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Research paper

Refinement of industrial kaolin by removal of iron-bearing impurities using thiourea dioxide under mechanical activation

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ABSTRACT

This study reports a series of experiments conducted to evaluate the suitability of thiourea dioxide (TD) under mechanical activation, in bleaching iron-bearing impurities from raw kaolin. The optimum conditions for the maximum whiteness of 76.32% were determined as follows: rotation speed of ball mill, 400 rpm; activation time, 1.5 h; TD dosage, 0.8% of kaolin mass; solid-to-liquid ratio, 1:2; pH, 8.0; room temperature. The effect of grinding causes the partial surface amorphization of kaolin particles and a decrease in the dehydroxylation temperature. The assistance of grinding leads to a higher iron removal when compared with the conventional bleaching method using sodium hydrosulfite.

1. Introduction

As an important industrial additive, kaolin is widely used in many industrial fields such as paper filling and coating, refractories and ceramic, fiberglass, cement, rubber and plastic, and paint (Murray 2002). The whiteness is one of the most important factors in determining the application and economic value of kaolin. Iron oxide is the most deleterious impurity for whiteness in kaolin. Thereupon, numerous investigations have focused on increasing the whiteness of kaolin to promote its commercial value (Taran and Aghaie 2015).

Iron oxide in kaolin can be removed by physical separation, e.g. flotation or magnetic separation, or by chemical leaching processes using chemicals such as Na_2SO_3, Cl_2, HCl, and dithionite, etc. However, the whitening efficiency of these traditional methods is usually low due to the complex form of iron (Cao et al. 2016). The reductive leaching of iron from kaolin with sodium hydrosulfite ($Na_2S_2O_4$) is efficient and is currently applied by the kaolin industry (Thurlow 2001). However, the utilization of hydrosulfites for bleaching kaolin must be performed under strong acidic conditions (pH < 3), leading to high operating costs and negative environmental impacts. Moreover, hydrosulfites require specific storage and transport arrangements due to the chemical instability.

Thiourea dioxide (TD, $(NH_2)_2CSO_2$) is a strong reductant, which has been widely used in leather processing industry, textile printing, paper, wool bleaching and so on for a long time (Xing et al. 2015). Compared to other reductants, TD has several advantages such as strong reducing capacity, environmental friendliness, lower decomposition rate, safe and cheap on bulk scale. The theoretical potential of TD is −1200 mV. Insoluble Fe^{3+} in kaolin can be reduced to soluble Fe^{2+} by TD. Subsequently, the whiteness of kaolin can be increased after filtering and washing processes. However, TD is very stable at room temperature and neutral pH conditions (Makarov et al. 2014). The strong reducing capacity of TD can only be obtained under strong alkaline (pH > 10) or heating (T > 70 °C) conditions (Cao et al. 2016), leading to higher operation costs and operating difficulty. Thereupon, there is an urgent need to develop an approach for activating TD under standard conditions.

Mechanical activation is an effective method to enhance the contact and interaction of the reactants by decreasing their particle size and increasing their homogeneity by the milling process (Ashrafi et al. 2015). Therefore, the aim of the present study is to investigate the feasibility of improving kaolin whiteness by chemical leaching using mechanically activated TD. Optimization of different operating parameters was also conducted.

2. Material and methods

2.1. Materials

The kaolin used in this study was obtained from Kuangshan Kaolin Factory, Xingzi, Jiangxi province, China. The kaolinite has an initial whiteness of 68.02%. The complete chemical analysis of the kaolin is listed in Table 1. All chemicals (NaOH, HCl, TD, $Al_2(SO_4)_3$, $Al_2(SO_4)_3$) used were of guaranteed-reagents grade and deionized water was used throughout the experiments.

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Table 1
Chemical composition of the dry kaolin clay.

Composition	Al_2O_3	SiO_2	Fe_2O_3	K_2O	CaO	LOI[a]
Content (wt%)	35.46	49.04	1.227	1.14	0.42	12.67

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

2.2. Experimental procedures

Kaolin slurry was prepared in a stirring reactor by mixing dry kaolin with deionized water with a mass ratio of 1:5, 1:4, 1:3 or 1:2. The slurry was stirred for 1 h at room temperature, and then the pH (7.2) of the slurry was adjusted to 8.0 using 0.1 M H_2SO_4 or 0.1 M NaOH. Single-factor experiments were conducted to investigate the effects of activation time, TD dosage, rotation speed of the ball mill, solid-to-liquid ratio and feeding mode on the bleaching efficiency of kaolin.

The leaching test was performed at room temperature. For each run, 100 mL of the slurry was poured into the ball mill. The leaching reaction was initiated by adding a certain amount of TD. After the appropriate time interval, the slurry was suction filtered. The resultant kaolin particles were rinsed three times with deionized water, and then dried at 110 °C.

2.3. Analysis and characterization

Iron content was determined using the 1,10-phenanthroline colorimetric method (Amonette and Templeton 1998). The whiteness index of kaolin was determined using a colorimeter (WSB-2A, Shanghai, China) after pressing and calcination (1220 °C, 20 min). The morphologies of samples were observed using field emission scanning electron microscopy (SEM, model JSM-6700F, Hitachi, Japan). The elements of samples were analyzed by wavelength dispersive X-ray fluorescence spectrometer (XRF, Axios advanced, PANalytical BV, Holland). The X-ray diffraction (XRD) patterns of samples were recorded with a Bruker D8 advance diffractometer (Bruker, Germany) with Cu Ka radiation. Fourier-transform infrared spectroscopy (FT-IR) (KBr pellets) were recorded on a Nicolet 5700 FT-IR spectrophotometer (ThermoElectron, Madison, WI, USA) running at 2 cm^{-1} resolution. Differential thermal analysis (DTA) was conducted using a thermogravimetric analyzer (model STA449C, NETZSCH Group, Selb, Germany) from room temperature to 800 °C at a heating rate of 10 °C min^{-1} under air.

3. Results and discussion

3.1. Effect of activation time

The variation in whiteness and iron content (as Fe_2O_3) with activation time is shown in Fig. 1. As shown, the whiteness increases quickly within the first 0.5 h, but there is no significant change of the leaching efficiency when activation time is prolonged from 1.5 to 2.5 h. The change of iron content with activation time is similar with that of whiteness since the increase of whiteness is a consequence of decrease of iron content in the kaolin sample. The possible reason for these two distinct rates is explained as follows: iron hydroxyl-oxides on the surface of kaolin are first leached out, and then, iron oxides on the surface of kaolin react with TD 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 (Lee et al. 2006, 2007). Thus, the optimum activation time is determined to be 1.5 h.

3.2. Effect of TD dosage

The influences of TD dosage on the iron removal and whiteness increase were studied with the dosage range of 0.2%–1.0%. According to Fig. 2, the leaching efficiency increases with increasing TD dosage until 0.8%, but no improvement occurs with further increase in the dosage. Therefore, 0.8% can be chosen as an optimal TD dosage for the subsequent experiments.

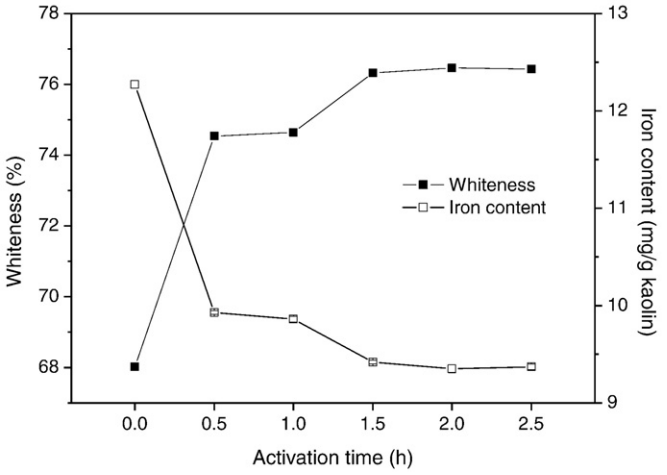

Fig. 1. Effect of activation time on the changes of iron content and whiteness of kaolin samples during leaching by TD. Experimental conditions: rotation speed = 400 rpm; TD dosage = 0.8% of kaolin mass; solid-to-liquid ratio = 1:2; pH = 8.0. Error bars represent standard deviations from four independent trials.

3.3. Effect of rotation speed

The influence of rotation speed of the ball mill on the iron removal and whiteness increase is investigated at rotation speeds of 200, 300, 400 and 500 rpm. According to Fig. 3, the leaching efficiency increases with increasing rotation speed until 400 rpm, but it is nearly independent of rotation speed from 400 to 500 rpm, which points to the fact that the reaction is incompletely controlled by film diffusion. For this reason, all subsequent experiments were carried out with a rotation speed of 400 rpm.

3.4. Effect of solid-to-liquid ratio

The influence of solid-to-liquid ratio on the iron removal and whiteness increase was performed with solid-to-liquid ratios of 1:5, 1:4, 1:3

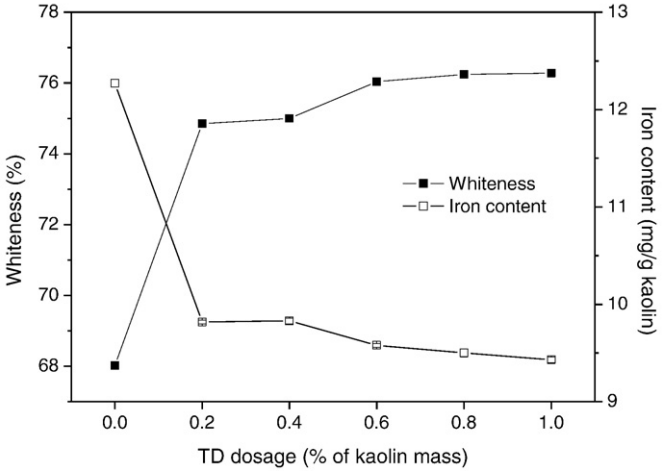

Fig. 2. Effect of TD dosage on the changes of iron content and whiteness of kaolin samples during leaching by TD. Experimental conditions: rotation speed = 400 rpm; activation time = 1.5 h; solid-to-liquid ratio = 1:2; pH = 8.0. Error bars represent standard deviations from four independent trials.