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Iron removal from kaolin using binuclear rare earth complex activated thiourea dioxide

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ABSTRACT

A binuclear rare earth complex was prepared by using Ce^{3+} and Y^{3+} as the central ion, and acetyl acetone (Hacac) as the ligand. Thiourea dioxide (TD) had strong reductive properties and good bleaching performance on kaolin after being activated by the complex. The concentrations of TD and the activator were fixed at 30 g/L and 0.6 g/L respectively, and the influences of raw material proportion, solution pH and reaction time on the activating efficiency of TD were investigated. The results show that TD reached its optimum activating efficiency after activation with the complex prepared under the conditions: the molar ratio of Ce^{3+} :Y³⁺:Hacac = 1:1:7, solution pH = 7, and reaction time = 3 h. The highest reductive potential of TD could reach up to -662 mV under the mild conditions (T = 25 °C, pH = 7.2). The influence of the dosage of activated TD on the bleaching effect of kaolin was characterized by colorimeter, XRD, SEM and EDS. The results show that the bleaching effect of kaolin reached the highest when the dosage of activated TD was 0.5 wt% (relative to the mass of kaolin). The calcined whiteness index of kaolin was raised from 82.6% to 88.7%.

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1. Introduction

Kaolin plays an important role in many industrial applications, such as ceramics, paper and rubber (Murray and Kogel, 2005; Alshameri and Rong, 2009; White et al., 2009; Qiu et al., 2014). Iron is the contaminating element in kaolin and gives an undesirable color to this type of mineral (Chandrasekhar and Ramaswamy, 2007; Zhou et al., 2014). Natural kaolin popularly contains various levels of iron impurity, which greatly affects its qualities and thus decreases its commercial value (Hart et al., 2003: Chen et al., 2004: Nkoumbou et al., 2009). Therefore, numerous investigations have focused on increasing the whiteness of the kaolin raw material to promote their commercial values (Taran and Aghaie, 2015). The methods of increasing whiteness can be classified as physical method, chemical method and bioleaching method (Xia et al., 2012). Physical method makes use of separation techniques such as flotation and high-gradient magnetic separation (Maurya and Dixit, 1990; Chandrasekhar and Ramaswamy, 2006). However, these traditional methods usually have low whitening efficiency due to the complex form of iron (Hosseini et al., 2007). Hydrosulfites have been used in industry as the reductive bleaching agent for whitening kaolin. However, this chemical bleaching must be conducted under acidic conditions (Chen et al., 2014). Recently, the bioleaching method using heterotrophic bacteria and fungi has drawn research interest, but there are still

* Corresponding author. *E-mail address:* hghuangjci@hotmail.com (H. Huang). some unsettled problems concerning its industrial application (Zegeye et al., 2013). Thus, kaolin industry urgently requires a new bleaching approach, which should contain economic, efficient and environmentally friendly features.

Thiourea dioxide (TD) is widely used in various fields because of its good and special characteristics, such as low decomposition rate, strong reductive property, safety and nontoxicity. The potential of TD can reach -1200 mV in theory. Insoluble Fe³⁺ in kaolin can be reduced to soluble Fe²⁺ by the strong reductive property of TD. The whiteness of kaolin can be increased after filtering and washing. However, this strong reductive property of TD can only be obtained under strong alkaline (pH > 10) or heating (T > 70 °C) conditions. At room temperature and under neutral conditions, TD is very stable (Fang et al., 2007; Makarov et al., 2014). The most difficult problem of the present technique is to prepare one kind of TD which has strong reductive property under mild conditions (T = 25 °C, pH = 7.2).

Rare earth elements have special electronic structure, they contain 4f electron layer, and their outermost electron configuration is 4f $^{n + 1}5d^{0-1}6s^2$. Rare earth elements often exist in trivalent ions, and their outermost electron configuration is 4fⁿ. As 5d orbital of rare earth ions has no electron, that can make them be used as the intermediate station of electron transfer, and makes the rare earth ions possess high catalytic activity (Savinkina et al., 2013; Zhan et al., 2014).

This study reported the preparation method of a binuclear rare earth complex with good activating efficiency on TD. The influences of raw material proportion, reaction solution pH and reaction time on the



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activating efficiency of TD were investigated. Furthermore, the influence of the dosage of activated TD on the bleaching effect of kaolin was also studied.

2. Experimental

2.1. Materials and reagents

The kaolin sample used in this study was provided by Yankuang Beihai Kaolin Co., Ltd. (Hepu County, Guangxi Province, PR China). The kaolin slurry was passed through a 250-mesh sieve to collect the <63 µm fraction. The final kaolin slurry had a mineral content of around 250 g/L. All chemicals used were of guaranteed-reagents grade (Shanghai Jiuyi Chemical Reagent Co., Ltd., China) and deionized water was used throughout the experiments.

2.2. Preparation of the activators

A certain amount of CeO₂ and Y₂O₃ was dissolved in concentrated hydrochloric acid (HCl, 18.4 mol/L), and then stirred for 0.5 h. After 48 h of vacuum drying at 80 °C, the solids were put into plastic bags until used. CeCl₃, YCl₃ and acetyl acetone (Hacac) were weighed according to a certain molar ratio (k), and then they were dissolved in an appropriate amount of deionized water. Under continuous stirring, acetyl acetone was added by drops to the rare earth chloride solution. The solution pH was adjusted with dilute H₂SO₄ (0.5 mol/L) or NaOH solution (1 mol/L), and stirred for a period (t). The mixture was then suction filtered after 48 h settling. The obtained powders were washed with deionized water for three times. The binuclear rare earth complex was obtained after 48 h of vacuum drying at 80 °C.

2.3. Tests and characterizations of activating efficiency

1.5 g TD was dissolved in 50 mL deionized water, and then 0.03 g activator was added. The activation reaction was performed under the mild conditions (T = 25 °C, pH = 7.2) (at this time, the concentrations of TD and activator were 30 and 0.6 g/L, respectively). Then, the potential of TD was detected with the instrument (converted by a type 990 pH/conductivity meter, Beijing, China) every 10 min in 1 h.

2.4. Tests and characterizations of bleaching effect

Quantitative activated TD was added into kaolin slurry, stirred for 20 min, and then suction filtered. The resulting kaolin particles were



Fig. 1. The influence of raw material proportion of the activators on the activating efficiency of TD (pH = 7, t = 2 h).



Fig. 2. The influence of reaction solution pH of the activators on the activating efficiency of TD (k = 1:1:7, t = 2 h).

washed with deionized water for three times, and then dried for 48 h at 80 °C. Then the kaolin was granulated, pressed into slices, and calcined at 1220 °C for 20 min.

To compare color changes in the kaolin samples before and after bleaching, the calcined whiteness index (R_{457}) of the samples were measured by colorimeter (WSB-2A, Shanghai, China). The X-ray diffraction (XRD) patterns were recorded with a Germany Bruker D8 advance powder X-ray diffractometer with Cu K_{\alpha} radiation. The chemical compositions were analyzed by X-ray fluorescent spectrometer (Axios Advanced, Panalytical, the Netherlands). The micro-morphological features were examined using field emission scanning electron microscope (SU8000, Hitachi, Japan) fitted with an Oxford Microanalysis X-ray dispersive system.

3. Results and discussion

3.1. The influence of raw material proportion of the activators on the activating efficiency of TD

The influence of raw material proportion (the molar ratio of Ce^{3+} :-Y³⁺:Hacac) on the activating efficiency of TD at pH 7 and reaction time 2 h is shown in Fig. 1. The reductive potential of TD increases

Table 1

The stability constant of the rare earth complex	(log K ₁)) (Dean,	1999).
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The central ion	The ligand			
	Cl-	SO_{4}^{2-}	Hacac	OH-
Ce^{3+} Y^{3+}	0.48 Unknown	3.40 3.47	5.30 6.40	14.60 5.00

Table 2

The pH while the rare earth chloride beginning to be hydrolyzed and the solubility product constant of its hydrolysate (K_{sp}) (Dean, 1999).

The rare earth chloride	pH	K _{sp} (25 °C)
CeCl ₃	7.41	1.5×10^{-20}
VCla	6.78	1.6×10^{-23}

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