Phosphate removal from domestic wastewater using thermally modified steel slag

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ABSTRACT

This study was performed to investigate the removal of phosphate from domestic wastewater using a modified steel slag as the adsorbent. The adsorption effects of alkalinity, salt, water, and thermal modification were investigated. The results showed that thermal activation at 800°C for 1 hr was the optimum operation to improve the adsorption capacity. The adsorption process of the thermally modified slag was well described by the Elovich kinetic model and the Langmuir isotherm model. The maximum adsorption capacity calculated from the Langmuir model reached 13.62 mg/g. Scanning electron microscopy indicated that the surface of the modified slag was cracked and that the texture became loose after heating. The surface area and pore volume did not change after thermal modification. In the treatment of domestic wastewater, the modified slag bed (35.5 kg) removed phosphate effectively and operated for 158 days until the effluent P rose above the limit concentration of 0.5 mg/L. The phosphate fractionation method, which is often applied in soil research, was used to analyze the phosphate adsorption behavior in the slag bed. The analysis revealed that the total contents of various Ca–P forms accounted for 81.4%–91.1%, i.e., Ca_{10}–P 50.6%–65.1%, Ca_8–P 17.8%–25.0%, and Ca_2–P 4.66%–9.20%. The forms of Al–P, Fe–P, and O–P accounted for only 8.9%–18.6%. The formation of Ca_{10}–P precipitates was considered to be the main mechanism of phosphate removal in the thermally modified slag bed.

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Introduction

Phosphorus-rich wastewater discharge often causes eutrophication, which leads to the abundant growth of aquatic plants and algae. Therefore, domestic wastewater treatment plants are required to meet maximum P discharge limits. A control target of total phosphate (TP) for secondary effluent is between 0.5 and 1.0 mg P/L (Xiong et al., 2008). Accordingly,

biological techniques are currently used in domestic wastewater treatment, including activated sludge treatment (Coma et al., 2012), sequencing batch reactors (Jin et al., 2012), and biological contact oxidation (Lu et al., 2011). Biological treatments reduce most of the organic carbon and nitrogen in wastewater. The main obstacle is that they have been less effective in phosphorus removal. Therefore, these biological processes usually need to be combined with post-treatment procedures to remove phosphorus in advanced wastewater treatment.

In the case of phosphorus removal, the adsorption technique has been widely studied in the past decades. Inorganic

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adsorbents, such as slag (Barca et al., 2012; Claveau-Mallet et al., 2012; Kostura et al., 2005), fly ash (Chen et al., 2007), red mud (Akay et al., 1997), alunite (Özacar, 2003), zeolite (Chen et al., 2006), soils (Gimsing et al., 2007; Moon et al., 2007), and iron oxide tailings (Zeng et al., 2004), have been widely used for phosphorus removal. Steel slag, a byproduct of the steel industry, has been considered a promising post-treatment option in terms of effluent quality, cost-efficiency, and operation simplicity. The application of steel slag as the adsorptive agent to remove phosphate from aqueous solution has been intensively attempted (Cucarella and Renman, 2009; Oguz, 2004). Batch experiments are commonly performed to evaluate the phosphate removal capacity of steel slag, which has been found to range from 1 to 80 mg/g (Bowden et al., 2009; Drizo et al., 2002; Jha et al., 2008; Xue et al., 2009). The main parameters affecting the efficiency of phosphate adsorption are the aggregate size, the ratio of material to solution, contact time, agitation, temperature, pH, and initial phosphate concentration (Cucarella and Renman, 2009). According to Xue et al. (2009), the anions Cl^-, SO_4^{2-}, and NO_3^- found in wastewater had insignificant effects on phosphate adsorption. Based on investigation of the effects of pH as well as chemical modeling, Baker et al. (1998) concluded that precipitation was the main mechanism of phosphate removal by slag treatment. In addition to precipitation, phosphate can also be removed by ion exchange and weak physical interactions between the surface of the sorbent and the metallic phosphate salts (Oguz, 2004). However, the use of slag in phosphate adsorption from aqueous solutions faces disadvantages, for example having a low specific surface area and a poor pore structure (Kostura et al., 2005). The internal chemical components cannot be used efficiently. Therefore, activating the steel slag surface is one effective way to utilize this waste. The methods of calcination, acidification, and basification have been applied to the slag to facilitate adsorption of ions such as PO_4^{3-}, F^-, Ni^{2+}, and NH_4^+, achieving an improvement of adsorption capacity (Islam and Patel, 2011; Jha et al., 2004, 2008; Li et al., 2011).

Slag is mainly composed of calcium, iron, aluminum, and silicon oxides, similar to the composition of calcareous soils. Methods to analyze phosphate fractionation in calcareous soils are often used to understand the phosphate reaction mechanism when studying phosphate adsorption by sepiolite and palygorskite (Gan et al., 2009; Yin et al., 2011). According to the nature of the different cations that bind with phosphate, inorganic phosphate can be divided into calcium phosphate (Ca–P), iron phosphate (Fe–P), aluminum phosphate (Al–P), and occluded phosphate (O–P) (Jiang and Gu, 1989). Based on the numbers of combined phosphate groups, Ca–P can be further classified into dicalcium phosphate ($Ca_2(HPO_4)_2$, Ca_2–P), tricalcium phosphate ($Ca_3(PO_4)_2$, Ca_3–P), octacalcium phosphate ($Ca_8H_2(PO_4)_6$, Ca_8–P), and ten-calcium phosphate ($Ca_{10}(PO_4)_6(OH)_2$, Ca_{10}–P) (Celen et al., 2007; Yin et al., 2011).

Thus, in the present study, the steel slag was first activated to improve its adsorption capacity using alkaline, water, salt, or thermal modification. The surface properties of the modified slag were investigated. The phosphate adsorption isotherm and kinetics of the modified slag were evaluated in batch experiments. Then, a reactor filled with the modified slag followed the biological treatment in series to dispose of real domestic wastewater. The effectiveness of phosphate removal was evaluated. Phosphate fractions in different parts of the slag bed were measured to quantify the amount of phosphate bound to mineral compounds in the slag and to understand the phosphate binding during treatment.

1. Materials and methods

1.1. Steel slag

The steel slag was obtained from a steel plant in Jiangxi Province, China. Elemental analysis (expressed as oxides) using X-ray fluorescence spectroscopy (S4-Explorer, Bruker Co., Billerica, Massachusetts, Germany) showed that the proportional mass composition of the slag was Fe_2O_3 27.8%, CaO 49.75%, SiO_2 10.5%, MnO 3.91%, MgO 2.28%, P_2O_5 1.80%, Al_2O_3 1.64%, V_2O_5 0.73%, TiO_2 0.66%, Cr_2O_3 0.30%, SO_3 0.28%, Na_2O 0.25%, CuO 0.07%, and Nb_2O_5 0.03%.

1.2. Modification

Before the experiments, the slag was sieved to yield the size fractions of 150–420 μm (mesh 100–40), 420–841 μm (mesh 40–20), 841–2000 μm (mesh 20–10), and 2000–4000 μm (mesh 10–5) using ASTM standard sieves, respectively. For thermal modification, the slag was heated directly at 800°C for 1 hr. For the alkaline, salt, or water modification, approximately 10 g of steel slag was immersed in 100 mL NaOH (3 mol/L), $NaNO_3$ (1 mol/L), or distilled water for 24 hr. The screened slag was then heated at 800°C for 1 hr. In the evaluation of adsorption capacity, 0.5 g of slag was added to 100 mL of a PO_4^{3-} solution (100 mg P/L) prepared with KH_2PO_4. After the mixture was stirred at 160 r/min for 24 hr in a thermostatic shaker (25°C), the solution was centrifuged, and the filtrate was used to measure the PO_4^{3-} concentration. The PO_4^{3-} adsorption capacity at equilibrium was calculated using Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where, C_0 (mg P/L) and C_e (mg P/L) are the initial and equilibrium concentrations of PO_4^{3-}, m (g) is the dry mass of the slag, and V (L) is the solution volume.

1.3. Reaction devices

As shown in Fig. 1, the experimental system included two parts, namely, biological contact oxidation (BCO) and steel slag adsorption (SSA). The BCO and SSA reactors, with working volumes of 20 and 40 L, respectively, were fabricated from polymethyl methacrylate. Volcanic stones and ceramic rings were chosen as the biofilter media due to their specific area and low cost. The adsorption bed in the SSA reactor was composed of two layers: 5 cm of gravel and 30 cm of the thermally modified slag (35.5 kg, size 2000–4000 μm).

1.4. Reactor operation

The raw wastewater discharge from the student dormitories was used, with the characteristics of pH 6.8–7.6, chemical oxygen demand (COD) 129.5–308.7 mg/L, ammonia nitrogen