



Fly ash as reactive sorbent for phosphate removal from treated waste water as a potential slow release fertilizer



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ABSTRACT

There is interest in recovering phosphate (P(V)) from secondary sources, such as waste water streams for potential use as fertilizers reducing the environmental impacts of P(V) discharges and providing alternative phosphorus sources. The goal of this work was to provide an understanding of P(V) removal by fly ash (FA) from coal power plants. Phosphate removal using Ca(II) rich FA was evaluated in terms of i) sorption equilibrium, ii) sorption kinetics under the expected pH values and P(V) concentrations in wastewaters effluents, and iii) P(V) availability of the FAs in agricultural applications. At the pH values (6–9) expected for wastewater effluents, P(V) removal proceeds as a combination of CaO(s) dissolution and brushite (CaHPO₄(s)) formation on the FA particles. This process avoids the formation of relatively insoluble Ca–phosphates, such as, hydroxyapatite (Hap) with limited fertilizing properties. High P-loadings were achieved (up to 50 mgP-PO₄/g FA (5% P(V) by weight)) at a pH of 8. The removal kinetics data were well described as a diffusion-based process of phosphate ions (H₂PO₄⁻ and HPO₄²⁻) on FA particles, and the CaO(s) dissolution process was discarded as the rate controlling step. The P(V) availability from loaded samples was determined via an agronomical assay with NaHCO₃ solutions with P(V) release ratios of 10–30 mgP-PO₄/g in FA, confirming the appropriateness of this material as a potential fertilizer, even in calcareous soils.

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1. Introduction

Increasing energy demands worldwide have led to increased utilisation of coal and, thus, the production of large quantities of fly ash (FA) as a waste product [1–3]. In 2011, coal-fired generation accounted for 30% of the world's electricity supply, and its share is anticipated to reach 46% by 2030. Sustained prices for oil and natural gas make coal-fired generation relatively economically attractive, particularly in nations with rich coal resources, such as China, the USA and India [4,5]. Recycling coal fly ash (CFA) can be a good alternative disposal method and could provide significant economic and environmental benefits. The global average FA utilisation ratio is estimated to be nearly 25% [6,7]. Most FA is alkaline, and its surface is negatively charged at high pH values; thus, it could be used to remove metal ions from solutions by

precipitation [8] or sorption [3,8,9]. Furthermore, it contains a certain amount of unburnt carbon, which has a high adsorption capacity for organic compounds [5].

Phosphorous (P) is an important element in industry and agriculture and is frequently present in domestic, industrial, and farming wastewaters. In the last decades, phosphate has been considered an environmental concern because of its role in the eutrophication of water bodies [10,11]. Currently, it is becoming increasingly economically concerning because its natural deposits are diminishing because of the continuous growth of the world population. Then, such wastewaters and sludge containing P (less than 1% by weight) are considered secondary P sources that should be mined [12]. In the European Union, P has been included in the list of Critical Elements, and new technologies to recover P from secondary sources are being promoted. Most of these technologies have focused on the recovery of P from solid wastes (e.g., incineration ashes), whereas for its recovery from liquid wastes, most technologies have focused on the recovery of struvite (MAP) from concentrated streams.

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Few efforts have been devoted to P recovery from diluted streams, although various removal techniques are available [13]. Chemical precipitation and coagulation processes are not cost effective and polymeric ion exchangers are not applicable because of the presence of dissolved and particulate organic matter. Thus, phosphate-removal/recovery solutions have focused on the use of low-cost inorganic materials with high performance in terms of equilibrium and kinetics. CFA has attracted substantial attention as a potential material for phosphate removal because it is easily available and cost effective [14–16]. The presence of aluminium, iron, calcium and magnesium oxides imbues FA with suitable properties for phosphate removal by complexation or precipitation of Ca/Mg-phosphates [3,17]. Cheung and Venkitachalam [18] associated the removal of phosphate by FA containing high- and low-calcium contents with Ca-phosphate precipitation. Johansson and Gustafsson [19] proposed the formation of amorphous calcium phosphate and/or octacalcium phosphate as the major P-removal mechanism and suggested the direct formation of hydroxyapatite (Hap) as the predominant removal mechanism. Although it is generally accepted that phosphate removal by FA involves adsorption and/or precipitation mechanisms, the interaction between phosphate and Ca(II) remains incompletely described [12].

Additionally, reduced progress has been done to obtain a solution for the exhausted ash, and recently, the possibility of using this material to improve the soil quality of areas degraded or for forestry applications has been proposed [5]. However, because of the low solubility and bio-availability of the Ca-phosphate mineral that is typically precipitated ($\text{Ca}_5(\text{PO}_4)_3\text{OH}(\text{s})$, $\log K_{\text{so}} = 116.8$) [20], efforts have been made to prepare more soluble minerals, such as brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\log K_{\text{so}} = 6.59$) [21] with properties suitable as slow-release fertilizers. These materials include Ca-silicates, such as wollastonite [22]; Ca-Al layered double hydroxide [23,24]; natural zeolites [25]; and FA [26]. However, the utilisation of powdered inorganic adsorbents for selective P removal and its potential use as slow-release fertilizers remain under development.

In this study, two different types of FA from two coal power stations with different CaO(s) contents (Los Barrios (FA-LB (2.8% w)) and Teruel (FA-TE (4.8% w))) were evaluated as adsorbents for phosphate recovery. The equilibrium and kinetic performances for phosphate sorption were studied and characterised by varying the experimental conditions, such as the solution pH and initial phosphate concentration. The phosphate-sorption mechanism was evaluated using a speciation method. Although the phosphate-removal mechanism is complex, the results are presented in terms of equilibrium isotherms and kinetic parameters.

2. Materials and methods

2.1. Batch equilibrium experiments of FA dissolution

FA samples (0.2 g) were mechanically mixed in polyethylene tubes with deionised water (10 mL) at different initial pH values (6–9) and at room temperature ($21 \pm 1^\circ\text{C}$) until equilibrium was achieved. The influence of the initial pH on FA dissolution was evaluated by varying the initial pH with 0.1-mol/L HCl or NaOH

solution. After phase separation with a 0.2- μm syringe filter, the equilibrium pH was measured using a pH glass electrode (Crison GLP22); the total Ca, Na, Mg, and K concentrations were measured by ion chromatography (Thermo Scientific Dionex ICS-1100); and the total Si, Al, Fe, P, and Ti concentrations were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Atomic Emission Spectrophotometry (ICP-AES) (X-Series II, Thermo Fisher SCIENTIFIC).

FA selection samples in this study (LB, TE) was based on having the highest Ca(II) and Mg content and the lowest toxic metallic and non-metallic traces. This selection was based on leaching studies for both samples that were published previously [27].

2.2. Batch equilibrium experiments of phosphate removal

Phosphate solutions were prepared by dissolving a weighed amount of $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ in deionized water (Milli-Q-Academic-A10 apparatus). FA samples from Teruel (FA-TE) and Los Barrios (FA-LB) (0.2 g) were mechanically mixed in polyethylene tubes with an aqueous phosphate solution (10 mL) at different initial concentrations (100–16000 mgP- PO_4/L) at room temperature ($21 \pm 1^\circ\text{C}$) until equilibrium was achieved. The influence of pH on the phosphate sorption was evaluated by varying the initial pH with 0.1 mol/L HCl or NaOH solution. After phase separation, the equilibrium pH was measured and the total phosphate concentration was measured by ion chromatography or by visible absorption spectrophotometry (UVmini-1240) [28]. The P(V) equilibrium sorption capacity was determined using Eq. (1).

$$q_e = \frac{(C_0 - C_e)v}{m_s} \quad (1)$$

where C_0 (mg/L) and C_e (mgP- PO_4/L) represent the initial and equilibrium total P(V) concentrations, respectively; v (L) is the aqueous solution volume; and m_s (g) is the mass of the FA sample.

2.3. Batch kinetic experiments of phosphate removal

Batch kinetic experiments were performed by adding of 0.2 g of FA to solutions containing 100 and 500 mgP- PO_4/L . The tubes were mechanically shaken at $21 \pm 1^\circ\text{C}$, and samples were withdrawn sequentially at specified times. All tests were performed in triplicate and the average values are reported. The samples were centrifuged for 10 min and then filtered. The total phosphate concentration and pH of the initial and remaining aqueous solutions were measured.

2.4. Speciation of phosphate-loaded FA samples

The speciation of the adsorbed P in both FA samples (FA-TE and FA-LB) was achieved using a modified four-step sequential extraction methodology [29–31]. First, 30 mL aliquots of 1000 mg P- PO_4/L at pH 7 were equilibrated with pre-weighed tubes containing 3 g of FA. After shaking for 24 h at room temperature, the suspensions were centrifuged, and the FA powders were dried at 50–60 $^\circ\text{C}$. The adsorbed phosphate was sequentially extracted using 1 g samples and 50 mL of the extraction solutions described in Table 1. The samples were

Table 1
Chemical extraction scheme for phosphorus speciation of loaded FA samples.

Extraction solutions	Speciation name	P Speciation	Step
40-mL 2 M KCl for 2 h	KCl-P	Soluble and exchangeable P	1
40-mL 0.1 M NaOH for 17 h	NaOH-P	Fe- and Al-bound P	2
40-mL 0.5 M HCl for 24 h	HCl-P	Ca-bound P	3
40-mL 10 M $\text{HNO}_3/10\text{M HClO}_4$ (5/2)	Res-P	Residual P	4

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