



Effects of pH on phosphorus removal capacities of basic oxygen furnace slag



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ARTICLE INFO

Article history:

Received 5 May 2015

Received in revised form

18 November 2015

Accepted 7 January 2016

Available online 3 February 2016

Keywords:

Phosphorus

Basic oxygen furnace slag

pH

Adsorption

Precipitation

ABSTRACT

Phosphorus removal capacities (PRCs) of basic oxygen furnace slag (BOF-slag) in different pH ranges were investigated using batch experiments. The fractions of different phosphorus containing compounds in fresh and reacted BOF-slag were measured by chemical extraction methods. Fresh and reacted BOF-slag was characterized through combining several methods. The results show that BOF-slag had high PRCs (21–30 mg P/g) and that the PRCs of BOF-slag at alkaline pH were comparable to the ones at neutral and acidic pH. At alkaline pH, phosphorus removal occurred via both the weak adsorption onto BOF-slag and the precipitation of calcium phosphates. At neutral and acidic pH, phosphorus removal was achieved through the chemical adsorption onto Fe containing minerals in BOF-slag. Influences of the pH on weakly bound phosphorus, Ca associated phosphorus, and Fe associated phosphorus in the reacted BOF-slag were also discussed in detail.

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1. Introduction

Phosphorus is an essential but limiting nutrient element for growth of organisms in water bodies. Excessive loads of phosphorus from domestic, agricultural and industrial wastewater can cause abnormal growth of hydrophytes, which results in the deterioration of water quality and finally leads to eutrophication. To protect surrounding environment, therefore, phosphorus should be efficiently removed from various wastewater before being discharged into the ecosystems. Many low cost and easily available materials such as natural minerals (limestone (Johansson-Westholm, 2006), zeolites (Johansson-Westholm, 2006), bauxite (Johansson-Westholm, 2006), and dolomite (Karaca et al., 2006)) and industrial by-products (fly ash (Cheung and Venkitachalam, 2000; Li et al., 2006), dewatered alum sludge (Yang et al., 2006), coal cinder (Wang et al., 2010), iron oxide tailing (Zeng et al., 2004), and blast furnace slag (Kostura et al., 2005; Oguz, 2005)) have been assessed for their capacity to sequester phosphorus.

Steel slag, which is a by-product of steel industry, mainly refers to basic oxygen furnace slag (BOF-slag) and electric arc furnace slag (EAF-slag). BOF-slag originates from the further refining of iron in a basic oxygen furnace while EAF-slag is derived from melting recycled scrap in an electric arc furnace (Barca et al., 2013). Steel

slag is heterogeneous oxide materials that primarily consist of components containing iron, calcium, aluminum and silicon (Xue et al., 2009). Through kinds of methods such as batch tests (Barca et al., 2012; Bowden et al., 2009; Jha et al., 2004, 2008; Xiong et al., 2008; Xue et al., 2009), column tests (Cha et al., 2006; Claveau-Mallet et al., 2012, 2013; Yang et al., 2009), and field tests (Barca et al., 2013; Lee et al., 2010; Shilton et al., 2006), the affinity of steel slag for phosphorus retention has been widely investigated to achieve its use as a filter substrate to treat wastewater. The phosphorus removal through steel slag mainly involve two prevailing mechanisms. Many studies have interpreted the precipitation between phosphates and calcium ions from the dissolution of steel slag to be a key phosphorus removal process (Barca et al., 2012, 2013; Bowden et al., 2009; Claveau-Mallet et al., 2012, 2013). Nevertheless, others have demonstrated the adsorption onto metal oxides or oxyhydroxides on steel slag surface to be a significant phosphorus removal mechanism (Jha et al., 2008; Pratt et al., 2007a,b; Xiong et al., 2008; Xue et al., 2009).

Barca et al. (2012) have reported that the phosphorus removal capacities (PRCs) of steel slag greatly varied from 0.8 mg P/g to 89.9 mg P/g. The huge discrepancy in the PRCs of steel slag significantly depended on various factors including exposure duration of phosphorus to steel slag, reaction temperature, wastewater pH, phosphorus concentration, and dosage, size and chemical compositions of steel slag. Particularly, wastewater pH has attracted more and more attentions to measure its important effects on the PRCs of steel slag.

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Claveau-Mallet et al. (2012, 2013) suggested a strong positive relationship between high effluent pH and low effluent phosphorus concentration during column tests with EAF-slag as a filter substrate. Based on batch experiments, Bowden et al. (2009) also confirmed that the highest phosphorus removal by BOF-slag was observed at the highest initial and equilibrium pH. These may be ascribed to the enhancement of the precipitation of phosphates with calcium ions at higher pH (precipitation mechanism). However, Xue et al. (2009) found that the PRCs of BOF-slag tended to decrease with the increase of pH, which is due to the fact that a higher pH causes BOF-slag surface to carry more negative charges and thus can more significantly repulse the negatively charged phosphates in wastewater (adsorption mechanism). The results mentioned above clearly suggest that effects of pH on the PRCs of steel slag are still open questions. To better remove phosphorus from wastewater using steel slag, therefore, more efforts should be further performed to expose the nature of the role of pH in the PRCs of steel slag.

In this work, effects of the pH on the PRCs of BOF-slag were analyzed in detail through batch tests. Chemical extraction methods were used to investigate the fractions of different phosphorus containing compounds in fresh and reacted BOF-slag. Fresh and reacted BOF-slag was characterized through the scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) system, the Fourier transform infrared spectrophotometer (FT-IR), and X-ray diffractometer (XRD). Concentrations of calcium and iron ions in wastewater were also measured by the atomic absorption spectrometric method (AAS). It is hoped that this can help to enhance the understanding of effects of pH on the PRCs of BOF-slag in practice.

2. Materials and methods

2.1. Materials

BOF-slag was collected from Anshan Iron and Steel Group Corporation in Liaoning province of China. To obtain fine powders, BOF-slag was ground for 3 min using the vibration mill (MZ100, Nanchang Hengye Mining and Metallurgy Machine Factory, China). Then, the fine powders were sieved by the sieves of 250 and 325 mesh number. The samples with a size range of 0.045–0.058 mm were used in batch tests. According to analysis of X-ray fluorescence (XRF, ZSX100e, Rigaku Corporation, Japan), chemical compositions of BOF-slag was predominately composed of CaO (47.08%), Fe₂O₃ (36.12%), SiO₂ (8.04%), and MgO (4.94%).

2.2. Batch tests

A series of batch tests were conducted to investigate influences of pH on the PRCs of BOF-slag. Synthetic wastewater with initial phosphorus concentrations of 300 mg P/L was prepared using tap water and KH₂PO₄ as phosphorus sources. BOF-slag of 2.0 g was put into the beaker containing 200 mL synthetic wastewater. The pH ranges can be adjusted using the buffering reagents of CH₃CO₂H/CH₃CO₂Na. The dissolution of alkaline species in BOF-slag may cause changes of the pH (Cha et al., 2006). By controlling the buffering capacity of CH₃CO₂H/CH₃CO₂Na, the different pH ranges were achieved to be 5.42–8.72, 5.50–7.21, and 4.50–4.51, respectively. For the pH range of 6.48–9.83, no chemical buffering reagents were required since BOF-slag in tap water can create the desirable pH range. The former values in the pH ranges were initial pH while the later ones were equilibrium pH. The pH was measured through a pH meter (PHS-3C Model). The solution in the beaker was continuously stirred for 24 h by a stirring apparatus with temperature controlling system. The reaction temperature can

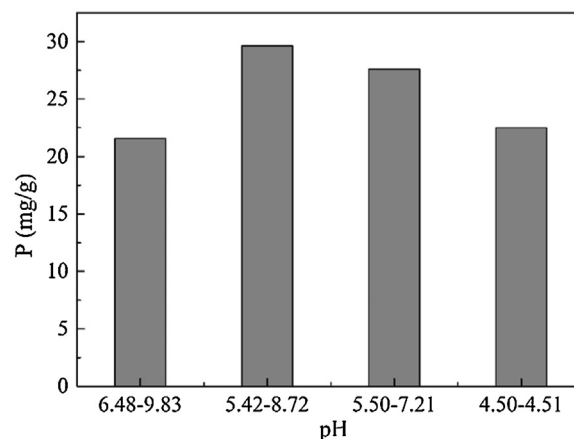


Fig. 1. PRCs of BOF-slag in different pH ranges.

be exactly controlled at 25 °C. After tests, the solution was sampled and centrifuged at 3000 rpm for 5.0 min to separate BOF-slag from the liquid phase. The reacted BOF-slag was dried at 100 °C and used in the following extraction procedures and analysis methods. Each batch test was carried out three times and the average value was adopted to better determine PRCs of BOF-slag.

2.3. Chemical extraction

To further determine effects of the pH on the PRCs of BOF-slag, the sequential extraction procedures were used to measure the fractions of different phosphorus compounds in fresh and reacted BOF-slag (Barca et al., 2013; Drizo et al., 2002; Headley et al., 2003). Three fractions of phosphorus can be sequentially extracted from BOF-slag of 2.0 g using different extractants and the duration of every step was 24 h. The bicarbonate extractable phosphorus was extracted in 0.5 mol/L NaHCO₃ of 200 mL and was related to weakly bound phosphorus. The hydroxide extractable phosphorus was extracted in 0.1 mol/L NaOH of 200 mL and was assigned to Fe and Al associated phosphorus. The hydrochloric acid extractable phosphorus was extracted in 1.0 mol/L HCl of 200 mL and represented Ca associated phosphorus.

2.4. Analysis methods

The phosphorus concentration was measured by the ammonium molybdate spectrometric method using the UV-vis spectrophotometer (UV-vis, UV-2550) (Barca et al., 2012, 2013). Analyses of calcium and iron ions concentrations were performed through the atomic absorption spectrometric method (AAS, TAS-990) (Barca et al., 2012, 2013; Claveau-Mallet et al., 2013; Pratt et al., 2007b). SEM-EDS (S-3400N) was employed to investigate the morphology and elemental compositions of fresh and reacted BOF-slag. Functional groups of fresh and reacted BOF-slag were examined by FT-IR spectra (Thermo Nicolet-380). Mineral compositions of fresh and reacted BOF-slag were investigated through XRD (DX-2600).

3. Results and discussion

3.1. PRCs of BOF-slag in different pH ranges

Fig. 1 shows the PRCs of BOF-slag in different pH ranges. The PRCs of BOF-slag was 21.57 mg P/g and 29.64 mg P/g in the pH range of 6.48–9.83 and 5.42–8.72, respectively. Unexpectedly, it was also rather high and was 27.60 mg P/g and 22.48 mg P/g in the pH range of 5.50–7.21 and 4.50–4.51, respectively. The PRCs of BOF-slag at

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