Ultrasonics Sonochemistry 19 (2012) 38–42

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultsonch

Iron removal from kaolin using thiourea assisted by ultrasonic wave

Guang-hua Xia [a,b,*], Mang Lu [a], Xiao-li Su [a], Xiao-dong Zhao [a]

[a] School of Materials Science and Engineering, Jingdezhen Ceramic Institute, Jingdezhen 333001, Jiangxi Province, China
[b] Jiangxi Provincial Key Laboratory for Advanced Ceramic Material, Jingdezhen Ceramic Institute, Jingdezhen 333001, Jiangxi Province, China

ARTICLE INFO

Article history:
Received 4 April 2011
Received in revised form 15 May 2011
Accepted 15 May 2011
Available online 19 May 2011

Keywords:
Bleaching
Kaolinite
Whiteness
Ultrasound

ABSTRACT

In the present study a bleaching process of a kaolinite was carried out using thiourea as the leachant agent in the iron removal process, in the absence and presence of ultrasound. The effect of thiourea was investigated together with other factors, such as thiourea concentration, temperature, treatment time, and ultrasonic parameters. The optimum conditions for the maximum whiteness of 89% with ultrasound were determined as follows: reaction temperature, 20 °C; ultrasound frequency, 80 kHz; ultrasound power, 500 W; thiourea concentration, 0.4 wt.%; pH, 3.0; reaction time, 20 min. The assistance of ultrasound led to a remarkable acceleration for the iron leaching process, and dramatic reduction in the concentration of leach reagent, irradiation time, and reaction temperature, when compared with the conventional bleaching method using thiourea in the absence of ultrasound.

1. Introduction

Kaolin is a fine, white clay, whose principal mineral is kaolinite [$Al_2Si_2O_5(OH)_4$]. Due to its properties, it is widely used in many industrial fields such as paper filling and coating, refractories and ceramic, fiberglass, cement, rubber and plastic, and paint [1].

The whiteness is one of the most important factors in determining the application and economic value of kaolinite. In general, the most deleterious impurities for whiteness of kaolin are iron oxide and titanium oxide minerals. Iron oxide is present mainly as the following minerals: goethite, hematite, magnetite, pyrite and ilmenite [2]. These impurities can be reduced by physical separation, e.g. flotation or magnetic separation, or by chemical leaching processes using chemicals such as Na_2SO_3, $C1_2$, HCl, and dithionite, etc. However, the removal efficiency of iron is low, and extraction yields of 60–70% can be obtained using the above mentioned processes [3]. Recently, the bioleaching processes have drawn research interesting using heterotrophic bacteria and fungi [4–6], but there are still some unresolved problems concerning its industrial application.

Hydrosulfites, such as sodium hydrosulfite and zinc hydrosulfite, have been used in industry as the reductive bleaching agent for brightening kaolin clay. However, the use of hydrosulfites for bleaching kaolin must be performed under acidic conditions, which has relatively high operating costs and environmental impacts. Moreover, hydrosulfites are chemically unstable, leading to decrease in the processing efficiency.

Thiourea (NH_2CSNH_2) is a strong reducing agent and has good chemical stability. Thiourea is widely used in photography as a fixing agent and to remove stains from negatives, and in wet purification of precious metals such as Au and Ag. Thiourea is seldom applied to iron removal from kaolin. Veglio' used thiourea as the leachant agent in the iron removal process from kaolin, and the largest iron extraction yield (94%) was obtained [7]. The chemical reactions can be summarized as follows:

$$Fe_2O_3 + 3H^+ \rightarrow 2Fe^{3+} + 3H_2O \quad (1)$$

$$Fe^{3+} + Tu \rightarrow Fe^{2+} + 1/2FDS + H^+. \quad (2)$$

where: $Tu = NH_2CSNH_2$ $FDS = NH_2CSSC(NH)NH_2$

However, this bleaching process must be conducted at 90 °C for 150 min, resulting in great limitations in the practical application of thiourea for kaolin bleaching. Therefore, there is an urgent need for full activation of thiourea at normal temperatures.

Ultrasonic energy can enhance reaction rates or induce chemical reactions because of the formation of highly reactive radical species formed during cavitation [8]. As an auxiliary energy, ultrasound has been successfully applied in the mining industry as an assistant means to clean mineral surfaces of oxidation products and fine coatings [9]. Some researchers have found that the iron oxide impurity on the surface of silica sand can be removed more efficiently by ultrasound than by mechanical scrubbing [10,11]. In addition, the iron elimination rate can be enhanced when the ultrasound technology is combined with chemicals (such as water glass, soda, sodium pyrophosphate, and oxalic acid) in solution due to their synergistic action [9–12]. This study reports the use of

* Corresponding author at: School of Materials Science and Engineering, Jingdezhen Ceramic Institute, Jingdezhen 333001, Jiangxi Province, China. Tel./fax: +86 798 8499678.
E-mail address: xiagh6565@163.com (G.-h. Xia).

1350-4177/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ultsonch.2011.05.008

ultrasound-assisted thiourea leaching for iron elimination from kaolinite and its comparison with the thiourea leaching process without ultrasound assistance. Optimization of different operating parameters has also been investigated.

2. Material and methods

2.1. Materials and reagents

The kaolinite comes from Beihai Kaolin Co., Ltd., of Yan Mine, located in the south of Guangxi Province, China. The kaolinite has a firing whiteness of 83%. The complete chemical analysis of the ore is reported in Table 1. The minerals under study were sieved at 100 mesh. All chemicals used were of guaranteed-reagents grade (Shanghai Jiuyi Chemical Reagent Co., Ltd., China) and deionized water was used throughout the experiment.

2.2. Leaching tests

A 42 wt.% kaolin slurry was prepared in a stirring reactor. The dispersion was facilitated by 0.1% (w/w) anhydrous sodium carbonate and sodium hexametaphosphate, respectively. The slurry was stirred for 1 h at room temperature, and then the pH of slurry was adjusted to three using dilute sulfuric acid.

For the first part of the experiment, the leaching process was conducted without ultrasound assistance at 20 °C (room temperature) and 90 °C, respectively. For each run, 500 mL volume of the mineral slurry was poured into a 1-L beaker in a constant temperature magnetic stirrer (CJJ-931, Beijing Kewei, China). Water bath was used to control the solution temperature. The beaker was covered to prevent losses by evaporation. The bleaching reaction was initiated by the addition of a certain amount of thiourea powder. After the appropriate time interval, aluminum sulfate, with an amount of 0.3% based on the weight of slurry, was introduced into the reaction suspension, continuously stirred for 20 min. Afterwards, the pH was adjusted to 5, and then 0.2% ethylene diamino tetraacetic acid (based on the weight of slurry) was added to the slurry. After 10 min, the reaction mixture was allowed to stand for 1.5 h. An amount of sample of the reaction mixture was taken out at the pre-determined time intervals, filtered immediately, rinsed three times with deionized water. The sample was dried at 110 °C, pressed into slices, and then calcined at 1200 °C in air for 2 h.

The second part of the experiment was performed under ultrasound assistance at 20 °C, using a digital ultrasonic cleaner (KQ-400DB, Kunshan, China). The contents of the beaker were simultaneously stirred and sonicated at a certain frequency and power for a specified duration. The ultrasonic power dissipated into the beaker was adjusted and determined by calorimetric measurement [13] in order to ensure comparative ultrasonic conditions. All the other experimental processes and parameters were designed identically with those in the first part. All the experiments were carried out in triplicate, and the mean values were reported.

2.3. Analysis and characterization

The morphologies of the kaolin clay and the leached solid samples were observed using field emission scanning electron microscopy (SEM, Hitachi, JSM-6700F). Iron leached from the kaolin was determined using the 1,10-phenanthroline colorimetric method [14]. The X-ray diffraction (XRD) patterns of samples were recorded with a Bruker D8 advance diffractometer (Bruker, Germany) with Cu Ka radiation. The measurement conditions of XRD are: 50 kV, 40–50 mA. To compare color changes in the kaolin samples before and after leaching, the whiteness index of the samples was measured using a colorimeter (WSB-IIIA, Beijing, China).

Table 1
Chemical composition of the dry kaolin clay.

Element	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	K_2O	CaO	LOI[a]
Content (wt.%)	34.28	52.36	0.85	0.11	1.55	0.1	10.75

[a] Ignition loss (1050 °C) and other trace components.

3. Results and discussion

3.1. Effect of temperature and thiourea dosage

The influences of temperature and thiourea dosage on the iron removal were studied for temperatures of 20 and 90 °C in solutions containing thiourea, in the absence of ultrasound. Fig. 1 shows the result of kaolin bleaching at 20 °C with the dosage range of 0.3–1.2% of thiourea dosage. It can be observed that both the dose of thiourea and reaction time had significant effects on bleaching efficacy. The whiteness had a progressive increase with time at the initial phase within 50 min, and then was approaching a stable level. The possible reason for these two distinct rates is explained as follows: in the initial phase of the leaching, iron hydroxyl-oxides which were possibly on the surface of the kaolin clay had been leaching out, and then, during the second phase of the leaching, iron oxides which were possibly on the surface of kaolin clay reacted with thiourea slowly. In other words, it is easier to dissolve hydroxyl-oxides such as goethite where dissolution can take place via both reduction (solid and aqueous species) and complexation, whereas oxides such as hematite dissolve mainly via solid reduction [12].

According to Fig. 1, the leaching rate increased with increasing concentration of thiourea until 0.9%, but only slightly increased with further increase in thiourea concentration, in the absence of ultrasound. This behavior may be attributed to the formation of thiourea precipitation when the thiourea concentration was over 0.9%. The precipitation of thiourea can form a product layer around the mineral coatings, which decreases the leaching rate. When the thiourea concentration was 0.9%, the Fe_2O_3 content of kaolin sample was reduced to 0.72%, and the whiteness was increased to 87%.

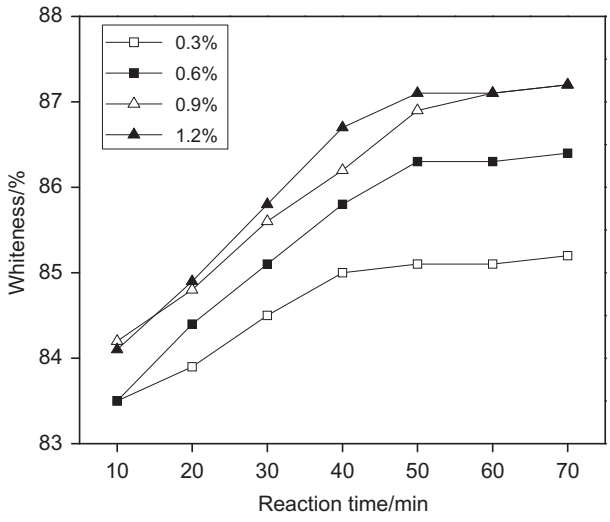

Fig. 1. Effect of thiourea concentration (wt.%) on whiteness increase in the absence of ultrasound. The experiments were conducted at 20 °C in the absence of ultrasound.