ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Preparation and performance of ceramic filter material by recovered silicon dioxide as major leached component from red mud

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ARTICLE INFO

Keywords:
Red mud
Two-step leaching process
Ceramic filter material
Ammonia nitrogen

ABSTRACT

In this study, a new ceramic filter material was prepared by recovering red mud from red mud at atmospheric pressure. The primary objective of this research was to investigate the effects of SiO_2 quantity and sintering temperature (ST) on the porosity, stability, microstructure, and performance of the resulting materials. The results demonstrated that after a two-step leaching process with 3 M HCl and 90% sulfuric acid, the recovery of SiO_2 from red mud exceeded 80%. The SiO_2 extracted from red mud was used as the main material and mixed with other materials including Na-bentonite, limestone and pulverized coal at a ratio of 65:25:8:2, resulting in a ceramic filter material with favorable chemical stability, high strength, and nontoxicity. The enhanced surface activity of the material can be attributed to the abundant Si-OH groups, which enable it suitable for the ammonia nitrogen removal from drinking water. Overall, silicon dioxide extracted from red mud will help solve the stockpile and pollution problems of it in China.

1. Introduction

With an overall improvement in living standards, the regulations for the quality of drinking water quality in China have become stricter during past decades alongside. At present, water quality is generally insufficient in both the urban and rural areas. Accordingly, water purification devices have been integrated into the water terminal process in several areas to remedy poor water quality [1,2]. Filter material is the core component of the household water purifiers, and ceramic filter material represents an economical and environmentally friendly approach to removing impurities and bacteria from water by filtration and adsorption without generating secondary pollution [3,4].

Ammonia nitrogen (NH_4-N) infiltrates the water supply network via chloramines produced during the chlorination process [5], after which it exists as ammonium ($NH_4^{+)}$ and ammonia (NH_3) under certain pH and temperature equilibrium. Although the proportion of NH_4^+ decreases with increasing pH, more than 70% of the NH_4-N exists in the form of NH_4^+, even in solution with a pH value greater than 9 [6]. The maximum acceptable contaminant level of ammonia nitrogen in drinking water has been defined as 0.5 mg/L set by the World Health Organization (WHO, 2011) [7]. To date, a variety of techniques have been developed to remove ammonia nitrogen, including break point chlorination, wet air oxidation, electrochemical treatment, adsorption, and ion exchange [8–11], of which adsorption is the most common [12].

Red mud is the by-product of alumina produced through the Bayer chemical process [13,14]. The global annual generation of red mud is approximately 120 million tons, and 3 billion tons of this material has already been stockpiled [15]. Red mud poses significant risks to the local environment because of its extreme alkalinity and its potential impacts on surface and groundwater quality [16,17]. Only a small percentage of this waste is currently utilized in China, mainly in cement and powder adsorbent. Red mud is a complex material with a chemical and mineralogical composition that varies widely depending on the source of bauxite and the technological process parameters [18,19]. Red mud contains many metallic oxides and small quantities of numerous trace elements in addition to its six major constituents, SiO_2, Fe_2O_3, Al_2O_3, CaO, Na_2O, and TiO_2 [20]. As natural resources are increasingly depleted, many researchers have attempted to develop techniques for recovering valuable elements [21–23]. Borra et al. [24], observed that the extraction rate of rare earth elements with hydrochloric acid solution is higher than that of other acids. Specifically, the maximum extraction rate of rare earth elements is approximately 80%, and sodium and calcium in the leaching process can be completely dissolved while 30–50% of aluminum, silicon, and titanium can be dissolved.

Recent studies have shown that red mud contains rich stores of iron and silicon. The main component of red mud is SiO_2, which is primary material utilized in ceramic filter materials [25]. Due to the varying

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http://dx.doi.org/10.1016/j.ceramint.2017.03.048
Received 5 December 2016; Received in revised form 7 March 2017; Accepted 7 March 2017

Please cite this article as: Man, K., Ceramics International (2017), http://dx.doi.org/10.1016/j.ceramint.2017.03.048

acid solubility of the oxides in red mud, the reaction between dilute hydrochloric acid and raw red mud can be described by several reactions:

$$Fe_2O_3+6HCl=2FeCl_3+3H_2O$$

$$Al_2O_3+6HCl=2AlCl_3+3H_2O$$

$$CaO+2HCl=CaCl_2+H_2O$$

$$Na_2O+2HCl=2NaCl+H_2O,$$

The reaction can reasonably be classified as a liquid-solid reaction, where most metallic oxides are dissolved. The contents of these elements account for more than half of the total amount of red mud. Leaching by concentrated sulfuric acid can be expressed as follows:

$$TiO_2+H_2SO_4=Ti(SO4)_2+H_2O=TiOSO_4+H_2SO_4,$$

where TiO_2 becomes soluble, and SiO_2 is enriched in the residue [26].

This study was conducted to investigate the possibility of SiO_2 recovery from red mud by a two-step acid leaching process. Specifically, SiO_2 extracted from red mud was used as the main material into which Na-bentonite, limestone, and pulverized coal were added to produce ceramic filter materials. The effects of various ratios of mixed materials and sintering temperatures on sample properties were then examined in detail. The sample exhibited favorable chemical stability and nontoxicity, suggesting that it can be used for the removal of ammonia nitrogen from drinking water. The ultimate goal of this research was to develop a sustainable and environmentally friendly process for red mud treatment.

2. Experimental method

2.1. Materials and analysis

The red mud was taken from the China Shandong Aluminum Industry Company. Hydrochloric acid, sulfuric acid, pulverized coal, limestone, polyvinyl alcohol (PVA), and Na-bentonite were analytical grade and were obtained from Tianjin Kermel Reagent Co. All solutions were prepared with deionized water. The chemical composition of the red mud is listed in Table 1, and its XRD patterns are shown in Fig. 1. The results revealed that three major phases, quartz SiO_2, hematite Fe_2O_3 and gibbsite $Al(OH)_3$, were presented in air-dried red mud.

The chemical composition of red mud was determined by X-ray fluorescence analysis (PANalytical, AXIOS-PW4400, Netherlands). The X-ray diffraction (XRD) patterns of samples were obtained on a Rigaku D/max-IIIB X-ray diffractometer with Cu Kα radiation (λ=1.5406 °A) generated at 40 kV and 20 mA. The micromorphological characteristics of the samples were characterized by Hitachi S-4800 scanning electron microscopy (SEM) at an accelerating voltage of 5.0 kV. The Brunauer–Emmett–Teller (BET) surface areas of the samples were determined using N_2 adsorption on a Micromeritics ASAP2420 instrument, and the plot of the pore-diameter distribution was determined using the Barrett–Joyner–Halenda (BJH) method from the desorption branch of the isotherm. TG/DTA analysis was conducted with a Setaram-Labsys thermal analyzer Functional groups on the samples were analyzed by Fourier Transform Infrared Spectroscopy (FTIR, Nicolet IS10). The content of iron in the leaching solution was determined by the phenanthroline spectrophotometric method. Aluminum was determined by EDTA complexometric method. Elements such as calcium and sodium in leaching solution were identified by inductively coupled plasma (ICP) emission spectroscopy.

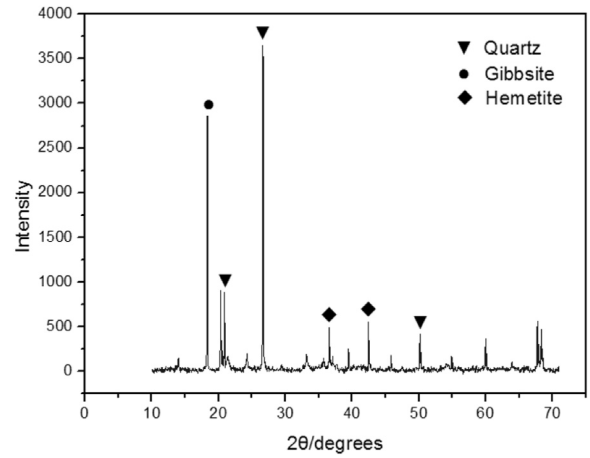

Fig. 1. XRD patterns of raw red mud.

2.2. Experiments procedure

The experiments were performed according to the summary procedure shown in Fig. 2. The red mud leaching procedure was conducted in a round bottomed split reactor with three-necks: one for the condenser, one for the thermometer, and one for the mechanical stirrer. The grinded red mud was dried in an oven at 105 °C before weighing. Briefly, 0.5*g* of red mud was added into the reactor, then leached with dilute hydrochloric acid using the parameters listed in Table 2. Subsequently, the leaching liquor and the leached residues were analyzed chemically. The residues of first step were leached with concentrated sulfuric acid (90%) at 90 °C at a solid to liquid ratio 1:10, after which the slurry was filtered through a centrifuge and washed with deionized water. The SiO_2 produced comprising the resulting leached residue was then dried at 110 °C and weighed. The chemical composition of the leaching residue is shown in Table 3.

The SiO_2 extracted from red mud was applied as the main raw material for manufacturing ceramic filter material, which can be used for the terminal drinking water treatment. Na-bentonite, limestone, and pulverized coal were then injected as adminicular materials, after which the mixture was sieved through a 200 mesh screen. Next, the mixture were subjected to high temperature to decompose the limestone and release CO_2, which plays a role in pore formation. The materials were mixed at mass ratios of 60–80:10–30:4–8:2–6. After the powder was evenly blended, 2 g of mixed powder was added into 2 ml of polyvinyl alcohol (5%), and the mixture was churned continuously at 75 °C until becoming gunk form. Next, an aperture board was used to squeeze the gunk form before shreds with diameter of 1.0–2.0 mm, which was drawn out. After being dried, the mixtures were preheated in a muffle furnace at 400 °C for 50 min, then sintered at the relevant temperature determined in preliminary experiments for 40 min. The ST ranged from 900 to 1100 °C. Finally, various types of ceramic filter materials were obtained after being naturally cooled to room temperature.

2.3. Solubility in hydrochloric acid and apparent porosity

The hydrochloric acid soluble rate is used to assess the chemical stability of granule filter materials. The limit of the hydrochloric acid

Table 1
Chemical composition of red mud.

Component	SiO_2	Fe_2O_3	Al_2O_3	Na_2O	TiO_2	CaO	SO_3	K_2O	P_2O_5
Contents (wt%)	36.338	28.030	22.846	8.864	1.781	1.078	0.399	0.121	0.168