Research article

Soluble phosphate fertilizer production using acid effluent from metallurgical industry

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ABSTRACT

Preventive and effective waste management requires cleaner production strategies and technologies for recycling and reuse. Metallurgical industries produce a great amount of acid effluent that must be discarded in a responsible manner, protecting the environment. The focus of this study was to examine the use of this effluent to increase reactivity of some phosphate rocks, thus enabling soluble phosphate fertilizer production. The effluent was diluted in deionized water with the following concentrations 0; 12.5; 25; 50; 75% (v v^{-1}), which were added to four natural phosphate rocks: Araxá, Patos, Bayovar and Catalão and then left to react for 1 h and 24 h. There was an increase in water (P_W), neutral ammonium citrate (P_{NAC}) and citric acid (P_{CA}) soluble phosphorus fractions. Such increases were dependent of rock type while the reaction time had no significant effect ($p < 0.05$) on the chemical and mineralogical phosphate characteristics. Phosphate fertilizers with low toxic metal concentrations and a high level of micronutrients were produced compared to the original natural rocks. The minimum amount of total P_2O_5, P_{NAC} and P_W, required for national legislation for phosphate partially acidulated fertilizer, were met when using Catalão and the effluent at the concentration of 55% (v v^{-1}). Fertilizer similar to partially acidulated phosphate was obtained when Bayovar with effluent at 37.5% (v v^{-1}) was used. Even though fertilizers obtained from Araxá and Patos did not contain the minimum levels of total P_2O_5 required by legislation, they can be used as a nutrient source and for acid effluent recycling and reuse.

1. Introduction

In many countries, appropriate industrial waste disposal is impaired by a lack of suitable landfill facilities in an era of expanding industrialization (Fang et al., 2013; Zamorano et al., 2011). This causes economic and operational problems, raising costs and often results in waste-disposal malpractice by companies. Effective management should aim to prevent or at least minimise waste generation by developing feasible technologies for waste recycling and reuse (Barik et al., 2014; Capón-García et al., 2014; Ghiani et al., 2014; Jadhav and Hocheng, 2012; Puig et al., 2013).

The metallurgical industry processes large amounts of ore that often contains low concentrations of the target metal. This results in the production of large amounts of solid, liquid and gaseous waste and therefore this industry is considered to have the greatest potential for hazardous waste generation (Agrawal et al., 2004; Leonard, 1978; Zheng and Kozinsk, 2006). In particular, the metallurgical industry produces significant amounts of effluent with high concentrations of toxic metals, which can cause several illnesses and serious physiological problems; these metals generally have a cumulative effect in the human body (Hegazi, 2013). Effluents that contain toxic metals can be treated by several processes including chemical precipitation, ion exchange, membrane filtration, electrodialysis and reverse osmosis (Adebowale et al., 2008; Fu et al., 2012; Inoue et al., 2010; Sadyrbaeva, 2014; Vinodh et al., 2011). However, these processes have high operational cost and low efficiency when a large amount of effluent has to be decontaminated (Post et al., 2009). Thus, it is important to develop alternative methods that are economically viable. Ideally these should involve effluent recycling and reuse.

Tantalum (Ta) and niobium (Nb) are additives used in special alloy manufacturing and have high aggregated value. These elements are extracted from the mineral pegmatite using a process

known as "three acid leaching" because it uses a mixture of sulfuric acid (H_2SO_4), hydrofluoric acid (HF) and hydrochloric acid (HCl). This extraction procedure generates a large volume of acid effluent whose composition makes it unsuitable and illegal for direct disposal into a receiving body (CONAMA, 2011). These effluents are therefore usually mixed with calcium hydroxide [$Ca(OH)_2$] to neutralize the acid and precipitate the heavy metals in their metal hydroxide forms. This process generates liquid waste and a metal-rich solid residue known as "mud" that is disposed to landfill, generating an environmental liability. Although this process accords with current waste legislation (CONAMA, 2011), it has a high cost and runs counter to the principles of recycling.

A potential alternative use for the acid effluent is the production of phosphate fertilizer. According to Braithwaite (1986) and Bolan et al. (1993) production of fully acidulated phosphate fertilizer, such as single superphosphate (SSP) involves reaction of H_2SO_4 with phosphate rock (PR) to produce monocalcium phosphate (MCP). The SSP product has a total P_2O_5 concentration of 16–20%, most of which is highly water-soluble (Bolland and Gilkes, 2008; Chien et al., 2010; Prochnow, 2003a). SSP is the most used phosphate fertilizer but its use is decreasing in favour of fertilizers with higher P concentrations (triple superphosphate – TSP and mono-ammonium phosphate – MAP). By using acid effluent from the metallurgical industry in place of H_2SO_4, it may be possible to reduce the cost of SSP at the same time as achieving significant industrial waste reuse. Such approach is in line with principles of "green chemistry" and "green engineering" for the development of new processes and elimination of waste, which is essential to achieve P sustainability (Withers et al., 2015). Therefore, this study aimed to evaluate the use of acid effluent from the metallurgical industry to increase phosphate rock reactivity, thereby producing a low-cost soluble phosphate fertilizer.

2. Materials and methods

2.1. Acid effluent and phosphate rocks

An effluent with high residual acidity was collected from the LSM Brasil S.A. chemical plant located in São João Del Rei, Minas Gerais State, Brazil. This effluent is the by-product of tantalum (Ta) and niobium (Nb) production from pegmatite using the three-acid ($H_2SO_4/HF/HCl$) leaching process. This process generates approximately 17,250 m^3 of effluent and 12,700 tons of mud at the plant each year, which needs to be treated before discharge into landfill and is currently an important part of the company's environmental liability.

The density and chemical composition of the effluent were determined using standard techniques. Concentrations of Cl^-, F^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, and Br^- were quantified using ion chromatography (DX500; Dionex, Sunnyvale–CA) with an electrochemical detector employing chemically suppressed conductivity and a mobile phase gradient of ultra-pure water, methanol and 0.1 mol L^{-1} NaOH as proposed by Silva et al. (2001). Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the contentrations of Cd, Ni, Pb, Cr, Al, Fe, Mn, Cu, Zn, Ca and Mg (PerkinElmer, Optima TM 4300DV); flame spectrophotometry was used to determine the concentration of K. The effluent had a high acidity and concentrations of cations and anions above those permitted by national legal limits (CONAMA, 2011) for disposal into a receiving watercourse (Table 1).

Three low-reactivity sources of natural phosphate rock (Araxá, Patos, and Catalão) and one high-reactivity source (Bayovar) were used. Table 2 shows the total P_2O_5, water-soluble P (P_W), citric acid soluble P (P_{CA}) and neutral ammonium citrate soluble P (P_{NAC}) concentrations of the PR.

Table 1
Acid effluent density, acidity and total content of chemical elements.

Density	Acidity[a]	Ca	Mg	K	Fe	Zn	Cu	Mn
g L^{-1}	(mol L^{-1})	mg L^{-1}						
1623	5.75	46	4.7	3438	13,595	44	57	1199

Al	Cr	Ni	Pb	Cd	F^-	SO_4^{2-}	NO_3^-	PO_4^{3-}	Cl^-
		mg L^{-1}					g L^{-1}		
897	59	126	56	11	109	791	18	19	128

[a] Acid buffering measured by neutralization of effluent to pH 7 with 0.5 mol L^{-1} of NaOH.

2.2. Phosphate rock solubilization

Effluent was added to each natural phosphate at the following dilutions with distilled water: 12.5; 25; 50 and 75% (v v^{-1}). Treatment with undiluted effluent was found impractical because the resulting product could not be completely dried.

Treatments were designed in a factorial scheme ($5 \times 4 \times 2$) evaluating five effluent concentrations diluted in deionized water (0; 12.5; 25; 50 and 75), four natural phosphate rocks (Araxá, Patos, Bayovar and Catalão) and two reaction times (1 and 24 h); there were three replications of each treatment.

Natural phosphates were sieved through a 0.149-mm sieve (100-mesh), and acid effluent (20 mL) added to 5 g aliquots of phosphate. The samples were placed into 50-mL centrifuge tubes and stirred at 150 rpm on a horizontal shaker table for 1 or 24 h at 25 °C. After stirring, open tubes were placed in a water bath at 80 ± 5 °C for 4 h inside an exhaustion chamber to reduce or eliminate excess fluorine. The samples were then dried in a forced-air oven at 105 °C for 72 h; they were subsequently weighed to determine mass increase. Final products were ground in an agate mortar, sieved through a 140-mesh sieve for standardization and stored in acrylic tubes.

2.3. Chemical analysis

Total P, water-soluble P (P_W), neutral ammonium citrate soluble P (P_{NAC}) and citric acid soluble P (P_{CA}) concentrations were determined as described by the Brazilian Ministry of Agriculture, Livestock and Food Supply Normative Instruction #5 (Brasil, 2007).

In each case, P was detected as the yellow phospho-vanado-molybdate complex. Concentrations of Ca, Cu, Zn, Cr, Ni, Fe, Al, Mn, Cd, Pb, As and Hg in each extract were determined by ICP-OES.

2.4. X-ray diffraction analysis

X-ray diffraction analysis of samples before and after effluent treatment was carried out using an X'Pert Pro MPD Panalytical diffractometer in the 4–60° 2θ range with Co-Kα radiation ($\lambda = 1.7889$ nm Å), at a rate of 0.02° 2θ s^{-1}, operated at 40 kV and 30 mA. The samples were ground to a grain size of about 200 mesh and placed on an excavated slide.

Table 2
Total, water (P_w), neutral ammonium citrate (P_{NAC}), and citric acid (P_{CA}) soluble P_2O_5 content in Araxá, Patos, Catalão and Bayovar phosphate rocks (PR).

PR	Total P_2O_5 (% w w^{-1})	Soluble P_2O_5 (% w w^{-1} total P)		
		Water	Citric acid	NAC + H_2O
Araxá	30	0.2	12	5
Patos	24	0.3	20	7
Bayovar	29	1.2	48	2
Catalão	37	0.2	13	4

NAC = neutral ammonium citrate.

2.5. Statistical analysis

Initially, error normality and variance homogeneity were tested. For non-conformity data, a log transformation was performed as proposed by Box and Cox (1964) through Statistica 5.0 software. Then, data were submitted to variance analysis evaluating effluent concentration over 1 h and 24 h reaction for each phosphate type by means of regression.

3. Results and discussion

3.1. Phosphate rock solubilization

Treatment of natural phosphates with acid effluent of increasing concentration generally increased P_W, P_{NAC} and P_{CA} fractions, indicating a positive effect of acid effluent on phosphate solubilization (Figs. 1–3). Phosphorus solubility is an important agronomical index of fertilizer efficiency, since soluble phosphates are more readily available to plants. Consequently, it can be expected that the acid effluent treated materials should enhance plant growth and production in P-limited soils, especially for shorter cycle crops (Bolland and Gilkes, 2008; Chien et al., 2010; Hammond et al., 1980; Prochnow et al., 2002).

Increasing effluent concentration resulted in an approximately linear increase in P_W for Araxá, Catalão and Bayovar phosphate rocks at both reaction times (Fig. 1; Table 3). At the highest acid effluent concentration (75%), 25, 50 and 72% of P in the treated product was water-soluble following 1-h treatments for Araxá, Catalão and Bayovar, respectively. Corresponding values for 24-h treatments were similar at 23, 53 and 92%, respectively. The most

striking result was observed for the Patos phosphate rock. The P_W fraction reached maximum values of 28% of total P at an effluent concentration of 45% (1 h reaction) and 25% at an effluent concentration of 52% (24 h reaction) (Fig. 1, Table 3).

The P_{NAC} fraction increased linearly with effluent concentration for all products. At the highest concentration (75%) for 1 h reaction, the P_{NAC} fraction represented 60, 53, 61 and 93% of total P for Araxá, Patos, Catalão and Bayovar, respectively. For 24 h reaction time, corresponding values were 52, 74, 62 and 97%, respectively (Fig. 2, Table 3).

The higher proportion of P_{NAC} compared to P_W, mainly for Araxá, can be attributed to impurities in the phosphates, especially Fe and Al. High Fe and Al contents were observed in Araxá phosphate (7.1% Fe_2O_3 and 11.6% Al_2O_3, w w^{-1}). These metals may react with the effluent forming Fe and Al phosphates, which are insoluble in water (Lehr, 1980; Prochnow et al., 2003a,b). At neutral pH, the citrate anion complexes metallic cations, conferring to the neutral ammonium citrate the ability to retrieve part of the P precipitated with Fe and/or Al (Braithwaite, 1987; Charleston, 1984). This highlights the need for high quality raw materials in the manufacture of fertilizers with high water solubility (Chien et al., 2010; Lehr, 1984; Syers et al., 2008).

Phosphorus solubility in 2% citric acid (P_{CA}) increased linearly with effluent concentration for both times, except for Patos (Fig. 3, Table 3). Further analysis showed that at the highest effluent concentration (75%) for a 1 h reaction time, the P_{CA} fraction reached values of 40, 57, and 80% (w w^{-1}) for Araxá, Catalão and Bayovar, respectively. Moreover, for Patos phosphate, the P_{CA} fraction reached 44% (w w^{-1}) at 47% (v v^{-1}) effluent concentration. For the 24 h reaction time, the P_{CA} fraction represented 32, 65, 56 and 82%
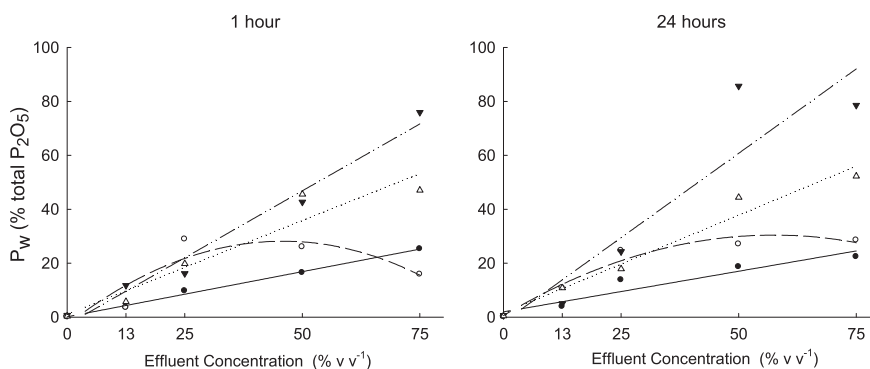

Fig. 1. Increasing Pw percentage in phosphate rocks with effluent addition, after 1 and 24 h reaction. The Pw content increased linearly with effluent concentrations using Araxá (A●), Catalão (C△), and Bayovar (B▼) rocks; and curvilinear using Patos (P○) one.

Fig. 2. Increasing P_{NAC} percentage in phosphate rocks with acid effluent addition, after 1 and 24 h reaction. The P_{NAC} content increased linearly with effluent concentrations using Araxá (A●), Catalão (C△), Bayovar (B▼), and Patos (P○).

Fig. 3. Increasing P_{CA} percentage in phosphate rocks with acid effluent addition, after 1 and 24 h reaction. The P_{NAC} content increased linearly with effluent concentration using Araxá (A●), Catalão (CΔ), and Bayovar (B▼) rocks; and curvilinear using Patos (P°) one, during 1 h reaction.
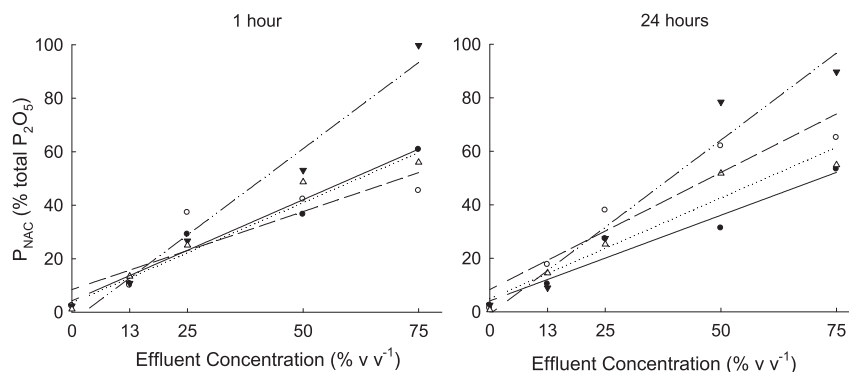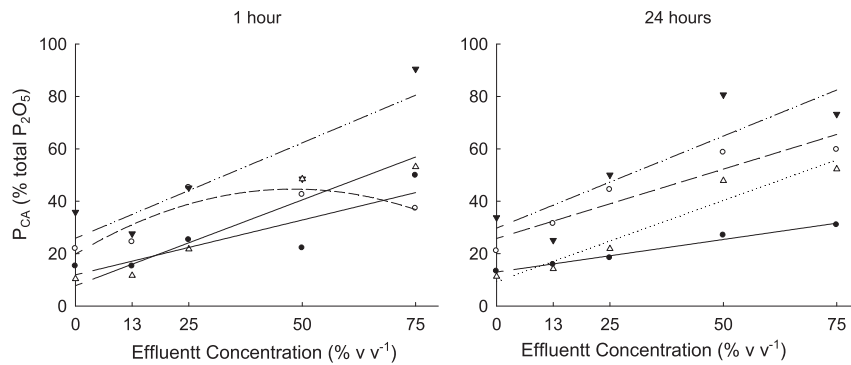
of total P for Araxá, Patos, Catalão, and Bayovar, respectively (Fig. 3, Table 3).

Treatment with acid effluent resulted in a mass increase and a consequent dilution of total P content in the treated products (Fig. 4, Table 3). This increase can be attributed to the incorporation of several elements sourced from the effluent into the final products, especially S, Cl, Fe, Mn and K (Table 1). The treated product exhibited mass increases of 151, 131, 118 and 129% (w w^{-1}) for Araxá, Patos, Bayovar and Catalão, respectively, at the highest effluent concentration (75%) after 1 h reaction (Fig. 4, Table 3).

The lowest phosphorus (P$_2$O$_5$) contents of 12, 16, and 11% (w w^{-1}) were found for products treated with the highest (75%) effluent concentration for Araxá, Catalão, and Bayovar, respectively. Interestingly, the lowest phosphorus content for Patos did not correspond with treatment with the highest effluent concentration, as shown in Table 3 and Fig. 4. The relatively low P$_2$O$_5$ content of these treated products relative to those of commercial fertilizers may limit their use, as they incur higher transportation and application costs per unit P. However, the approach may still be practical with the use of phosphate rock with higher P concentrations. Besides, the reuse of acid waste effluent for the dissolution and to increase solubility of phosphate rocks might reduce the costs

of fertilizer production and is an environmentally friendly approach.

Treatment of phosphate rocks with acidic effluent produced materials with characteristics similar to partially acidulated phosphates. However, their use as partially acidulated phosphates is dependent on achieving criteria based on minimum total and available P concentrations and maximum toxic element concentrations.

Regarding minimum P concentrations, Brazilian legislation requires that partially acidulated phosphate should have at least 20% total P$_2$O$_5$ (w w^{-1}), of which 45% is soluble in neutral ammonium citrate (P$_{NAC}$), and 25% is soluble in water (P$_W$) (Brasil 5/2007). Based on our results, these criteria would be met by adding effluent at 55% concentration to the Catalão PR, which has the highest initial total P$_2$O$_5$ content. This should produce a partially acidulated phosphate with 21% (w w^{-1}) total P$_2$O$_5$, 46% (w w^{-1}) P$_{NAC}$, and 26% P$_W$. Treating the Bayovar phosphate with effluent diluted to 37.5% (v v^{-1}) should produce a fertilizer with 19% (w w^{-1}) total P$_2$O$_5$, 45% (w w^{-1}) P$_{NAC}$, and 34% (w w^{-1}) P$_W$, which nearly satisfies all minimum requirements. For the other phosphate sources, it would not be possible to obtain partially acidulated fertilizers that meet the national legislation requirements for P$_W$ and P$_{NAC}$ concentrations.

Table 3
Regression equations for P$_W$, P$_{NAC}$, P$_{CA}$, and total P mass increase in phosphate rocks (PR) according to acid effluent concentration, after 1 and 24 h reaction.

PR	Reaction time (hours)			
	1		24	
	Equation	R^2	Equation	R^2
	P$_W$ (% total P$_2$O$_5$)			
Araxá	y = 0.125 + 0.335**x	0.99	y = 1.93 + 0.301**x	0.91
Patos	y = −2.79 + 1.35**x-0.015*x^2	0.81	y = 0.583 + 1.04*x-0.009*x^2	0.96
Catalão	y = 1.039 + 0.656**x	0.92	y = −1.51 + 0.726**x	0.97
Bayovar	y = −2.79 + 0.992**x	0.98	y = −1.84 + 1.25**x	0.86
	P$_{NAC}$ (% total P$_2$O$_5$)			
Araxá	y = 3.503 + 0.749**x	0.96	y = 4.04 + 0.641*x	0.95
Patos	y = 8.84 + 0.583*x	0.79	y = 8.29 + 0.875*x	0.91
Catalão	y = 4.243 + 0.756**x	0.96	y = 4.85 + 0.758**x	0.93
Bayovar	y = −3.49 + 1.289**x	0.98	y = −0.88 + 1.301*x	0.95
	P$_{CA}$ (% total P$_2$O$_5$)			
Araxá	y = 11.88 + 0.419*x	0.78	y = 12.95 + 0.249*x	0.98
Patos	y = 19.74 + 1.03*x-0.011*x^2	0.79	y = 25.77 + 0.529*x	0.99
Catalão	y = 7.74 + 0.655**x	0.93	y = 9.32 + 0.619**x	0.94
Bayovar	y = 25.84 + 0.728**x	0.82	y = 29.71 + 0.703*x	0.77
	Mass increase[1]/(% w w^{-1})		Total P[1]/(% w w^{-1} P$_2$O$_5$)	
Araxá	y = −8.54 + 2.13**x	0.97	y = 28.68−0.228*x	0.85
Patos	y = −1.72 + 1.77*x	0.99	y = 29.0−0.449*x + 0.005*x^2	0.92
Catalão	y = −1.45 + 1.75*x	0.99	y = 32.76−0.217*x	0.79
Bayovar	y = −3.06 + 1.62*x	0.99	y = 17.18−0.214*x	0.88

*, and** means significant at p ≤ 0.05 and 0.01, respectively; by "t" test. 1/After 1 h reaction.
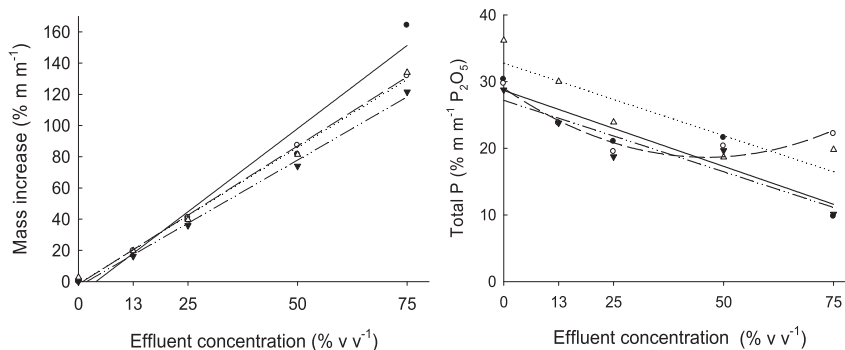
Fig. 4. Mass increased and total P_2O_5 content decreased in phosphate rocks with acid effluent addition, after 1 h reaction. Mass increased linearly and total P_2O_5 content decreased linearly with effluent concentrations using Araxá (A•), Catalão (C△), and Bayovar (B▼) rocks; except for Patos (P○), in which the total P_2O_5 content increased at effluent concentrations higher than 45%.

Nevertheless, the chemical improvements in Patos and Araxá PR achieved through treatment with the effluent should be recognised. Even though, according to legislation, they could not be classified and marketed as fertilizers, their production still results in improved natural phosphate rock solubility and acid waste exploitation.

Regarding potentially toxic elements, current legislation dictates maximum concentrations of 2.0; 0.05; 4.0; 20 and 40 mg kg^{-1} for As, Hg, Cd, Pb and Cr, respectively, per each P_2O_5 percentage point (Brasil, 2006). As and Hg were not detected in the samples. Natural rock phosphates and all products had Cd, Cr and Pb contents below maximum limits (Table 4) and therefore represent low or no risk when applied to soil. Among the PR, the highest Cr and Cd concentrations were observed for the Bayovar phosphate and the highest Pb concentration was observed for the Araxá phosphate. Effluent treatment at 75% (v v^{-1}) concentration increased Cr, Cd and Pb concentrations.

Additionally, it should also be noted that there was an increase in the concentrations of the micronutrients Cu, Mn, Fe, Zn and Ni following PR acidification (Table 4). These nutrients are essential to plant growth and their presence in increased concentrations and increased water solubility might be an important benefit in fertilization. Carvalho et al. (2012) asserted that phosphate fertilizers are an indirect source of micronutrients due to residual impurities derived from the manufacture process.

3.2. Rock minerals and soluble P fertilizers

X-ray diffraction analysis was used to track changes in the minerals present in the PR after acid effluent addition at 0; 12.5; 25; 50 and 75% concentrations and 1 h of reaction time (Fig. 5). The diffractogram for the Catalão phosphate showed a reduction in the width and intensity of apatite (tricalcium phosphate) peaks as effluent concentration increased, with these peaks disappearing completely at 75% of effluent concentration (Fig. 5). On the other hand, calcium sulfate (gypsum) peaks were already observed in the products at the lowest acid effluent concentration used (12.5%).

The diffraction pattern for untreated Bayovar phosphate indicated a poorly crystalline apatite (less, broader and lower intensity peaks) compared to Catalão phosphate (Fig. 5). The less crystalline peaks of apatite in the Bayóvar phosphate were more susceptible to acidification by the effluent, declining easily with the increasing acid concentration. And as for the Catalão phosphate, calcium sulfate (gypsum) was already formed at the lowest acid effluent concentration (12.5%).

Acid effluent was effective in solubilizing apatites, which were probably converted to amorphous Ca-phosphate forms (no XRD peaks) including Fe–P, Ca–P, Al–P and Mn–P (the main cations present in the effluent) and gypsum. These amorphous P species have higher solubility (Lehr, 1984). These results are consistent with the observed increase in P_W, P_{NAC} and P_{CA} fractions with increasing effluent concentration (Figs. 1–3). Regarding the reaction time, there was not much difference between 1 and 24 h in terms of P solubility in the different extractants. It means that 1-h was enough time for most of the reactions to occur. The only marked differences were in the P_W fraction of the Bayovar RP (Fig. 1) and in the P_{CA} of the Patos PR (Fig. 3). For the first, P_W increased in the 24 h for the 50% effluent concentration. For the Patos PR, more time was necessary for the 75% effluent concentration to react and give a linear response for the P_{CA}.

In general, effluent reaction on PR was similar to pure acids, such as sulfuric acid, in the production of simple superphosphate (SSP) or partially acidulated phosphate rock (PAPR) (Dorozhkin, 2012). In the apatites, each O atom bound to the P is also bounded to a surrounding Ca atom. When protons are provided, these Ca–O–P bonds start to break, substituting Ca by H and breaking the crystal structure. When there is only pure H_2SO_4 and a PR where Ca is the main cation, the main phosphate product of the acidification of apatite is $Ca(H_2PO_4)_2$. However, when other cations are also present, intermediate phosphate species are formed. And, besides the fact that the effluent is a mixture of three acids, the mainly difference between using pure acids or the acid effluent to acidify the apatite is the presence of other cations in the effluent, in particular Fe.

The presence of these other cations would allow the precipitation of amorphous intermediate forms of phosphate, which cannot be detected by XRD. These recently precipitated amorphous forms of phosphate are usually soluble in the short term. However, these forms can crystallize with time, decreasing P solubility (Biswas and Mukheriee, 1994).
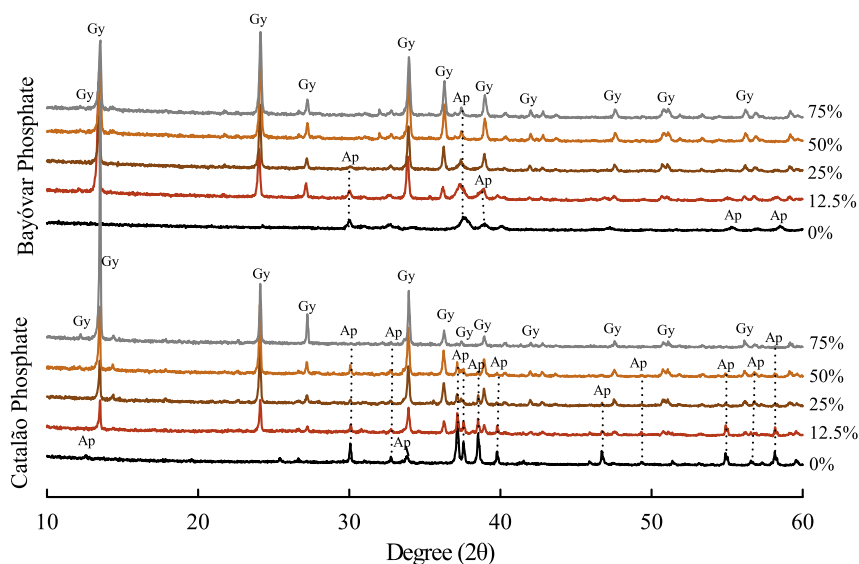
Many factors are relatated to apatite dissolution; including rock composition, particle size and strength and composition of the reacting acid (Dorozhkin, 2012). The three-acid (H_2SO_4/HF/HCl) mixture was effective to transform apatite (tricalcium phosphate) mineral in more soluble P-forms as verified by increasing P_W and P_{NAC} fractions. Since phosphate rocks contain low P_w or P_{NAC}, their acidification improves P solubility and their agronomic performance tends to increase accordingly (Bolland and Gilkes, 2008; Braithwaite, 1987).

4. Conclusions

This study demonstrates that metallurgical industry effluent can be used to increase phosphate rock reactivity, potentially producing

Table 4
Total P_2O_5 contents, nutrients and potentially toxic elements in the phosphate rock (PR) used in the experiment.

PR	Effluent concentration (% v v^{-1})	Total P_2O_5	Mn	Fe	Al	Cu	Ni	Zn	Cr	Cd	Pb
		(%w w^{-1})	(g kg^{-1})			(mg kg^{-1})					
Araxá	0	30	1.7	44	4.5	50	69	264	37	1.1	52
	12.5	24	1.6	56	5.1	67	85	267	53	1.0	93
	25	21	2.1	61	5.6	92	106	270	62	1.2	94
	50	22	2.1	53	4.4	103	149	218	80	1.5	81
	75	10	4.0	80	6.2	209	294	358	145	2.5	139
Patos	0	30	0.1	9.1	7.8	22	5.5	63	16	0.1	29
	12.5	24	0.2	14	10	31	15	60	26	0.5	35
	25	19	0.6	18	11	61	58	74	44	0.6	36
	50	17	1.0	18	8.5	78	92	66	54	0.2	29
	75	12	1.3	18	6.6	89	109	63	60	0.7	38
Catalão	0	36	0.3	8.6	1.4	23	7	33	5	0.7	26
	12.5	30	0.4	11	1.3	33	19	34	12	0.7	30
	25	24	0.7	14	1.7	54	45	39	21	0.5	40
	50	19	1.5	22	2.5	102	118	61	52	0.6	42
	75	20	1.5	21	1.9	100	116	51	57	0.8	48
Bayovar	0	29	0.1	4.8	2.9	23	3	106	129	26	30
	12.5	24	0.3	9.1	38	51	20	113	154	31	35
	25	19	0.5	15	5.5	84	38	121	179	23	46
	50	20	1.0	18	3.9	96	98	100	140	20	36
	75	10	2.4	36	8.0	203	239	181	186	36	70

Fig. 5. X-ray diffraction (XRD) patterns from rock phosphates (Catalão and Bayóvar) following treatment with different concentrations of acid effluent (AE): 0 (−), 12.5 (−), 25 (−), 50 (−), or 75% (−) (v/v). Gy-gypsum, Ap-apatite. X-ray diffraction shows the disappearance of apatite and the appearance of gypsum (CaSO$_4$.2H$_2$O) with increasing AE concentration. Data were collected using Co K$_{α1}$ radiation (0.1789 nm).

soluble phosphate fertilizers at low cost through the reuse of industrial waste. Moreover, this procedure produced fertilizers with lower concentrations of toxic metals and higher concentrations of micronutrients compared to natural phosphates. X-ray diffraction analysis clearly showed that effluent treatment converted tricalcium phosphate into amorphous P forms. The similarity of products resulting from treatment for 1 h and 24 h demonstrated that the reactions involved are rapid. Overall, effluent concentration and the source of natural phosphate were the most important factors affecting the composition of the partially acidulated phosphate products.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2015.10.012.

References

Adebowale, K.O., Unuabonah, E.I., Olu-Owolabi, B.I., 2008. Kinetic and thermodynamic aspects of the adsorption of Pb^{2+} and Cd^{2+} ions on tripolyphosphate-modified kaolinite clay. Chem. Eng. J. 136, 99–107.

Agrawal, A., Sahu, K.K., Pandey, B.D., 2004. Solid waste management in non-ferrous industries in India. Resour. Conserv. Recycl. 42, 99–120.

Barik, S.P., Park, K.H., Nam, C.W., 2014. Process development for recovery of vanadium and nickel from an industrial solid waste by a leaching solvent extraction technique. J. Environ. Manag. 146, 22–28.

Biswas, T.D., Mukherjee, S.K., 1994. Textbook of Soil Science, second ed. Tata McGraw-Hill Publishing Company Limited, New Delhi.

Bolan, N.S., Hedley, M.J., Loganathan, P., 1993. Preparation, forms and properties of controlled-release phosphate fertilizers. Fertilizer Res. 35, 13—24.

Bolland, M.D.A., Gilkes, R.J., 2008. The chemistry and agronomic effectiveness of phosphate fertilizers. J. Crop Prod. 1, 139—163.

Box, G.E.P., Cox, D.R., 1964. Analysis of transformations (with discussion). J. R. Stat. Soc. Brighton 26, 211—252.

Braithwaite, A.C., 1986. A comparison of fertilizers made by partially and fully acidulated phosphate rocks with phosphoric acid. NZJ Technol. 2, 3—42.

Braithwaite, A.C., 1987. The use of chemical solubility tests in comparing phosphate Fertilizers. Fertilizer Res. 12, 185—192.

BRASIL. Ministério da Agricultura Pecuária e Abastecimento - MAPA. Instrução normativa n. 27, de 05 de Junho de 2006. Disponível em: < extra-net.agricultura.gov.br/sislegis-consulta/consultarLegislacao>. Acesso em 28 de fevereiro de 2014.

BRASIL. Ministério da Agricultura Pecuária e Abastecimento - MAPA. Instrução normativa n. 5, de 23 de fevereiro de 2007. Disponível em: < extra-net.agricultura.gov.br/sislegis-consulta/consultarLegislacao>. Acesso em 27 de junho de 2014.

Capón-García, E., Papadokonstantakis, S., Hungerbühler, K., 2014. Multi-objective optimization of industrial waste management in chemical sites coupled with heat integration issues. Comput. Chem. Eng. 62, 21—36.

Carvalho, V.G.B., Nascimento, C.W.A., Biondi, C.M., 2012. Potential de fertilizantes e corretivos no aporte de micronutrientes ao solo. R. Bras. Ci. Solo 36, 931—938.

Charleston, A.G., 1984. Solubilities of single superphosphate components in water, 2% citric acid, and neutral ammonium citrate solutions. N. Z. J. Sci. 27, 269—277.

Chien, S.H., Prochnow, L.I., TU, S., Snyder, C.S., 2010. Agronomic and environmental aspects of phosphate fertilizers varying in source and solubility: an update review. Nutr. Cycl. Agroecosyst 89, 229—255.

CONAMA, Conselho Nacional do Meio Ambiente. Resolução CONAMA N° 430, de 13 de maio de 2011. Disponível em: <www.mma.gov.br/port/conama/res/res11/res43011.pdf> Acesso em 28 de fevereiro de 2014.

Dorozhkin, S.V., 2012. Dissolution mechanism of calcium apatites in acids: a review of literature. World J. Methodol. 2, 1—17.

Fang, H., Xia, J., Zhu, K., Su, Y., Jiang, Y., 2013. Industrial waste heat utilization for low temperature district heating. Energy Policy 62, 236—246.

Fu, F., Liping, X., Bing, Tang, Qi, W., Shuxian, J., 2012. Application of a novel strat-egy—Advanced Fenton-chemical precipitation to the treatment of strong sta-bility chelated heavy metal containing wastewater. Chem. Eng. J. 189, 283—287.

Ghiani, G., Laganà, D., Manni, E., Musmanno, R., Vigo, D., 2014. Operations research in solid waste management: a survey of strategic and tactical issues. Comput. Oper. Res. 44, 22—32.

Hammond, L.L., Chien, S.H., Polo, J.R., 1980. Phosphorus availability from partial acidulation of phosphate rocks. Fertiliser Res. 1, 37—49.

Hegazi, H.A., 2013. Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. HBRC J. 9, 276—282.

Inoue, K., Paudyal, H., Nakagawa, H., Kawakita, H., Ohto, K., 2010. Selective adsorption of chromium(VI) from zinc(II) and other metal ions using persimmon waste gel. Hydrometallurgy 104, 123—128.

Jadhav, U.U., Hocheng, H., 2012. A review of recovery of metals from industrial waste. J. Achiev. Mater. Manuf. Eng. 54, 159—167.

Lehr, J.R., 1980. Phosphate raw materials and fertilizers, Part I — a look ahead. In: Khasawneh, F.E., Sample, E.C., Kamprath, E.J. (Eds.), The Role of Phosphorus in Agriculture. American Society of Agronomy, Madison, pp. 81—120.

Lehr, J.R., 1984. Impact of phosphate rock quality on fertilizer marketcuses. Ind. Min. 200, 127—153.

Leonard, R.P., 1978. Hazardous solid waste from metallurgical industries. Environ. Health Perspect. 27, 251—260.

Post, J.W., Hamelers, H.V.M., Buisman, C.J.N., 2009. Influence of multivalent ions on power production from mixing salt and fresh water with a reverse electrodi-alysis system. J. Membr. Sci. 330, 65—72.

Prochnow, L.I., Chien, S.H., Taylor, R.W., Carmona, G., Henao, J., Dillard, E.F., 2003a. Characterization and agronomic evaluation of single superphosphates varying in iron phosphate impurities. Agron. J. 95, 293—302.

Prochnow, L.I., Chien, S.H., Dillard, E.F., Austin, E.R., Carmona, G., Henao, J., Singh, U., 2003b. Synthesis, characterization, and agronomic evaluation of iron phosphate impurities in single superphosphates. Soil Sci. Soc. Am. J. 67, 1551—1563.

Prochnow, L.I., Van Raij, B., Kiehl, J.C., 2002. Effect of water and citrate solubility on agronomic effectiveness of acidulated phosphates in three consecutive corn crops. R. Bras. Ci. Solo 26, 729—736.

Puig, R., Fullana-i-Palmer, P., Baquero, G., Riba, j. J., Bala, A., 2013. A cumulative energy demand indicator (CED), life cycle based, for industrial waste manage-ment decision making. Waste Manage 33, 2789—2797.

Sadyrbaeva, 2014. Recovery of cobalto(II) by the hybrid liquid membrane-electrodialysis -electrolysis process. Electrochim. Acta 133, 161—168.

Silva, I.R., Smyth, T.J., Raper, C.D., Carter, T.E., Rufty, T.W., 2001. Differential aluminum tolerance in soybean: an evaluation of the role of organic acids. Physiol. Plant 112, 200—210.

Syers, J.K., Johnston, A.E., Curtin, D., 2008. Efficiency of soil and fertilizer phos-phorus use. FAO Fertilizer Plant Nutr. Bull. 18 (FAO, Rome, Italy).

Vinodh, R., Padmavathi, R., Sangeetha, D., 2011. Separation of heavy metals from water samples using anion exchange polymers by adsorption process. Desali-nation 267, 267—276.

Withers, P.J.A., van Dijk, K.C., Neset, T.-S.S., Nesme, T., Oenema, O., Rubæk, G.H., Schoumans, O.F., Smit, B., Pellerin, S., 2015. Stewardship to tackle global phos-phorus inefficiency: the case of Europe. AMBIO 44, 193—206.

Zamorano, M., Grindlay, A., Molero, E., Rodríguez, M.I., 2011. Diagnosis and pro-posals for waste management in industrial areas in the service sector: case study in the metropolitan area of Granada (Spain). J. Clean. Prod. 19, 1946—1955.

Zheng, G.H., Kozinsk, J.A., 2006. Solid waste remediation in the metallurgical in-dustry: application and environmental impact. Environ. Prog. 15, 283—292.