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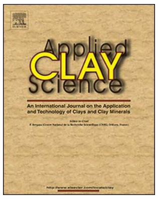

Research paper

Preparation and characterization of a granular bentonite composite adsorbent and its application for Pb^{2+} adsorption

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ABSTRACT

Bentonite is an important clay for preparation of adsorbents for potential treatment of industrial effluents. However, due to its natural occurrence as fine particles and swelling after moisture absorption, bentonite is difficult to be separated from the liquid for regeneration purpose, which limits its application in effluent treatment. In this study, two different bentonite-polypropylene composites were synthesized, i.e., with and without pore-enlarging treatment. They both showed strong ability to resist hydraulic agitation damage with a small breakage rate in water. The obtained results from SEM and XRD characterization revealed that the compounding of bentonite with the polypropylene was a physical process, and the structural characteristics of bentonite particles were maintained in the new products. The granular composite adsorbents were effective in removing Pb^{2+} in aqueous solution. The suggested pore-enlarging treatment was verified as a successful operation to increase greatly the adsorption rate of contaminants on the granular bentonite composite.

1. Introduction

Bentonites are clays that consist mainly of montmorillonite (Mt) and are formed from the alteration of volcanic ash and tuff. Mt has drawn great interests due to their useful chemical and physical properties, such as rheological and adsorption properties, cation exchange capacity, plasticity, high bonding strength, and swelling capacity (Yuan et al., 2013; Zhu et al., 2016). Conventionally bentonites are mainly used as foundry moulding sands (Chojecki et al., 2013), drilling mud (Huang et al., 2016), and iron ore pelletizing (Huang et al., 2014). A lot of special and new uses include filtering agents, water impedance, cosmetics, foods, pharmaceuticals, thickeners and extenders for paints, additives in ceramics, coating and filling of paper, organic clays and acid-activated bleaching earths (Allo and Murray, 2004).

With increasing environmental concerns, bentonites play an important role in the treatment of effluents (Zhu and Zhu, 2007; Zhu et al., 2016), which represents one of new applications of bentonite. The potential product forms of bentonites for effluent treatment involve raw or purified bentonites without pre-chemical treatment (Viraraghavan and Maria Alfaro, 1998; Tahir and Rauf, 2004; Tahir and Rauf, 2006), acid-activated bentonite (Bayrak et al., 2006), synthesized bentonites (Ayari et al., 2007; Zhu et al., 2014), pillared bentonites (Altunlu and Yapar, 2006; Manohar et al., 2006; Ma et al., 2015), organically modified bentonites (Bors et al., 2000; Yapar et al., 2005; Anirudhan and Ramachandran, 2006), and other complexes containing bentonites (Bacquet et al., 2004; Nguyen-Thanh and Bandosz, 2005). Bentonite naturally occurs as fine particles with a large specific surface area, which is beneficial to the adsorption ability and efficiency when being used as wastewater adsorbents. However, fine particles of bentonite are difficult to settle in aqueous medium, thus resulting in the difficult solid/liquid separation and regeneration, even causing the secondary water pollution. Furthermore, the aggregation and coagulation of clay particles under varying conditions of temperature and electrolytes lead variations in flow properties of clay minerals, which is an undesired feature for their practical use as adsorbents (Luckham and Rossi, 1999; Starodoubtsev et al., 2002; Godelitsas and Armbruster, 2003). These disadvantages maybe partly explain why most of bentonite applications in wastewater treatment remain on a laboratory scale. It is well known that settling speeds of solid particles are proportional to their sizes. As such the solid/liquid separation could be greatly improved if the sizes of solid particles increased. Ulusoy and Simsek (2005) developed a granular composite of polyacrylamide-bentonite with a size of 1 mm, which was prepared by direct polymerization of acrylamide monomer in the clay suspension to form gel for further drying and grinding. By now, the researches of manufacturing macroscopically granular composites or granulation of bentonite with polymers as adsorbents are drawing increasing interests.

To overcome the above-mentioned negative effects of fine particles

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of bentonite used in aqueous medium, this work presented a new technique to prepare granular composites of bentonite and resin materials with 3–5 mm in size for wastewater treatment as adsorbents. In this technique, the resin material was melt to form filiform frames to fasten bentonite particles and then squeezed out of a screw type extruder. This manufacturing process is simple and easy to operate with controllable product size. Using this technique, two types of granular bentonite composite adsorbents were prepared, i.e., with and without pore-enlarging treatment. In addition, characterizations of the strength, micro-structure, and adsorption behavior of the composite adsorbents were also performed.

2. Materials and methods

2.1. Materials

The raw bentonite used in this study was produced from Ningming Bentonite Mine, Guangxi Zhuang Autonomous Region of China. It contains about 65.6% Mt with the chemical composition of 64.5% SiO_2, 17.9% Al_2O_3, 1.69% CaO, 3.05% MgO, 3.23% Fe_2O_3, 1.27% Na_2O, 1.17% K_2O, and 0.38% TiO_2 which was determined using XRF, which indicates that the bentonite belongs to Ca, Mg-bentonite type with a low content of Mt. The cation exchange capacity (CEC) of the bentonite is 68.8 meq/100 g (NH_4AC method). The maximum particle size in terms of 90% passing aperture (D_{90}) is 54.36 μm determined using a Malvern Laser Particle Analyzer (Model MS2000, Britain).

The powder polypropylene (PP) was employed as the resin material to compound the bentonite. Its apparent density is > 0.45 g/cm^3.

2.2. Preparation of granular composites

The composites consisted mainly of two components, bentonite and polypropylene. A small amount of other materials such as activated carbon, metallurgy slag powder, fly ash, cenosphere, anti-friction materials, or plasticity promoting additives was added as needed depending on the requirement of the designed products. First of all, raw materials, with mass percentages of bentonite in the range of 45–80% and resin material in the range of 20–40% for burdening, were premixed for 15 min using a pug mill type mixer with double-axle paddles of horizontal rotation. After completion of the pre-mixing, the mixture was taken out of the mixer and transferred to the feed hopper of a twin-screw extruder for further processing. The extruder was an ordinary plastic processing and forming equipment. The feed was added through a delivery screw into the barrel of the extruder which was wrapped with heating resistance to obtain different temperatures along the screw axial direction. The barrel was classified into four parts on the basis of the heated temperature from the feed end to the discharge end. The first part closest to the feed hopper inlet was conveying region at 160–190 °C, the second plastication region at 180–200 °C, the third melting region at 200–220 °C, and the final part next to the outlet was extrusion region at 200–230 °C. The appropriate temperature of each region was selected based on the trial tests and controlled using an electromagnetic valve to connect or block cooling water. In addition, a gas exit was used to vacuum the barrel. When the fed mixture went through the barrel, the mixture was compounded, incorporating further mixing, plastication, compression, and ejection out of a multi-hole die in the barrel. Finally the composite was extruded through a 3 mm exit hole at the discharge end in the form of rod-like products which immediately went through a water trough for cooling, which was followed by naturally drying and cutting into granular products with 3 to 5 mm size in length. This type of granular product underwent high pressure compression and so particles in the product were dense with very small pores. Primary adsorption tests showed that this product had a low adsorption rate. Therefore, a further process was invented to enlarge the pore size of the extruded product. That was, firstly, the granular product was underwent the treatment of water bath to be contained a certain content of water; and then was put into a bulking machine, after being heated to a certain of temperature and pressure, the water in the granular product was gasification, so when the bulking machine was open, with the instantaneous pressure releasing, the granular product was puffed to become a porous material with rich porosity at last. For the sake of convenience to distinguish the extruded granular products with or without further enlarging pores treatment, the former is designated as granular extrusion composites (GEC) and the latter as granular pore-enlarged composites (GPEC). Thus, two types of composites will be referred to as adsorbents in the subsequent discussion.

2.3. Characterization of composite adsorbents

Micrographs of the raw bentonite particles and granular composites were taken using an S-570 scanning electronic microscope (Hitachi Ltd., Japan). Due to the non-conductivity of plastic material, the composite particles were treated to improve their conductivity before observation under the microscope with the following procedures: First, deep cooling was used by putting some sample particles in liquid nitrogen to cause brittle failure and then treated the fracture surface with gold plating in vacuum. After the treatment, the composite products were put under scanning electronic microscope and observed its surface at acceleration voltage of 10 kV.

A self-designed method was used to measure the strength of the composites. Since the composites is prepared as adsorbents for wastewater treatment, its strength must meet the basic requirements of adsorbing operation in which the adsorbents may undergo water immersion, transportation and low-speed agitation to be damaged and ruptured. Therefore, an agitation breakage method with the adsorbents immersed in water was used to test the strength of the composite products. It involved the following detailed procedures: a given mass of dry composite product larger than 2.5 mm was added, together with a fixed volume of water, into a container for agitation. Then, the content was stirred on an agitator for 60 min by controlling the rotary speed of the agitator in the range of 200–500 rpm. Once the stirring was completed, the composite adsorbent was taken out and sieved with 2.5 mm sieving aperture to obtain the mass of the oversized part on the basis of dry weight. Finally, the mass of the composite before and after an agitation was determined to calculate the percentage change of the composite, which is defined as the breakage rate of the composite. It is easy to understand that the breakage of the composite adsorbent in agitation experiment was caused by hydraulic shear, collision and friction between particles and/or between particles and container wall, which to some extent match the breakage mechanisms of adsorbents in practical use of wastewater treatment. Apparently, the smaller the breakage rate, the stronger the composite product is.

The crystal structure of the raw bentonite and the compounded bentonite were determined by X-ray diffraction with Cu Kα radiation (Rigaku, Japan). The operation parameters of this diffraction instrument were: the incident wave length of 1.54178 Å, the power voltage of 40 kV, the electrical current of 120 mA, and the scanning speed of 2°/min.

The surface area of the composite product was obtained by the multiple Point BET method using an aperture and ratio surface analyzer (kubo × 1000, China).

Adsorption tests were performed on the composite products to discuss their adsorption behavior. The wastewater used in the adsorption tests was artificial Pb^{2+} solution. Adsorption experiments were conducted as follows: 100 mL of 100 mg/L Pb^{2+} solution was added to a 250 mL conical flask containing 2 g composite adsorbent, and the flasks with the contents were then agitated on a shaker. After 120 min oscillatory adsorption under several adsorption temperatures and oscillation speed of 200 rpm, the solution was filtered to obtain the filtrate for determining Pb^{2+} concentration using an AA-240FS spectrometer (Varian Ltd). The parameters of the spectrometer for Pb^{2+} measurement were: wavelength 283.3 nm, slit width 0.5 nm, lamp current