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Removal kinetics of phosphorus from synthetic wastewater using basic oxygen furnace slag

*Chong Han**, *Zhen Wang, He Yang, Xiangxin Xue*

School of Materials & Metallurgy, Northeastern University, Shenyang 110819, China. E-mail: hanch@smm.neu.edu.cn

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ABSTRACT

Removal kinetics of phosphorus through use of basic oxygen furnace slag (BOF-slag) was investigated through batch experiments. Effects of several parameters such as initial phosphorus concentration, temperature, BOF-slag size, initial pH, and BOF-slag dosage on phosphorus removal kinetics were measured in detail. It was demonstrated that the removal process of phosphorus through BOF-slag followed pseudo-first-order reaction kinetics. The apparent rate constant (k_{obs}) significantly decreased with increasing initial phosphorus concentration, BOF-slag size, and initial pH, whereas it exhibited an opposite trend with increasing reaction temperature and BOF-slag dosage. A linear dependence of k_{obs} on total removed phosphorus (TRP) was established with $k_{obs} = (3.51 \pm 0.11) \times 10^{-4} \times \text{TRP}$. Finally, it was suggested that the Langmuir–Rideal (L–R) or Langmuir–Hinshelwood (L–H) mechanism may be used to describe the removal process of phosphorus using BOF-slag.

Introduction

Phosphorus is an essential nutrient for the growth of plants and animals. However, the enrichment of phosphorus in water bodies including rivers, lakes, and lagoons can give rise to abnormal growth of hydrophytes, which results in the deterioration of water quality and finally leads to eutrophication. Thus, phosphorus should be removed from domestic and industrial wastewater before being discharged into the surrounding environment. Constructed wetland systems (CWS) have been demonstrated as an effective treatment method for phosphorus removal (Barca et al., 2013; Johansson-Westholm, 2006; Shilton et al., 2006; Vohla et al., 2011). The selection of the materials for wetland substrates plays a key role in designing the CWS (Drizo et al., 2006). 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 such as fly ash (Cheung and Venkitachalam, 2000; Li et al., 2006), dewatered alum sludge (Yang et al., 2006), coal cinders (Wang et al., 2010), iron oxide tailings (Zeng et al., 2004), and blast furnace slag (Gong et al., 2009; Oguz, 2005; Kostura et al., 2005) have been assessed for their capacity to sequester phosphorus.

In the last decades, the by-products (basic oxygen furnace slag and electric arc furnace slag) from the steel industry have attracted considerable interest from researchers to investigate them as appropriate wetland substrates through various methods such as batch tests (Bowden et al., 2009; Barca et al., 2012; 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). Basic oxygen furnace slag (BOF-slag) is derived from the refining of iron in a basic oxygen furnace, whereas electric arc furnace slag (EAF-slag) originates from melting recycled scrap in an electric arc furnace (Barca et al.,

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* *Corresponding author.*

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2013). Steel slag consists of heterogeneous oxide materials and is primarily composed of species containing iron, calcium, aluminum and silicon (Xue et al., 2009).

According to the results of different studies, the removal rate of phosphorus by steel slag greatly varied in the range of 37%–100% and its phosphorus removal capacity drastically fluctuated from 0.13 to 89.9 mg P/g (Barca et al., 2012, 2013; Bowden et al., 2009; Claveau-Mallet et al., 2013; Drizo et al., 2006; Li et al., 2013; Wang et al., 2010; Xiong et al., 2008; Yang et al., 2009). These large discrepancies significantly depended on various factors such as exposure duration of phosphorus to steel slag, temperature, phosphorus concentration, wastewater pH, steel slag dosage, steel slag size, and chemical composition of steel slag. There have been two popular mechanisms for phosphorus removal by steel slag. A number of researchers have concluded that the main mechanism of phosphorus removal was related to CaO-slag dissolution followed by Ca–P precipitation (Barca et al., 2012, 2013; Bowden et al., 2009; Claveau-Mallet et al., 2012, 2013; Drizo et al., 2006). Nevertheless, other studies have suggested the adsorption of phosphorus onto metal oxides/oxyhydroxides on the surface of steel slag to be a primary phosphorus removal mechanism (Jha et al., 2008; Pratt et al., 2007a,b; Xiong et al., 2008; Xue et al., 2009).

To date, researchers have focused on the investigation of phosphorus removal capacity of steel slag as well as the mechanism. However, few studies have been performed to determine the kinetics of phosphorus removal by steel slag. Jha et al. (2008) suggested that a first order rate expression was more appropriate than the pseudo-second order equation for the data obtained from batch experiments. The phosphorus removal data of CWS with steel slag as filter substrates can be also well explained employing the model of Kadlec and Knight, which originated from the first-order kinetics equation proposed by the U.S. Environmental Protection Agency to model pollutant removal in CWS (Barca et al., 2013). It should be pointed out that the understanding of phosphorus removal kinetics using steel slag is still limited. The study of phosphorus removal kinetics can substantially contribute to the understanding of the whole process and the mechanism of phosphorus removal by steel slag.

In this work, therefore, the kinetics of phosphorus removal by BOF-slag was analyzed in detail through batch experiments. Fresh and reacted BOF-slag was characterized using an X-ray diffractometer (XRD) and scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) system. Effects of several parameters, including initial phosphorous concentration, temperature, steel slag size, initial pH, and steel slag dosage, on the reaction rate of phosphorus removal were investigated. A quantitative relationship between reaction rate of phosphorus removal and total removed phosphorus was also established. Finally, Langmuir–Hinshelwood (L–H) and Langmuir–Rideal (L–R) mechanisms were discussed and used to describe the phosphorus removal process, which may help reveal the mechanism of phosphorus removal by steel slag.

1. Experimental

1.1. Materials

BOF-slag was from Anshan Iron and Steel Group Corporation in Liaoning province of China. The chemical composition of BOF-slag was analyzed using X-ray fluorescence (XRF). The composition of BOF-slag was mainly CaO (47.08%), Fe_2O_3 (36.12%), SiO_2 (8.04%), and MgO (4.94%), with small amount of MnO (1.99%), Al_2O_3 (0.78%), TiO_2 (0.56%), P_2O_5 (0.30%), Cr_2O_3 (0.15%), SrO (0.03%), and Nb_2O_5 (0.02%). This is similar to steel slag used in previous studies (Barca et al., 2013; Bowden et al., 2009; Claveau-Mallet et al., 2012). To obtain samples with different sizes (0–0.038, 0.038–0.045, 0.045–0.058, 0.058–0.106, 0.106–0.180 mm), BOF-slag was ground into fine powders and sieved through sieves of different mesh sizes.

1.2. Batch experiments

A series of batch tests was conducted to investigate the influence of several parameters on the kinetics of phosphorus removal by BOF-slag. Synthetic wastewater with different initial phosphorus concentrations (50, 75, 100 and 125 mg P/L) was prepared using tap water and KH_2PO_4 as the phosphorus source. Then, BOF-slag with different sizes was added to beakers containing 250 mL synthetic wastewater. The BOF-slag dosage varied in the range 0.0–2.0 g. The solution in the beaker was continuously stirred for 4.0 hr employing a stirring apparatus with a temperature control system. The reaction temperature could be exactly controlled from 293 to 313 K. The initial solution pH was adjusted to desired values using 0.05 mol/L HCl and 0.05 mol/L NaOH. The pH was measured using a pH meter (PHS-3C Model, Shanghai Precision & Scientific Instrument Co.Ltd, Shanghai, China). The solution was sampled at certain time intervals and centrifuged at 3000 r/min for 5.0 min to separate BOF-slag from the liquid phase.

1.3. Kinetics analysis

The Langmuir–Rideal (L–R) mechanism is usually used to describe heterogeneous reaction processes. This mechanism indicates the reaction between liquid phase phosphorus ($[P_{liq}]$) and active species ([AS]) on the surface of BOF-slag as shown in Eq. (1).

$$[AS] + [P_{liq}] \rightarrow \text{Products} \tag{1}$$

The kinetics of Eq. (1) can be described using Eq. (2).

$$\frac{d[P_{liq}]}{dt} = -k^{II} \times [AS] \times [P_{liq}] \tag{2}$$

where, k^{II} is the second order rate constant. A pseudo first-order kinetics can be assumed by replacing $k^{II} \times [AS]$ with k_{obs}, which is the apparent rate constant.

$$\frac{d[P_{liq}]}{[P_{liq}]} = -k_{obs} \times dt \tag{3}$$

Eq. (4) derives from the integration of Eq. (3).

$$\frac{1}{t}\ln\left(\frac{[P_{liq}]_0}{[P_{liq}]_t}\right) = k_{obs} = k^{II} \times [AS] \tag{4}$$

Thus, k^{II} can be obtained through linear fitting of k_{obs} as a function of [AS].

Additionally, the Langmuir–Hinshelwood (L–H) mechanism may also occur during the phosphorus removal process using BOF-slag. According to this mechanism, the reaction can occur when active species on the surface of BOF-slag encounter phosphorus adsorbed on adjacent sites. The k_{obs} can be expressed by the following equation in the L–H mechanism,

$$\frac{k^{II}[SS]K_{AS}[AS]}{1 + K_{AS}[AS]} = k_{obs} \tag{5}$$