefore, in this study elemental carbon was chosen to investigate the capacity of *P. chrysosporium* for degradation of carbonaceous matter as a possibility for optimization of cyanide recovery of gold.

2. Materials and methods

2.1. Materials

The elemental carbon used in this study was extracted from a Carbonaceous gold ore in Shaanxi, China. The extraction was performed by an improved demineralization-density separation technique (Stenebraten et al., 1999; Tafuri, 1987). Firstly, the gangue minerals were removed through treatment by heated hydrochloric acid and hydrofluoric acid. Then, the metallic sulfide minerals and carbonaceous matter were separated by heavy liquid flotation. The heavy liquid was zinc chloride with the relative density of 2.5 g/L. The partial chemical analysis of the extracted elemental carbon is shown in Table 1. Its purity reached 85%. The pre-oxidized gold concentrate used for cyanide recovery was provided by the Jinchuan Group Company Limited, Gansu, China. As shown in Table 2, the total carbon content of the pre-oxidized gold concentrate is 2.3%, including 2.2% carbonate and 0.005% elemental carbon. Organic carbon was not detectable. This indicates that an interfering effect of carbonaceous matter in the pre-oxidized gold concentrate can be excluded. The particle size of elemental carbon and the pre-oxidized gold concentrate amounted to 72% of less than 75 μm and 86% of less than 38 μm, respectively.

P. chrysosporium (CCTCC M 2013616) was purchased from the China Center for Type Culture Collection. A nitrogen-limited culture medium was selected, since an excessive nitrogen supply can inhibit the formation of the ligninolytic enzyme system of *P. chrysosporium* (Sato et al., 2007; Tien and Kirk, 1988). The nitrogen limited liquid medium contains glucose 10 g/L, KH_2PO_4 0.2 g/L, $MgSO_4$•$7H_2O$ 1.0 g/L, ammonium tartrate 0.37 g/L, $CaCl_2$ 0.02 g/L, thiamin-HCl 1 mg/L and trace element solution 70 mL/L. The trace element solution is composed of glycine 0.586 g/L, NaCl 1.0 g/L, $CoSO_4$ 0.1 g/L, $CuSO_4$•$5H_2O$ 0.01 g/L, Na_2MoO_4 0.01 g/L, H_3BO_3 0.01 g/L, $KAl(SO_4)_2$•$12H_2O$ 0.01 g/L, $ZnSO_4$•$7H_2O$ 0.1 g/L, $CaCl_2$ 0.082 g/L, $FeSO_4$•$7H_2O$, 0.1 g/L, $MgSO_4$•$7H_2O$ 3.0 g/L and $MnSO_4$•$7H_2O$, 0.5 g/L.

2.2. Biodegradation of elemental carbon

Firstly, 200 mL medium and 10 g elemental carbon were mixed and autoclaved at 121 °C for 20 min. After cooling, 0.5 mL spore suspension of *P. chrysosporium* was inoculated into the medium with a content of 1×10^5 spores per mL and incubated at 150 rpm with a constant temperature of 30 °C. The initial pH of the pulp solution was controlled at 5. Each test was carried out in triplicate. The samples were filtered after treatment for 14 days. A lot of precipitates was produced, when the brown filtrate was adjusted to above pH 12. The fungal degradation residue and the water-soluble alkaline precipitate were washed with deionized water and treated by ultrasound to remove the remaining medium and the fungal biomass. Afterwards, they were filtered, dried and weighed to calculate the amount of degradation.

2.3. Assay for enzyme activity

During the fungal degradation of elemental carbon, the activities of LiP, MnP, Lac and cytochrome P450 were measured to evaluate their importance. LiP activity was measured using the change of absorbance of a reaction liquid for 2 min at 310 nm (Tien and Kirk, 1988). The activity of MnP was evaluated by the change of absorbance of a reaction liquid for 2 min at 240 nm (Paszczynski et al., 1988). Lac activity was determined by the guaiacol method (Aytar et al., 2011). Reduced (versus oxidized) P450-CO difference spectra were used to measure cytochrome P450 activity (Schenkman and Jansson, 1998).

2.4. Influence of elemental carbon on the cyanide recovery of gold before and after treatment with P. chrysosporium

Elemental carbon, fungal degradation residue and water-soluble alkaline precipitate with a content of 0.2% were added to the pre-oxidized gold concentrate to test the cyanidation efficiency. Cyanidation experiments were carried out for 24 h with a sodium cyanide concentration of 0.15%, a stirring speed of 1050 rpm and a pulp density of 20%. Control experiments were run under the same conditions, but without carbonaceous matter. The effect of *P. chrysosporium* treatment on the cyanide recovery of gold was evaluated by comparing the gold recovery amount.

2.5. Analytical methods

The chemical analysis of samples was carried out with an element analyzer (Vario EL cube, Elementar Analysensysteme GmbH, Germany). The pH of the fungal degradation system was measured with a pH meter (Lei-ci pHS-2F, Shanghai INESA Scientific Instrument Co., Ltd., China). The concentration of organic acids was determined using High Performance Liquid Chromatography (Agilent 1100, Agilent Technologies Corporation, USA). The phase analyses and the infrared analyses were performed using an X-ray diffractometer (D/MAX-RB, Panalytical Corporation, Holland) and a Fourier transform infrared spectrometer (VECTOR-22, Bruker, Germany), respectively. The morphology of samples was observed by a Scanning electron microscope (SSX-550, Shimadzu, Japan). An automatic physical adsorption analyzer (AUTOSORB-1, Quantachrome, USA) was employed to measure the specific surface area and pore volume. The concentration of gold in cyanide solution was determined by ICP-OES (PE Optima 8300, PerkinElmer, USA). All photometric measurements were performed on a Double-beam UV–Vis Spectrophotometer (Persee TU-190, Beijing Purkinje, China). The pyrolysis of samples was carried out in a Thermal Analyzer (METTLER TOLEDO DSC 1, Mettler-Toledo Group, Switzerland).

Table 1
Partial chemical analysis of elemental carbon (mean ± sd, wt.%).

C	Fe	Si	S	As	Ca	Al	H	N	O
85.34 ± 0.85	0.34 ± 0.04	2.78 ± 0.27	0.76 ± 0.06	0.12 ± 0.01	0.23 ± 0.02	1.06 ± 0.13	2.89 ± 0.35	0.28 ± 0.03	0.12 ± 0.02