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Processing of coal fly ash magnetic spheres for clay water flocculation

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ABSTRACT

The application of coal fly ash magnetic spheres (MSs) in water treatment is limited due to their complex mineral compositions, low magnetism, and large diameters. In this study, MSs were carefully ball milled and magnetically separated to improve their related properties. After the processing, the resultant magnetic ball-milled MSs (MBMSs) show a substantial change in composition, magnetism, and surface property in addition to a decrease in diameter. Compared with those of the original MSs, the Fe percentage, magnetism, and specific surface area of MBMSs are increased by 25.87%, 54.60%, and 810%, respectively. Dispersive spectrometer mapping investigation shows segregated high- and low-Fe areas with different structures in MS. These different structures enable purification. Highly turbid clay water flocculation experiments using MSs as flocculants indicate that MBMSs can cause fast flocculation whereas the compared samples exert less or slight flocculation effect. Zeta potential investigation suggests that the different flocculation effects are due to the change in the point of zero charge (pH_{PZC}). The pH_{PZC} increases from 3.91 for the original MS to 4.96 for MBMS. The reduction in the diameter, as well as the increase in magnetism, surface area, and pH_{PZC}, makes MSs applicable to water treatment.

1. Introduction

Coal fly ash (CFA) is a major industrial waste due to its tremendous output and widespread distribution, especially in developing countries where energy mainly comes from coal burning (Blissett and Rowson, 2012). Tremendous efforts have been made toward the harmless disposal and resource recovery of CFA in recent years. Most CFA applications are found in the construction industry; however, applications such as in cement additions, concrete processing, bricks and tiles, and roads and embankments employ CFA as a basic structural material and thus result in low added value (Yao et al., 2015). Only 10%–20% of CFA has found application in other fields, including valuable metal recovery, water treatment, and in the agricultural industry (Ukwattage et al., 2013; Yao et al., 2014; Liu et al., 2013). CFA contains various mineral resources, including SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, Na_2O, K_2O, and biochar (Sarkar et al., 2006). Promising applications with high added value can be expected if CFA is properly treated and separated. Recently, considerable research has been reported on the advanced use of separated CFA, including valuable metal recovery (Torralvo and Fernández-Pereira, 2011; Singh et al., 2015), zeolite fabrication (Ansari et al., 2014), catalyst carriers (Saputra et al., 2012), biochar sorbent (Lu et al., 2008), and heavy-media separation (Sarkar et al., 2011; Groppo and Honaker, 2009).

Magnetic spheres (MSs) are major compositions in CFA and can be easily separated from CFA by magnetic processing. The percentage of MS ranges from 2%–23% depending on the mining environment. MS is rich in Fe oxides, which show magnetism at room temperature. The morphology, composition, structure, and properties of MS have been comprehensively studied in previous works (De Boom et al., 2011; Bhattacharjee et al., 2011; Blaha et al., 2008; Gomes et al., 1999; Veneva et al., 2004; Yang et al., 2014; Wang, 2013; Payá et al., 1996). Considering its high Fe concentration, MS can be applied in iron recovery but can only produce very low added value with numerous useless byproducts. MS is also supposed to have potential applications in the water treatment industry as magnetic catalysts and carriers (Anshits et al., 2000; He et al., 2014), magnetic seeds for sewage treatment (Wang, 2013), microwave absorbents (Zhang et al., n.d.), heavy media for gravity separation (Sarkar et al., 2011; Groppo and Honaker, 2009), and magnetic sorbents (Jiang and Liu, 2014). However, research on the application of MS has been very limited. The limited application of MS is based on the wide variation in the ferrous compositions and structures, which leads to inconstant physical properties. The Fe element in MS presents mainly as FeO_x (e.g., Fe_3O_4, Fe_2O_3, FeO, and Fe^0) and other ferrites (e.g., magnesioferrite) (Sokol et al., 2002; Zyryanov et al., 2011). All these ferrous compositions evolve from the melting of Fe-bearing minerals, such as FeS_2 and $FeCO_3$ (Zhao et al., 2006). Therefore, the Fe distribution and structures of ferrous minerals in MS are

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related to not only the mining area but also the burning environment. As a result, the magnetism of MS is often low and uneven. MSs possess typical diameters of tens of microns and density of ~3.1–3.9 g/cm^3 (Sarkar et al., 2011). Thus, maintaining their suspension in water over a long time, which is crucial for water treatment application, is difficult. The diameter is also too large for their potential application in heavy-media separation. Given that magnetism and size are critical for water treatment application, processing and classification are highly desirable. In most previous works, MSs were investigated and used as a whole (Zyryanov et al., 2010; Vassilev et al., 2004).

In the current study, MSs collected from CFA were beneficiated by an additional magnetic separation, followed by a careful ball milling and further magnetic separation. The obtained MSs were carefully characterized and studied in terms of their structure, composition, magnetism, and zeta potential. Processed MSs possess not only small size and high magnetism but also high pH_{PZC}, thereby leading to effective flocculation in highly turbid water under pH = 4.5. After the processing, MSs become applicable to water treatment.

2. Material and methods

2.1. Sample collection and magnetic separation

2.1.1. Preparation of MS samples

The CFA sample was obtained from a typical pulverized coal-fired power plant in Huainan City, China. The CFA was collected by electrostatic precipitators without further treatment. The MSs, including all the magnetic content in the CFA (denoted as 1-MS), were separated using a high-field dry magnetic separation process. To obtain strongly magnetic MSs (denoted as 2-MS), a low magnetic-field wet magnetic separation process was conducted using a magnetic tube with a tunable magnetic field of 0–320 mT (CXG320-80, Tangshan Research Institute of China Coal Technology & Engineering Group, China). Further processing included ball milling and a subsequent wet separation. The 2-MS sample was ball milled with a planetary ball miller (XGB04, Nanjing Yunbotong Scientific Instruments Co., Ltd., China). Then, the magnetic tube was employed again for the wet magnetic separation under a 100 mT magnetic field. The magnetic ball-milled MS (MBMS) and the non-magnetic ball-milled MS (NBMS) after their final separation were dried at 110 °C for 2 h. Each magnetic separation process in this study was performed three times to ensure full collection of target magnetic particles.

2.1.2. Turbid water preparation

The highly turbid water used in this study was prepared in the laboratory. Typically, 1% of montmorillonite (−600 mesh) and 3% kaolin (−600 mesh) were mixed with water at 400 rpm for 1 h. The original pH value and electrokinetic ζ-potential were examined and found to be 8.09 and −22.40 mV, respectively. Only turbid water produced on the same day was used for the flocculation experiment and was stirred 3 min before use to ensure the uniformity of the suspended solids. The overall processing is illustrated in Fig. 1.

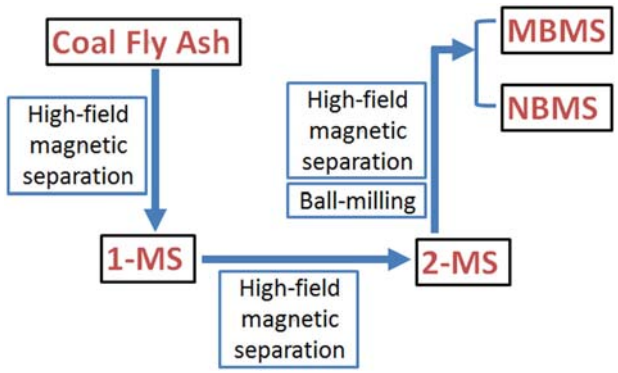

Fig. 1. Schematic of magnetic separation and further processing of MSs.

2.1.3. Flocculation experiments

The flocculation experiments were performed using a jar test apparatus (ZR4-6, Zhongruan Water Industry Technology Development Co., Ltd., China) without any flocculant or coagulant agents. Briefly, 3.0 g MBMS was mixed with 300 mL turbid water at 300 rpm for 1 min, then at 100 rpm for 5 min, and ultimately allowed to settle for 30 min in 500 mL glass beakers. The height of the bottom sediment and the turbidity of the supernatant liquor were recorded at the 0.5, 1, 3, 5, 10, 20, and 30 min points. A HCl aqueous solution (1 mol/L) and a NaOH aqueous solution (1 mol/L) were employed to tune the pH value of the turbid water. For comparison, the same dosages of 1-MS, 2-MS, and NBMS were added to the same volume of turbid water by the same process.

2.2. Analysis method

The particle size distribution of the magnetic spheres was examined using an SALD-7101 laser diffraction particle size analyzer (LDPAZ, Japan). The scanning electron microscope (SEM) images, element distribution mapping, and element composition of the MSs were obtained with a JEOL JSM-4990LV SEM (Japan) equipped with an Oxford energy dispersive spectrometer (EDS, England). The structures of the MSs were characterized using a Rigaku D/Max-2200 X-Ray diffractometer (XRD, Japan) with Cu (Kα) (1.54 Å) radiation. The magnetic properties were characterized with a vibrating sample magnetometer (VSM, Lake Shore 7410, USA) at 300 K. The turbidity of the supernatants was measured using a turbidimeter (HACH 2100 N, USA). The ζ-potentials of the MSs were measured with a zetaprobe measurement apparatus (Colloidal Dynamics, USA). Surface characterization was completed by porosity and BET surface analyses (Autosorb-IQ-MP, Quantachrome Instruments).

3. Results and discussion

3.1. Composition, structure, and physical properties of MSs

The original diameter of the MSs is 1.1–196.5 μm with a Φ50 value of 41.1 μm, as presented in the LDPAZ results (Fig. 2). By contrast, the particles in the ball-milled sample are significantly small in size. The diameter distribution of MBMSs is in the range of 0.1–16.7 μm with a Φ50 value of 5.3 μm. As shown in Fig. 3, most 2-MSs are spherical or

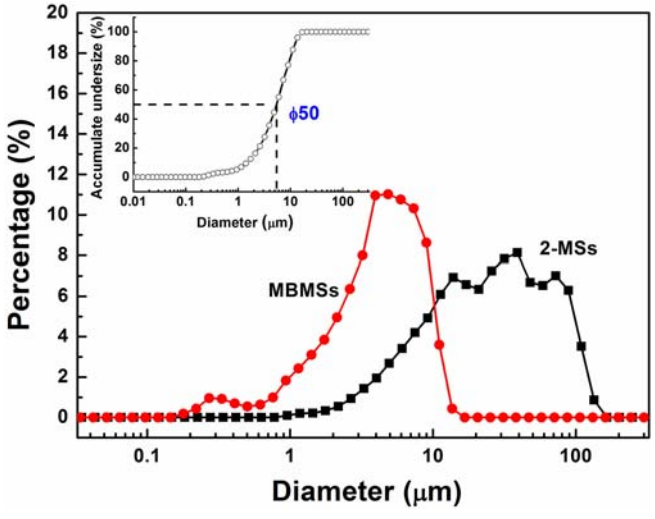

Fig. 2. Diameter distribution of 2-MSs and MBMSs; inset: the cumulative probability curve of MBMSs.