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Characteristics and mechanisms of phosphate adsorption onto basic oxygen furnace slag

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ABSTRACT

The adsorption characteristics of phosphate adsorption on the basic oxygen furnace (BOF) slag were identified as a function of pH and ion strengths in solution. In addition, adsorption mechanisms were investigated by conducting batch tests on both the hydrolysis and phosphate adsorption process of the BOF slag, and making a comparative analysis to gain newer insights into understanding the adsorption process. Results show that the adsorption capacity from 4.97 to 3.71 mg P/g slag when the solution pH was increased from 2.0 to 13.0 and phosphate initial concentration was 50 mg/L, indicating that adsorption capacity is largely dependent upon the pH of the system. The results of the competitive adsorption between phosphate and typical anions found in wastewater, such as NO_3^-, SO_4^{2-} and Cl^-, onto BOF slag reveal that BOF slag can selectively adsorb phosphate ions. The insignificant effect of NO_3^-, SO_4^{2-} and Cl^- on phosphate adsorption capacity indicates that phosphate adsorption is through a kind of inner-sphere complex reaction. During the adsorption process, the decrease of phosphate concentration in solution accompanied with an increase in pH values and concentrations of NO_3^-, SO_4^{2-} and Cl^- suggests that phosphate replaced the functional groups from the surface of BOF slag which infers that ligand exchange is the dominating mechanism for phosphate removal. At the same time, the simultaneous decreases in PO_4^{3-} and total calcium, magnesium and aluminum concentration in solution indicate that chemical reaction and precipitation are other mechanisms of phosphate removal.

1. Introduction

Phosphate is an essential, often limiting, nutrient for growth of organisms in most ecosystems. However, excessive supply of phosphorus from wastewater into water bodies, such as lakes, rivers and creeks causes eutrophication, resulting in the bloom of aquatic plants, growth of algae and depletion of dissolved oxygen. Phosphorus removal from wastewater has been widely studied during the past decades. Typical removal methods such as chemical and biological treatments have been successfully applied [1]. Nevertheless, increasing attention has been paid to adsorptive removal of phosphate from aqueous solutions. The application of low cost and easily available materials in wastewater treatment has been widely investigated during recent years, such as fly ash [2], blast furnace slag [2,3], red mud [4], alunite [5], aluminum hydroxide [6] and iron oxide tailings [7].

Basic oxygen furnace slag (BOF slag in short) is a final waste material in the basic oxygen furnace steel making process. In blast furnace iron making, limestone (as fluxes) is added to react with the gangue minerals (iron ore and coke) to form iron slag. Slag is separated from the molten iron owing to the different specific gravity of molten iron and slag. In a basic oxygen furnace, the molten iron is converted into steel with oxygen, which also requires some flux materials to react with gangues. The slag formed in the BOF, after being solidified, is called BOF slag [8]. In recent years, the management of BOF slag has become a significant issue in environmental engineering due to the enormous quantities generated and the associated disposal costs and constraints. BOF slag is heterogeneous oxide materials which are compounded by some main oxides such as CaO, Fe_2O_3, SiO_2, Al_2O_3, and MgO due to their mass percentage. These oxides are going to change with different steel making process, raw materials, even cooling and crash methods, and all these factors will lead to BOF slag show the heterogeneity characters which may affect the new application way for BOF slag like removal of phosphate from aqueous solution. It is known that BOF slag shows strongly heterogeneous surfaces. The heterogeneity of the BOF slag surface stems from two sources, namely geometrical and chemical. The geometrical heterogeneity (poros-

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ity) is the result of differences in the size and shape of pores, as well as pits, vacancies and steps. Chemical heterogeneity is associated with different functional groups at a surface, and with various surface contaminants. Both the chemical and geometrical heterogeneities contribute to the unique adsorption properties of BOF slag [9]. In other instances, conjunctive evidences from literature have also shown that BOF slag can help remove phosphorus in wastewater. This is attributed to the abundant calcium and aluminum ions in the treated BOF slag, which enhance the processes of adsorption and chemical precipitation that help to remove such pollutants from wastewater [10]. However, an in-depth understanding of the mechanisms and characteristics of phosphate adsorption by the BOF slag is crucial to its effective utilization as an adsorbent material.

Therefore, the objective of this work was to study the feasibility of using modified BOF slag as adsorbents for the removal of phosphate from aqueous solution. In doing so, the modified BOF slag was prepared by mechanochemistry and acid treatment. The surface structure of the materials was investigated by means of X-ray diffraction (XRD), scanning electron photograph, N_2 adsorption–desorption technique. The adsorption characteristics of these materials for phosphate removal from aqueous solutions were evaluated in batch adsorption experiments.

2. Materials and methods

2.1. Preparation of test materials

BOF slag used in this study generated from the local steel-making factory with 2 years setting time. The sieve size of BOF slag was controlled under 0.6 mm as original materials. There two kinds of modified BOF slag used in this study: (1) sample BTM (BOF slag treated by milling) meant that original materials were ground for 3 h by vertical planetary ball mill, while the ratio of materials versus ball was 1:10 by mass; (2) sample BTA (BOF slag treated by acid) meant that original materials were pretreated in dilute hydrochloric acid, then oven-dried powders were used as adsorbents after being washed by deionised water for five times.

Artificial wastewater was synthesized by dissolving pre-weighed potassium dihydrogen phosphate (KH_2PO_4) in deionised water. The solution was then incubated in the laboratory at $20 \pm 2\,^{\circ}$C, and adjusted to different pH (using sulphuric acid (0.01 M) and sodium hydroxide (0.1 M)). Solutions were kept air-tight to prevent CO_2 from affecting solution pH. Chloride stock solution (6.0 M), sulphate stock solution (3.0 M) and ammonia stock solution (3.0 M) were prepared by dissolving pre-weighed amount of NaCl and Na_2SO_4, $NaNO_3$ respectively, in deionised water.

2.2. Characterization, test method and equipment

Elemental, physical and chemical analyses of the BOF slag were carried out using Inductively coupled plasma-atomic emission spectrometer (ICP-AES, IRIS Advantage). The morphological structure of the dewatered BOF slag was examined by X-ray diffractometer (XRD, D/Max-RB Model XRD Analyzer) and scanning electron microscope (SEM, JSM-5610LV Model). The specific surface areas SBET of the samples were determined by the thermal desorption method using a "Chrom4" gas chromatograph fed with nitrogen as adsorbate. Physical properties and chemical compositions of BOF slag used in this study are shown in Table 1.

The pH control measurement (PHS-3C Model), a thermo-stated shaker (Orbital Model SHZ-88) were used in adsorption batch experiments; a vertical planetary ball mill (QM-1SP2 Model) was used for modification of BOF slag.

Table 1
Chemical compositions of BOFS

Chemical composition	Content (%)
Silica (as SiO_2)	13.7
Calcium (as CaO)	45.4
Iron (as Fe_2O_3 and FeO)	17.8
Magnesium (as MgO)	7.3
Alumina (as Al_2O_3)	6.8
H_2O at 105 °C	1.1
H_2O at 950 °C	2.4

To determine the theoretical saturation capacities of the BOF slag and to establish the adsorption isotherms, a series of suspensions in 250 mL plastic bottles were prepared, each containing 1.00 g of slag in 100 mL of phosphate solution; these solutions had different phosphate concentrations (10–500 mg/L). Experiments of effect of pH were conducted by adding same amount of the slag to a pH controlled deionised water and measuring the zeta potential. Sulphuric acid (0.01 M) and sodium hydroxide (0.1 M) were used to control the pH of the adsorption system to designed values (pH 2–13) to investigate the effect of pH on adsorption capacity and the amount of acid/alkaline required to maintain the pH was calculated from the concentration and volume added, including a correction for the dilution effect. Thereafter, standard aliquots of the phosphate stock solution were introduced, giving a resultant phosphate concentration of 50 mg/L. The mixtures were then mechanically agitated for promoting adsorption over a 3-h pre-determined equilibrium time. After adsorption, equilibrated samples were filtered using 0.45 mm millipore filter paper (Millipore) and analyzed for phosphate concentration. In order to determine the effect of NO_3^-, SO_4^{2-} and Cl^- on phosphate adsorption, different concentrations of solutions containing these ions were mixed with 100 mg/L phosphate. By following above test procedure, the selectivity adsorption of NO_3^-, SO_4^{2-}, Cl^- and PO_4^{3-} and structural identity of the BOF slag was studied by investigating the effect of the ionic strength on the equilibrium of the surface complex formed.

NO_3^-, SO_4^{2-}, PO_4^{3-} and Cl^- concentrations were obtained using a Hach spectrophotometer (DR/2400) by performing UV spectrophotometric, barium chromate, and molybdenum blue spectrophotometric methods for NO_3^-, SO_4^{2-}, and PO_4^{3-} concentrations determination; silver nitrate titration method for determination of Cl^- concentration. The concentrations of Ca^{2+}, Mg^{2+}, and Al^{3+} in the slag leachates were determined by using ICP-AES. The zeta potential of the BOF slag was measured at different pH using a zeta Potential Analyzer (ZC-2000). All the adsorption tests were repeated twice and the average value of measurements was reported. And test was conducted at 20 °C.

3. Results

3.1. Characterization of adsorbents

3.1.1. Chemical composition and properties

The principal chemical compositions of the BOF slag are shown in Table 1. The BOF slag adsorbents consisted mainly of CaO, Fe_2O_3, SiO_2, Al_2O_3, FeO, and MgO (more than 90% by mass). It is observed in Table 2 that for BTM by milling, density, surface area,

Table 2
Technical properties of BOFS and adsorbents

Materials properties	Original	BTM	BTA
Density (mg/cm^3)	3.11	3.29	2.98
Specific surface (m^2/g)	0.50	0.75	0.90
Total porosity (%)	5.76	7.18	9.22