

Characteristics and mechanisms of phosphate adsorption onto basic oxygen furnace slag

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ARTICLE INFO

Article history:

Received 21 August 2007

Received in revised form 26 May 2008

Accepted 27 May 2008

Available online 9 July 2008

Keywords:

Adsorption mechanisms
Basic oxygen furnace slag
Ligand exchange
Phosphate removal
Surface complex

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.

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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, N₂ 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 (KH₂PO₄) in deionised water. The solution was then incubated in the laboratory at 20 ± 2 °C, and adjusted to different pH (using sulphuric acid (0.01 M) and sodium hydroxide (0.1 M)). Solutions were kept airtight to prevent CO₂ 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 Na₂SO₄, NaNO₃ 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 ₂ O ₃ and FeO)	17.8
Magnesium (as MgO)	7.3
Alumina (as Al ₂ O ₃)	6.8
H ₂ O at 105 °C	1.1
H ₂ O 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 NO₃⁻, SO₄²⁻ 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 NO₃⁻, SO₄²⁻, Cl⁻ and PO₄³⁻ 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.

NO₃⁻, SO₄²⁻, PO₄³⁻ and Cl⁻ concentrations were obtained using a Hach spectrophotometer (DR/2400) by performing UV spectrophotometric, barium chromate, and molybdenum blue spectrophotometric methods for NO₃⁻, SO₄²⁻, and PO₄³⁻ concentrations determination; silver nitrate titration method for determination of Cl⁻ concentration. The concentrations of Ca²⁺, Mg²⁺, and Al³⁺ 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, Fe₂O₃, SiO₂, Al₂O₃, 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

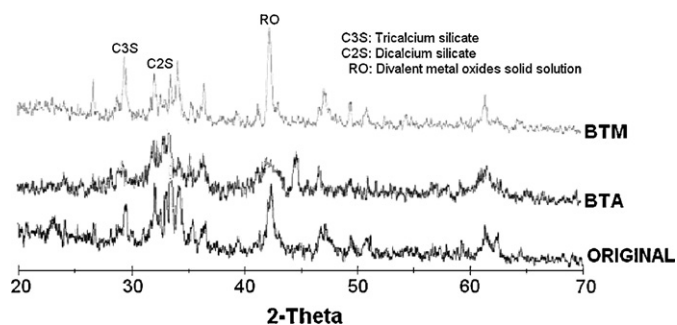


Fig. 1. XRD spectra of BOFS.

and total porosity increased. This could be regarded as effect of mechanochemistry while BOF slag was being ground. On the other hand, acid treatment led to show BTA more porous and bigger surface area than BTM, while density of materials decreased.

3.1.2. XRD and SEM analysis

The XRD spectrums are shown in Fig. 1. It shows peaks were complex in spectrum and some of them overlapped. Major minor products were RO phase (divalent metal oxides solid solution), dicalcium silicate and tricalcium silicate. With an increase in grinding time, strength of peaks fell down and this indicated crystal degree of BOF slag decreased by the effect of mechanochemistry. It also demonstrated ground surface was going to be amorphous and this always led to materials activated for its characteristics for BTM. For BTA sample, peaks were complex in spectrum too and some of them were weakened due to crystalline materials had reaction with acid.

The scanning electron microscope (SEM) observation of BOF slag adsorbents is shown in Fig. 2. It was observed that by 3 h ground for BTM, more and more pores were exposed, and it was predicted these pores would do positive effect on adsorption. It also showed that by acid treatment, surface of BTA was coarser. Acid treatment led to an increase of porosity volume and connects the pores.

3.2. Adsorption characteristics

3.2.1. Adsorption capacity

The results of the phosphate adsorption isotherm experiments are shown in Fig. 3. The phosphate adsorption capacity increased with the phosphate equilibrium concentration increasing from 10 to 500 mg/L (pH 7.0–7.2). This capacity of the BTM, BTA and original BOF slag was increasing approximately from 0.99 to 43.1, 0.98 to 41.6 and 0.82 to 37.6 mg P/g adsorbents, respectively. The results showed that with a further increase of the phosphate equilibrium concentration, the increase of the adsorption capacity was less significant. Especially at phosphate concentration of 10 mg/L which simulated the phosphate level in typical municipal wastewater, the phosphate adsorption removal rate was 98–99% by BTA and BTM adsorbents.

According to the results of the phosphate adsorption isotherm experiments, the modified BOF slag had higher adsorption capacities than the unmodified sample. It was believed that the surface structural changes and chemical composition of the material play the most important roles in the adsorption capacities of the phosphate. Table 2 clearly showed that by milling and acid treatment, the specific surface area of BOF slag increased from 0.4 to 0.75 and 0.9 m²/g, respectively, which resulted from opening of channels and enlargement of aperture diameter and the creation of microporosity. For another, the negative charges of the adsorbent surface may be decreased after treatment, and this would be more signif-

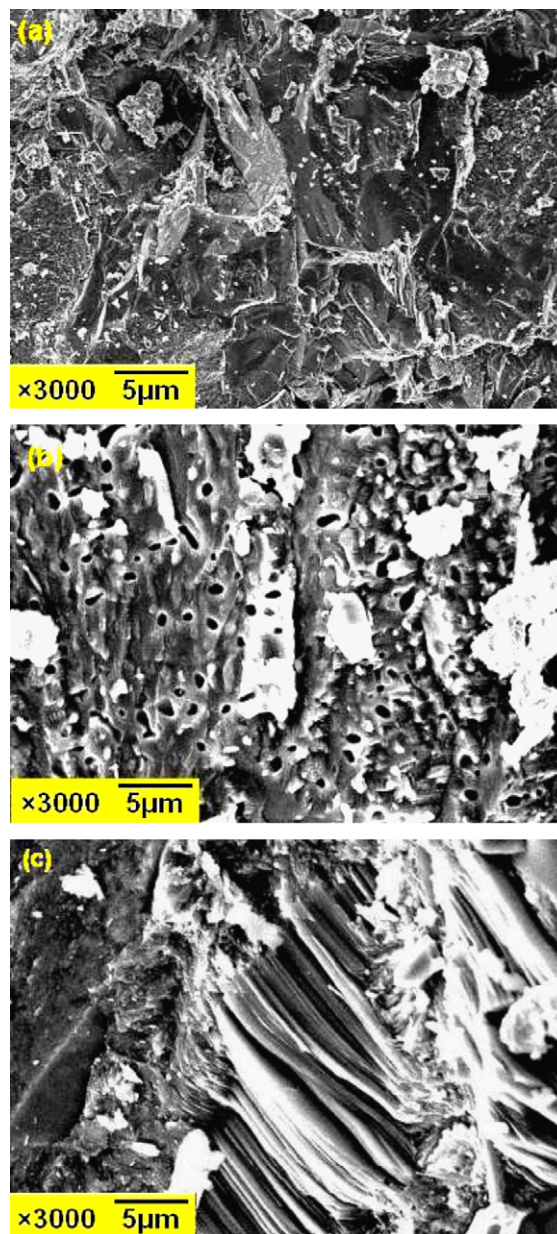


Fig. 2. SEM micrographs: (a) original BOFS; (b) 3 h ground by mill and (c) treated by acid.

icantly in favor of the adsorption of anions in solution. Chemical composition of adsorbents had great effect on phosphate adsorption. Due to BOF slag contains CaO (45.4%), Al₂O₃ (6.8%) and MgO (7.3%), the variation of soluble calcium, aluminum and magnesium hydrolysis during BOF slag hydrolysis and adsorption process revealed that chemical reaction occurred and precipitation was formed then [12].

Two typical isotherms, as described below in Eqs. (1) and (2), were used for fitting the experimental data:

$$\text{Freundlich equation: } q_e = KC_e^{1/n} \quad (1)$$

$$\text{Langmuir equation: } q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2)$$

where, q_m is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration (mg/L). The other parameters are different isotherm constants, which can be determined by regression of the experimental data. In this study, the isotherm data from

Table 3
Estimated isotherm parameters for phosphate adsorption

BOFS	Freundlich equation $q_e = KC_e^{1/n}$				Langmuir equation $q_e = \frac{q_m b C_e}{1 + b C_e}$			
	K	1/n	R ²	S.E.	q _m (mg/g)	b (L/mg)	R ²	S.E.
BTM	5.0262	0.508	0.9974	0.042	60.7	0.038	0.9754	0.125
BTA	2.6558	0.594	0.9972	0.035	43.1	0.018	0.9852	0.140
ORIGINAL	0.4833	0.918	0.9979	0.052	32.9	0.013	0.9821	0.135

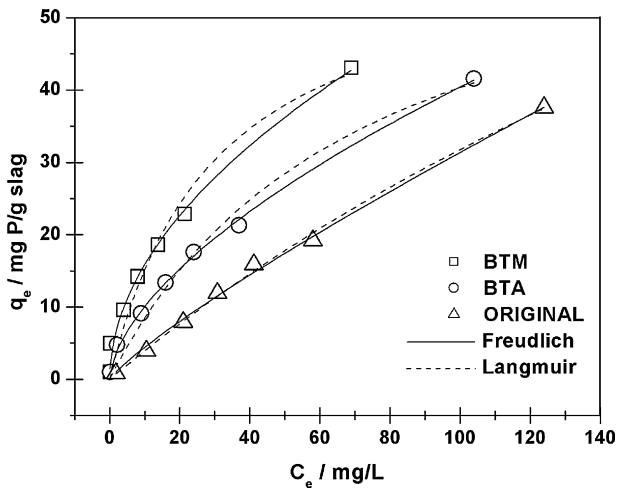


Fig. 3. Phosphate adsorption isotherm regression by Freundlich and Langmuir equations.

Fig. 3 were fitted to the above two models by non-linear regression using the method of least squares. The estimated model parameters with the correlation coefficient (R^2) and the standard error (S.E.) of estimate are shown in Table 3. The fitting curves from the two isotherms are also illustrated in Fig. 3. It is shown that the experimental data of phosphate adsorption on these samples could be well fitted by the isotherms. Clearly, the Freundlich equation provided better fitting in terms of R^2 and S.E. values.

The phosphate adsorption on different materials has been widely studied during recent years [2,3,7,12,13]. At respective optimal pH value and approximately the same phosphate equilibrium concentration, their reported phosphate adsorption capacities (mg P/g adsorbent) are given in Table 4. For comparison, the phosphate adsorption capacities of natural and modified BOF slag obtained in this study are also listed in Table 4. The modified basic oxygen furnace slag used in this study appeared to have a higher phosphate adsorption capacity than other materials, which may be attributed to its higher percentage of CaO, and chemical precipitation is a more significant contributory phenomenon to the removal of phosphate than physical adsorption. Test result was similar to literature [3], which used blast furnace slag as adsorbent. Hence, the relatively low cost and high capabilities of the modified BOF slag make them potentially attractive adsorbents for the removal of phosphate from aqueous solution.

Table 4
Phosphate adsorption by different low-cost adsorbents with 1 g of adsorbent and 150 mg/L of P initial concentration

Materials	Capacity (mg/g)	Literature
Fly ash	6.6	[2]
Blast furnace slag	10.5	[3]
Iron oxide	8	[7]
Montmorillonite	3.2	[12]
Basic oxygen furnace slag	14.2	This study

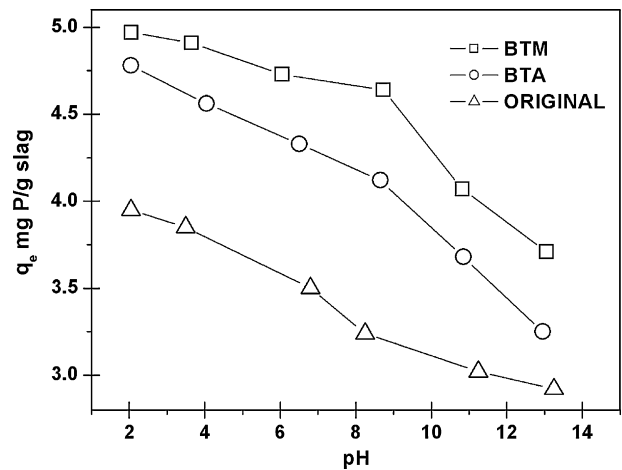


Fig. 4. Effect of pH on adsorption capacity.

3.2.2. Effect of pH on phosphate adsorption

The effect of pH on the phosphate adsorption on the three adsorbents for pH between 2 and 13 is presented in Fig. 4. It can be found that the phosphate adsorption tends to decrease with the increase of pH, for the BTM, from 4.97 mg P/g at pH 2.05 to 3.71 mg P/g at pH 13.05; for the BTA, from 4.87 mg P/g at pH 2.05 to 3.25 mg P/g at pH 12.95.

The pH of the aqueous solution is an important variable that influences the adsorption of anions and anions at the solid–liquid interfaces. As can be seen from Fig. 4, the pH value of the phosphate solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The phosphate adsorption on the three adsorbents tends to decrease with the increase of pH. Similar trends were also observed for phosphate adsorption from other researches [2–4]. This is likely attributed to the fact that a higher pH value causes the surface to carry more negative charges and thus would more significantly repulse the negatively charged species in solution. Therefore, the lower adsorption of phosphate at higher pH values resulted from an increased repulsion between the more negatively charged PO_4^{3-} species and negatively charged surface sites.

The values of zeta potential of the slag particles were measured and results were given in Fig. 5. The measured zeta potential shows the variation of surface charge from +85.8 to -40.7 and 80.2 to -35.6 mV, corresponding to a pH change from 2 to 13.

3.2.3. Desorption study

Phosphate desorption tests were conducted with the different initial phosphate concentrations (10–500 mg/L) at pH 7.0–7.2. Results were shown in Table 5. The phosphate desorbability can be defined as the ratio of the desorbed phosphate over the total adsorbed phosphate by the adsorbent. Therefore, the desorbability of phosphate can be used to indicate the degree of phosphate desorption from the adsorptive materials. The data in Table 5 show that the desorbability of phosphate is about 0.24–1.25% for all samples, regardless of the initial phosphate concentrations used for

Table 5
Desorbability of the adsorbed phosphate on BOFS

Initial concentration (mg/L)	Adsorbents	Adsorbed P (mg/g)	Desorbed P (mg/g)	Desorbability (%)
10	BTM	0.99	0.002	0.24
	BTA	0.98	0.011	1.08
	ORIGINAL	0.82	0.009	1.07
	BTM	4.97	0.013	0.26
50	BTA	4.78	0.057	1.20
	ORIGINAL	3.95	0.041	1.04
	BTM	9.6	0.031	0.32
100	BTA	9.1	0.107	1.18
	ORIGINAL	7.9	0.077	0.98
	BTM	14.2	0.062	0.44
150	BTA	13.4	0.167	1.25
	ORIGINAL	11.9	0.145	1.22

the batch adsorption experiments. The amount of the desorbed phosphate is slightly increased with the increase of the adsorbed phosphate. These results indicate that the phosphate adsorption on the BOF slag is not completely reversible and the bonding between the sample particles and adsorbed phosphate is likely strong. It is relatively difficult for the adsorbed phosphate to be desorbed from the samples. On the other hand, the result which the desorbability of BTA is more than that of BTM showed that chemical reaction, such as precipitation, was playing more important role than physical adsorption. This was due to BTM was more active on chemical reaction in solution, while BTA showed more specific surface area and porosity for physical adsorption of phosphate.

3.2.4. Selective adsorption

The effects of Cl^- , NO_3^- and SO_4^{2-} on the phosphate adsorption capacity of the BOF slag are shown in Fig. 6. The pH was 7.0–7.2 and added anion concentration varied from 100 to 1000 mg/L while phosphate initial concentration was 50 mg/L. At pH 4.0–4.2, despite the wide variation in the concentrations of Cl^- , SO_4^{2-} and NO_3^- , from 100 to 1000 mg/L, there was no significant difference in the adsorption capacity of the BTM, BTA, and original BOF slag. Results show that P adsorption capacity of BTM ranged from 4.75 to 4.33 with Cl^- , 4.65 to 4.20 with SO_4^{2-} , and 4.80 to 4.43 mg P/g slag with NO_3^- , respectively; for BTA, adsorption capacity ranged from 4.45 to 3.98 with Cl^- , 4.38–3.85 with SO_4^{2-} , and 4.42–4.02 mg P/g slag with NO_3^- ; while for original materials, 3.60–3.02, 3.52–2.85, and 3.48–3.12 mg P/g slag. It can be seen from Fig. 5, the effect of SO_4^{2-} on phosphate adsorption was more than any other anions. Based

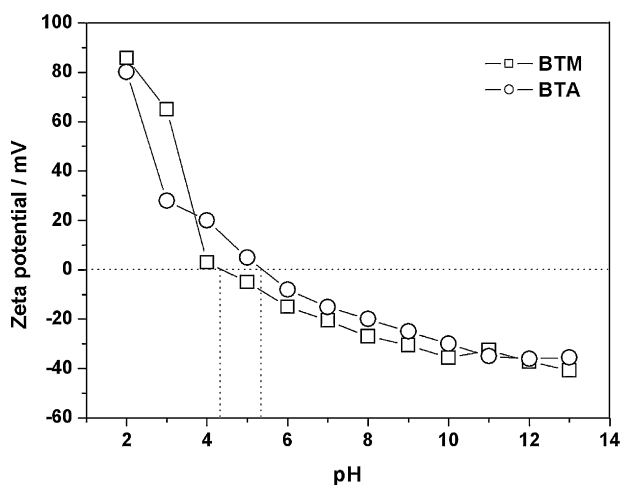


Fig. 5. Zeta potential results of BTM and BTA slags.

on results, the selectivity of anions adsorption onto BOF slag was in the order Cl^- , NO_3^- , SO_4^{2-} and PO_4^{3-} . The selectivity of phosphate adsorption onto BOF slag was 44–450 times that of different anions according to results from Table 6. This selectivity was weaker than those provided from previous researches [11,14] which concluded 1000–7000 and 1000–3000 times during phosphate adsorption. This was due to higher capacity of BOF slag for adsorption of various anions. On the other hand, various anions will have effect on phosphate adsorption onto BOF slag due to the amount of phosphate adsorbed in the presence of various anions solutions was less than that in single solutions. However, the results of selectivity experiment still indicate that BOF slag could selectively adsorb phosphate ion and was suitable for the removal of phosphate from aqueous solutions.

3.3. Adsorption mechanisms

Results of the pre-hydrolysis process of the BOF slag followed by the phosphate adsorption process are shown in Fig. 7. The studies were carried on BTM and BTA adsorbents. The change of pH and concentration of Ca(II), Mg(II) and Al(III) were emphasized. The results showed that the BOF slag appeared a strong hydrolysis potential characterized by an initial rapid release of OH^- in the first 7 days, as well as total calcium, magnesium, and aluminum in the 21 days followed by a slow release, which was monitored until an equilibrium value or concentration was reached. Thereafter, phosphate was added on 28th day to initialize the adsorption process.

During the hydrolysis stage, an increase of pH from 7.0 to 12 for BTM and 9.8 for BTA respectively were observed indicating complex reactions between the calcium magnesium, and aluminum oxide with H_2O , which leads to the increases in pH. Concurrently, the concentrations of total calcium, magnesium, and aluminum increased

Table 6
Selectivity of phosphate adsorption in presence of anions

Anion ^a	Adsorbents	P adsorbed (mg/g)	Anion adsorbed (mg/g)	Selectivity
Cl^-	BTM	4.75	0.015	317
	BTA	4.45	0.012	371
	ORIGINAL	3.60	0.008	450
NO_3^-	BTM	4.80	0.017	282
	BTA	4.38	0.016	273
	ORIGINAL	3.52	0.009	391
SO_4^{2-}	BTM	4.65	0.105	44
	BTA	4.42	0.080	55
	ORIGINAL	3.48	0.058	60

^a Concentration of Cl^- , NO_3^- and SO_4^{2-} was 100 mg/L; concentration of PO_4^{3-} was 50 mg/L.

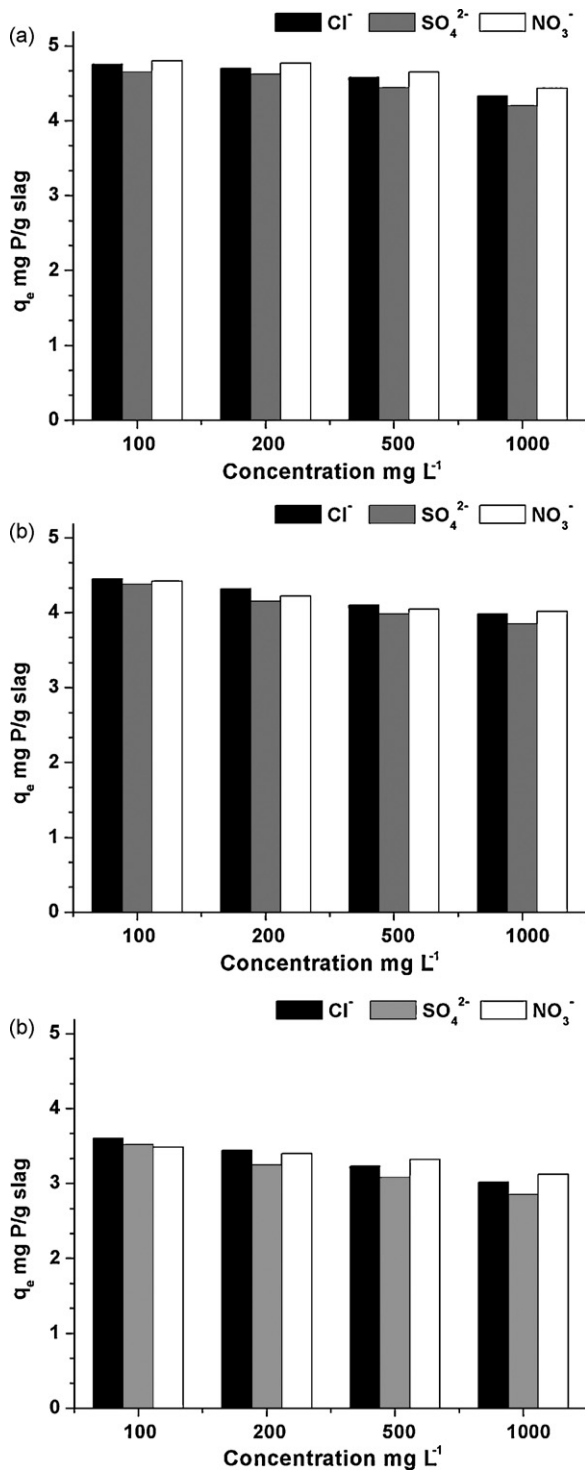


Fig. 6. Effects of Cl⁻, SO₄²⁻ and NO₃⁻ on phosphate adsorption (a) BTM; (b) BTA and (c) ORIGINAL slag.

from 0 to 98 mg/L, 10, and 8 mg/L for BTM, while from 0 to 30 mg/L, 4 and 3 mg/L for BTA respectively, as the hydrolysis progressed. The amount of total calcium, magnesium, and aluminum released from BTM was more than those from BTA, and this was thought that BTA was treated by acid and washed by deionised water for five times. Oxides in BOF slag were reacted with H⁺, and almost of calcium, magnesium and aluminum ions were washed away, hence, the hydrolysis of BTA was weak which led to lower pH and less

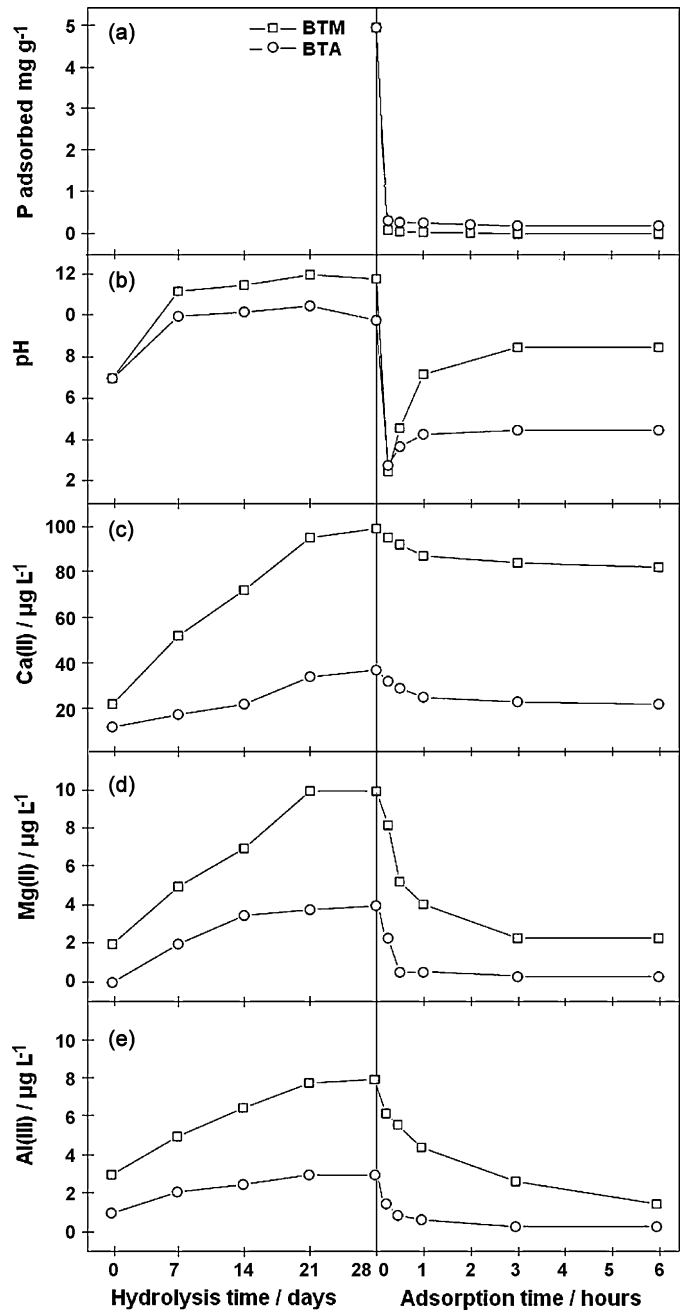


Fig. 7. Variation of pH, Ca(II), Mg(II) and Al(III) during hydrolysis and phosphate adsorption process (a) P adsorbed; (b) pH; (c) Ca(II); (d) Mg(II) and (e) Al(III).

total calcium, magnesium, and aluminum release. However, during the adsorption process, the decrease of phosphate occurred simultaneously with decrease of pH (12–2.5, 9.8–2.8), and concentration of total calcium, magnesium, and aluminum (Fig. 6, adsorption process). These results show valuable insights that are vital to the understanding of the adsorption mechanism and which are further discussed in this study.

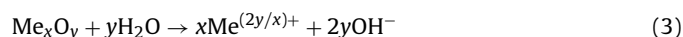
4. Discussion

4.1. Hydrolysis of BOF slag

The increase of pH from 7.0 to 12 during the hydrolysis stage of the BTM (Fig. 7b) shows that such material has a particularly strong

tendency to hydrolyze in water. When BOF slag is added to water, it can be expected that the BOF slag is surrounded by a tightly bound shell of oriented water molecules (HO–H) on its surface and the positive charge on the BOF slag tends to weaken the forces holding the protons (–H) to the oxygen, and thus the hydroxyl are relatively easy to release. The release of OH[–] causes the increase of pH which suggests a change in the number of OH[–] bonded on the surface of the BOF slag, leading to a hydroxylated surface [13,15]. These surface hydroxyl groups can take part in complex reactions with metal ions and ligand [16].

At the same time, the decrease in pH was accompanied by an increase in the concentration of total calcium, magnesium, and aluminum (Fig. 7c–e). The change in the concentration is attributable to hydrolysis and ionization reaction. The reactions occurring during the hydrolysis stage can be possibly explained by Eq. (3). This equation only reflects simple reaction between oxides with H₂O for explanation of pH changing after hydrolysis start.



While the acid-treated slag showed weak hydrolysis capacity due to oxides reacted with H⁺ and the cations were washed away from samples. Another explanation about strong hydrolysis of BTM was that, after being ground, slag was activated and more easily occurred hydrolysis reaction with H₂O.

4.2. The pH dependence of adsorption

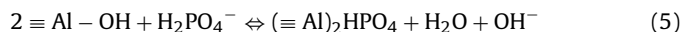
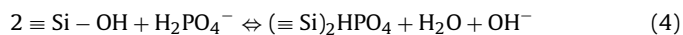
The results of the effect of pH on adsorption capacity show that the adsorption capacity of BOF slag is strongly dependent on solution pH and several reasons may be adduced to this. First, the change of surface characteristics can affect adsorption capacity to some extent. The surface characteristics of BOF slag, such as the surface charge (as related to the zeta potential measurements) as shown in Fig. 5 resulted from proton transfers at the surface [15]. It can be seen from Fig. 4 that as pH increases, the surface charge of the BOF slag, which is pH-dependent, changes from positive to negative. This gives information regarding the changing nature of the surface of the slag. The increase of OH[–] in solution could affect the electrostatic properties of the slag. The adsorption of –OH on the surface of slag leads to the formation of a new charged layer, making the slag surface being a comparable lower affinity to phosphate. With an increase in pH, OH[–] competes strongly with phosphate for active sites, which affects the adsorption capacity. This therefore implies that adsorption is favored by low pH values and that adsorption capacity would be higher at low pH values than at high pH values. This agrees with the lots of reports from previous researches [1,2].

4.3. Adsorption mechanisms

4.3.1. Ligand exchange

Unlike the hydrolysis process, the pH rapidly decreased at first several minutes from 12 and 9.8 to 2.5 and 2.8 coupled with decrease of phosphate, then increased and reached plateau after 1 h during adsorption process (Fig. 7a and b). The rapid decrease of pH was attributed to increase of H⁺ which was brought by adding H₂PO₄[–] (contains some H₂SO₄) into solution. The increase of pH is a sign of the release of OH[–] and consume of H⁺. This indicates that phosphate is adsorbed by surface complex such as the ligand exchange between phosphate (in solution) and –OH (on the surface of BOF slag). The –OH involved in the ligand exchange process is a kind of nonstructural OH, formed during either the formation process of BOF slag in acid treatment or the hydrolysis process. From Table 1 and Fig. 1, it can be concluded that BOF slag contains much more silicon and aluminum oxides that show its mineral composition as silicon oxide tetrahedron and aluminum oxide tetrahedron

in materials. The ligand, –OH would bond with such tetrahedron if Si–O and Al–O bond can be cut by some kinds of forces. It can be found that mechanochemistry by grind and acid treatment was such forces. Hence, when ligand exchange process occurred, the phosphate adsorption process could be described as



Although the ligand exchange may be one of the major mechanisms of phosphate adsorption onto BOF slag, it should be pointed out that the phosphate adsorption is a complicated process due to the differences in the formation of phosphate–silicon and phosphate–aluminum complexes. It was concluded that phosphate adsorbed onto silicon and aluminum oxides by forming not only the bidentate or binuclear complexes (products from above equations), but also the monodentate complexes [16,17]. Thus, the phosphate adsorption with silicon and aluminum in a real adsorption system could be far more complicated.

4.3.2. Precipitation effect

It is known that in wastewater applications, the most common and successful method to precipitate phosphate involves the dissolved cations such as Al³⁺, Ca²⁺, and Mg²⁺. Solubility diagrams for metal phosphates in pure water show that when iron and aluminum are present, iron phosphates (FePO₄) and aluminum phosphates (AlPO₄) are the stable solid phases in the low pH range (<6.5) [11]. However, total iron was not determined in this study. calcium phosphates (Ca₃(PO₄)₂) and magnesium phosphates (Mg₃(PO₄)₂) are the stable solid phases in the pH range of 6.6–7.2 in the presence of calcium and magnesium. As shown in Fig. 7b, the pH changed from 11.8 to 8.5 and 8 to 4.5 for BTM and BTA, respectively after phosphate adsorption. For BTM, there were stable solid precipitation phase such as calcium phosphates, magnesium phosphates and aluminum phosphates in the pH range of 11.8–8.5 accompanied with a rapid decrease of phosphate concentration. While for BTA, pH of phosphate adsorption was not fit for such precipitations. This might to be a reason why the concentration of total calcium, magnesium and aluminum during hydrolysis and phosphate adsorption changed largely through the Fig. 7c–e. It pointed out that calculated solubility limit of total calcium, magnesium and aluminum should be much more than that of determination from hydrolysis experiments. This was thought to be multi-ions interactions attributions in the system. It was thought from Fig. 5 and 7b that the precipitation of metallic salts such as Al³⁺, Ca²⁺, and Mg²⁺ was less effective as a result of the electrostatic attraction between adsorbate and adsorbent which affected the removal of phosphate from aqueous solution. This result indicates that the removal of phosphate is mainly based on physical interactions and hardly the precipitation of metallic salts such as Al³⁺, Ca²⁺, and Mg²⁺ on the BTA. However, the intricacies of the phosphate–BOF slag adsorption system make a distinctive quantitative analysis of the amount of adsorption and chemical precipitation rather difficult.

5. Conclusions

Results obtained from this study have provided some valuable information regarding the characteristics and mechanism of phosphate adsorption by basic oxygen furnace slag. In particular

- (1) The maximum adsorption capacities varied from 0.99 to 43.1, 0.98–41.6 and 0.82–37.6 mg P/g when the initial phosphate concentration ranged from 10 to 500 mg/L for basic oxygen furnace slag treated by mill (BTM), acid (BTA) and original (Original)

slag, respectively. Solution pH has been shown and established as a vital factor influencing the adsorption behavior. It can be found that the phosphate adsorption tends to decrease with the increase of pH. It is believed that phosphate adsorption by BOF slag is highly dependent on solution pH and the surface characteristics of the slag.

- (2) It is shown that the experimental data of phosphate adsorption on these samples could be well fitted by the isotherms. Clearly, the Freundlich equation provided better fitting. The desorbability of phosphate is about 0.24–1.25%, and it is relatively difficult for the adsorbed PO_4^{3-} to be desorbed. The selectivity of anions adsorption onto BOF slag was in the order Cl^- , NO_3^- , SO_4^{2-} and PO_4^{3-} . The selectivity of phosphate adsorption onto slag was 44–450 times.
- (3) Ligand exchange is shown to be the dominating mechanism based on exploratory evidence from the adsorption mechanism of phosphate onto the BOF slag. Ligand exchange and precipitation have effect on phosphate adsorption simultaneously. Although chemical reaction between phosphate and dissolved ions was demonstrated, it is believed that the chemical reaction played only a marginal role in the phosphate removal process.
- (4) Besides, all experiments were performed at room temperature and artificial wastewater containing phosphate. Hence, it is thought to be very interesting to study thermodynamic and kinetics characteristics while using phosphate wastewater derived from industry as adsorbates and basic oxygen furnace slag as adsorbents.

Acknowledgments

Financial and technical supports from ZhongGu New Materials Co. Ltd. and Wuhan University of Technology “Key Laboratory for Silicate Materials Science and Engineering Ministry of Education” in China are gratefully acknowledged.

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