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Recovery of manganese from low-grade pyrolusite ore by reductively acid leaching process using lignin as a low cost reductant

Shaofeng Xiong[a,1,*], Xie Li[a], Pingle Liu[a,1,**], Shihua Hao[a], Fang Hao[a], Zhoulan Yin[b], Jiaxin Liu[a]

[a] College of Chemical Engineering, Xiangtan University, Xiangtan, Hunan 411105, China
[b] School of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, China

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ABSTRACT

Recovery of manganese from low-grade pyrolusite was investigated by reductive leaching method using lignin as a reductant in the sulfuric acid medium. Lignin is a very abundant biopolymer available from the pulping wastewater in the pulp and textile industry. Effects of lignin amount, temperature, H_2SO_4 concentration and the leaching time on the leaching efficiency of Mn and main impurities (Fe, Al) were examined. The leaching temperature and H_2SO_4 concentration have a major effect on the extraction of Mn, Fe and Al. The maximum leaching efficiency of manganese can reach above 91% under the optimal experimental conditions. The experimental results demonstrated that lignin is a low cost, renewable and environmentally benign reductant for leaching low-grade manganese ore. The kinetic analysis further indicated that the behavior of reductively acid leaching Mn from pyrolusite in sulfuric acid solution follows Avrami equation well. The degradation mechanism of reductively acid leaching pyrolusite by lignin was also investigated by the gas chromatography-mass spectrometry, focusing on the cleavage of dimers into monolignols.

1. Introduction

Manganese has wide application in many fields such as steel production, preparation of dietary additives, non-ferrous alloys, fertilizers and carbon–zinc batteries. High grade manganese ores ($> 40\%$) are conventionally processed into manganese metal and its alloys by the pyro-metallurgical processes. With the rapid growing demand for manganese metal and the upcoming exhaustion of the high-grade manganese ore sources, the scientists and enterprises shift attention to the low-grade manganese ores ($< 40\%$) as well as manganese ocean nodules and secondary manganese sources. However, as Zhang and Cheng (2007) have implied, low-grade manganese ores has little commercial value and cannot be economically processed by the conventional pyro-metallurgical process or pyro-pretreatment. The reductively acid leaching process emerged in the past two decades aroused a strong research interest as a cost-effective alternative method and the corresponding principle is that the reductants are capable of converting insoluble MnO_2 of manganese ores into soluble MnO and further $MnSO_4$ in the acid solution without pre-calcination of manganese ores. Therefore, the reductive acid leaching method possesses the advantages of energy conservation and one-step leaching process (Cheng et al., 2009).

Many efforts have been devoted to developing reductants with high leaching efficiency and low price. The inorganic reductants were firstly used, such as $FeSO_4$ (Das et al., 1982), charcoal (Das et al., 1989), pyrite (Parida et al., 1990), SO_2 (Petrie et al., 1995) and H_2O_2 (Nayl et al. 2011). The usage of some inorganic reductants is beneficial to obtain high leaching efficiency but adverse to lessen the leaching cost due to their relatively high price. Some inorganic reductants are even harmful to the environment. For example, SO_2 is toxic and the control of solution acidity appears difficult (Zhang and Cheng, 2007).

As a promising alternative reductant for leaching low-grade ore, the renewable carbohydrate is regarded as environmentally friendly and effective. It includes sawdust (Sanigok, 1988; Ekmekyapar, 2012), sucrose (Veglio, 1994), lactose (Ali, 2002; Ismail, 2004) and cane molasses (Su, 2008), etc. However, there is also a concern over the limited annual output of foregoing renewable carbohydrates, such as sawdust, which is difficult to meet the need of mass production. Meng and Zhang (2013) further indicated that some cane molasses contained chloride ion, causing serious corrosion damage to the anode plate in the subsequent electrolytic section.

Lignin is the most abundant aromatic compound on earth and can

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* Corresponding author at: Chemical Engineering & Chemistry Building, No. C205, College of Chemical Engineering, Xiangtan University, Xiangtan, Hunan 411105, China.
** Corresponding author at: Chemical Engineering & Chemistry Building, No. A213, College of Chemical Engineering, Xiangtan University, Xiangtan, Hunan 411105, China.
E-mail addresses: shfxiong@163.com (S. Xiong), liupingle@xtu.edu.cn (P. Liu).

[1] Both corresponding authors contribute equally to this paper.

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be used as a source of carbohydrate. Lignin is a class of complex organic polymers composed of three common monolignols, i.e., guaiacyl units (G), syringyl units (S) and p-hydroxy phenyl units (H) (Jex et al., 2014). It accounts for ab. 50% of the pulping wastewater known as "black liquor" in the pulp and textile industry. 80–90% of the overall pollution load of the paper industry in China are caused by the black liquor (Ren, 1998). Therefore, the utilization of lignin as the leaching reductant is beneficial to slash the leaching cost and lessen water pollution. In addition, the lignin annual output is capable of meeting the demand for mass leaching production.

Lignin used in the form of purified solid or industrial wastewater after is feasible. After all, several methods including precipitation (Minu et al., 2012) and ultrafiltration (Wallberg et al., 2003) can be applied to recycle lignin from black liquor. In this work, lignin recycled from black liquor was employed as the leaching reductant with a view to facilitating the leaching kinetic study. The emphasis in present work is focused on optimizing the leaching experimental conditions and investigating the degradation mechanism by infra-red spectrum (IR) and gas chromatography mass spectrometry (GC–MS).

2. Materials and methods

2.1. Materials

Pyrolusite used in the present work was obtained from Hunan, China. The ore was crushed, ground and screened to obtain a material with particles of 100% < 100 μm size. The ore sample was first characterized by X-Ray fluorescence spectrometer and further calibrated by reference to Chinese national standard (GB/T 1506-2002) for its major and minor elements. According to the analysis results, the ore sample used in the experiment mainly contains 25.10 wt% Mn, 16.11 wt% Fe and 2.67 wt% Si, which indicates the pyrolusite is low grade.

The ore samples before and after leaching were also characterized by powder X-ray diffraction (XRD, Rigaku model D/max-2500) to define the mineralogical structure and its corresponding variation caused by leaching. From the XRD pattern shown in Fig. 1, the main components of the low-grade pyrolusite include pyrolusite (MnO_2), quartz (SiO_2) and aluminum silicate, whereas the peaks originating from pyrolusite disappear after leaching.

Solid lignin precipitated from wastewater was herein introduced into the acid leaching solution for the convenience of measuring the addition. It was then dried in a cabinet oven with air circulation at 60 °C for 16 h before use. All chemicals were of analytical grade and used without further purification.

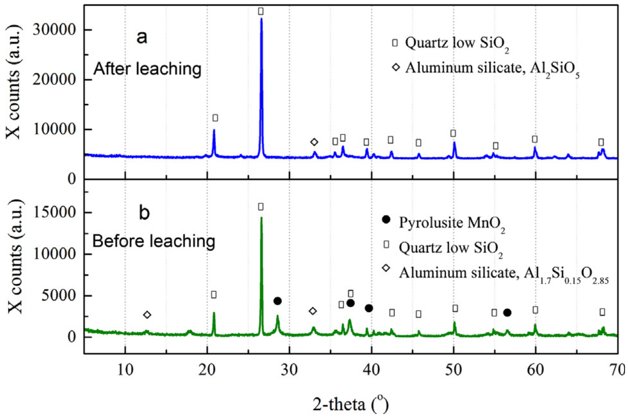

Fig. 1. XRD of manganese ore (a) before and (b) after acid leaching.

2.2. Methods

2.2.1. General leaching procedure

Leaching experiments were carried out in a 250 ml three-neck flask immersed in a thermostatically controlled water bath. In a typical experiment, the liquid-to-solid (L/S) ratio was fixed as 5:1 (mL/g). 20 g of pyrolusite sample was first added to 100 ml sulfuric acid solution under stirring at 30–80 °C for a certain period. Lignin of required amount was then added to the solution as the beginning of leaching that would keep over 180 min. The slurries sampled at various times (0–120 min) were further filtered for analysis of Mn, Fe and Al concentration, while the residues were washed with distilled water and dried for further infrared spectra (IR) analysis.

2.2.2. Analysis methods

Mn, Fe and Al concentration in the slurry was measured by an inductively coupled plasma spectrophotometer (ICP, PS-6, Baird). The leaching efficiency was calculated by referring the amount of leached metal in the solution to its original input quantity in the ore sample.

To identify the reduction products of MnO_2 contained in the pyrolusite, the single-sweep polarography was employed to detect the existence of Mn(2+), Mn(3+) or their complexes in the leaching solution. The single-sweep polarography is capable of determining various valent ions simultaneously by the identification of different redox peaks in the polarogram. The single-sweep polarogram can be obtained by the following procedure: (1) Preparation of the supporting electrolyte: typically, 0.05 ml of the leaching solution at 30 min was sampled and then diluted to 10 ml with the deionized water (DI water). The pH of the resulting sample solution was adjusted to 7 by dropwise addition of the diluted NaOH solution. The supporting electrolyte was then obtained by adding 1 ml of 20 vol.% ethanediamine, which was denoted as "s1-no". For comparison, another supporting electrolyte containing Mn(2+) was prepared by the same procedure except that 0.15 ml of $MnSO_4$ solution was mixed with the leaching solution in the first step. This Mn(2+)-contained supporting electrolyte was denoted as "s2-Mn". All chemicals used were reagent grade without further purification and the DI water was used throughout. (2) The procedure of the single-sweep polarography: A JP-303 polarographic analyzer (Chengdu Instrument Factory, China) was used for the electrochemical experiments. The setting for this analyzer mainly included 400 mV/s of the sweep rate and 5 s of the delay time. The single-sweep polarogram from − 800 mV was recorded and the current peak height was measured.

The degradation mechanism of lignin was investigated using the GC–MS analysis method. 50 ml of the leaching liquor was extracted with 20 ml chloroform to prepare sample solution for GC–MS analysis. GCMS-QP2010 Plus GC–MS system with a quadrupole mass spectrometer and a capillary gas-chromatograph (Varian 3700) were used. The fused silica capillary column (30 m × 0.25 mm i.d.) was coated with SE 30 (0.25 μm). Helium was used as carrier gas (0.7 bars) at a flow rate of 1.3 ml/min. The splitter/injector was kept at 300 °C with a split ratio of 5:1. The column temperature was programmed as follows: 50 °C (2 min)–8 °C/min–280 °C (5 min). The ion source temperature was 200 °C, the emission current was 0.6 to 0.7 mA. The chromatograms were recorded by ion monitoring in the m/e range of 50–500.

3. Results and discussion

3.1. Qualitative analysis of the reduction products of MnO_2

Mn(2+), Mn(3+) and their complexes are the possible reduction products of MnO_2 when lignin is employed as the reductant. To confirm the ability of lignin to reduce the pyrolusite, both the E_H-pH diagram and the single-sweep polarogram were used to detect the existence of Mn(2+), Mn(3+) and their complexes in the leaching solution. The E_H-pH diagram is capable of analyzing the thermodynamic stability of these Mn ions, which can be graphed by applying the HSC 6 software