



Phosphorous removal in batch systems using ferric chloride in the presence of activated sludges

Alejandro H. Caravelli^a, Edgardo M. Contreras^{a,b,*}, Noemí E. Zaritzky^{a,b}

^a Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA) CONICET La Plata, UNLP, 47 y 116 (B1900AJJ), La Plata, Argentina

^b Fac. de Ingeniería, UNLP, 47 y 1 (B1900AJJ), La Plata, Argentina

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ABSTRACT

The objectives of this work were: (a) to analyze the effect of alkalinity, pH and initial Fe:P molar ratio ($Fe_0:P_0$) on the precipitation of orthophosphate using ferric chloride in the presence of activated sludge in order to represent conditions of simultaneous precipitation, and in exhausted wastewater to simulate conditions of post-precipitation, (b) to compare the experimental results with predictions obtained from a chemical equilibrium model, and (c) to propose a mechanistic model to determine the dose of coagulant required to achieve a given orthophosphate removal degree at constant pH. Results showed that the presence of biomass did not affect the orthophosphate precipitation; however, addition of ferric chloride caused a drop of pH to values not compatible with the normal activity of activated sludges. For this reason, the wastewater was supplemented with $NaHCO_3$; when 1 g L^{-1} $NaHCO_3$ was added, orthophosphate removals higher than 97% and pH above 6.2 were obtained using $Fe_0:P_0 = 1.9$. Precipitation assays at constant pH showed that Fe(III) hydrolysis and $FePO_4$ precipitation reaction compete with each other.

Calculations using a chemical equilibrium model (CHEAQS) predicted that ferric phosphate precipitation should not take place if pH is higher than about 7.8. However, experimental results showed that ferric phosphate precipitation occurred even at pH 9. For this reason, a mechanistic model was proposed to predict orthophosphate concentrations as a function of $Fe_0:P_0$ at constant pH. The model can be applied to calculate the minimum Fe(III) concentration required to achieve a given discharge limit for orthophosphate as a function of its initial concentration and pH.

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1. Introduction

Municipal and industrial wastewaters often have high concentrations of phosphorous containing compounds. Orthophosphates, polyphosphates, and organic phosphates are the main forms of phosphorous that are present in wastewaters. If these wastewaters are not treated to remove phosphorous, nutrient enrichment of both groundwater and surface waters may occur leading to detrimental effects on water quality and eutrophication of surface water bodies. For this reason, many countries have adopted strict discharge limits concerning phosphorous in wastewaters. For example, the US discharge limit for phosphate is $0.5\text{--}1.0\text{ mg PL}^{-1}$ ($0.016\text{--}0.032\text{ mM}$); according to Argentinean standards, the discharge limit for phosphate ranges from 1.0 to 10 mg PL^{-1} ($0.032\text{--}0.32\text{ mM}$), depending on the wastewater receiving location.

Although reverse osmosis and electrodialysis have been suggested to remove phosphorous compounds, up to the present these methods are still expensive [1]. Chemical precipitation, biological processes such as EBPR (enhanced biological phosphorous removal), or a combination of both are usually adopted to remove phosphorous from wastewaters. In all cases, phosphorous is contained in chemical or microbiological flocs, which are removed by means of a settling tank [2]. EBPR has been adopted in many countries; however, actual facilities demonstrate that the EBPR process tends to be unstable [3,4]. In many cases, a practical solution to meet effluent standards consists of supplementing the biological system with a chemical precipitation process [5]. However, there is evidence that addition of coagulants such as calcium, aluminum, or iron salts have a deleterious effect on the EBPR process [6]. Besides, coagulants are more effective to remove orthophosphates than polyphosphates and organic phosphorous [7].

The main factors to consider in the precipitation of phosphorous are the selection of the coagulant, its dose, and pH [8]. Among the available precipitants, aluminum, iron and calcium salts are the most used. Phosphorous removal using calcium chloride works best when pH is above 10; therefore, pH must be adjusted close to a normal value before discharging [9]. Traditionally, aluminum

* Corresponding author at: Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA) CONICET La Plata, UNLP, 47 y 116 (B1900AJJ), La Plata, Argentina. Tel.: +54 221 4254853.

E-mail address: econtrer@quimica.unlp.edu.ar (E.M. Contreras).

Nomenclature

Fe_0	added ferric iron concentration (mM)
Fe_{0min}	minimum ferric iron concentration (mM)
Fe_{TS}	total soluble ferric iron concentration (mM)
$(Fe:P)_{prec}$	Fe:P molar ratio of the precipitate (Eq. (1))
k_{Fe}	first order conditional rate constant (s^{-1}) (Eq. (12))
k_p	second order conditional rate constant ($mM^{-1} s^{-1}$) (Eq. (11))
$K_{SP(Fe)}$	solubility constant of $Fe(OH)_3(s)$ (Eq. (9))
$K_{SP(P)}$	solubility constant of $FePO_4(s)$ (Eq. (10))
P	orthophosphate concentration (mM)
P_0	initial orthophosphate concentration (mM)
P_{max}	discharge limit orthophosphate concentration (mM)
r	initial Fe:P molar ratio ($Fe_0:P_0$) (Eq. (7))
α	total phosphorous fraction precipitated as $FePO_4(s)$ (Eq. (7))

chloride, alum, and poly-aluminum chloride are used to remove phosphorous. Considering the potential reuse of sludge as fertilizer, the dose applied of aluminum-based precipitants must be carefully controlled because phytotoxic sludges may be produced [10]. Ferric chloride ($FeCl_3$) and ferrous sulphate ($FeSO_4$) are the most used iron salts to remove phosphorous. One of the main disadvantages of using $FeSO_4$ is related to the decrease of dissolved oxygen due to the oxidation of Fe^{2+} ; for this reason, ferric chloride is preferred. From the stoichiometry of $FePO_4$ formation, 1 mol of Fe^{3+} is necessary to remove 1 mol of phosphorous. However, because iron undergoes side reactions such as formation of hydroxides, Fe:P molar ratios higher than 1:1 are often necessary; in addition, these side reactions consume alkalinity and decrease pH [6]. Reported optimal pH values for removing phosphorous with $FeCl_3$ range between 4.0 and 9.0 [11–13]. This wide range of optimal pH reflects the differences among the procedures employed to optimize phosphorous precipitation conditions and between the physicochemical characteristics of the studied wastewaters.

Coagulant addition may be applied to the primary settler (known as pre-precipitation), to the aeration basin (simultaneous precipitation), or during tertiary treatment (post-precipitation) [6]. Pre-precipitation offers the benefits of reducing 50–70% the organic loading of the biological treatment, providing savings in aeration. However, the main problem is the marked increase in the sludge production. In addition, a significant proportion of phosphorous may be present as organic compounds and hence may not be removed [14]. This problem is avoided with simultaneous precipitation because polyphosphates and organic phosphates are hydrolyzed to orthophosphate in the aeration tank. When coagulants are used in the aeration tank, they enhance compaction and thickening of activated sludge, preventing bulking problems [9]. However, the excess of coagulants may be deleterious to the biological process [15]. In post-precipitation, an almost pure chemical precipitation process without much interference from organic matter or particles is achieved. However, an additional settling tank is necessary, increasing both investment and operating costs. In addition, the obtained chemical sludge is often voluminous and difficult to dewater [14].

The objectives of this work were (a) to analyze the effect of alkalinity, pH and initial Fe:P molar ratio on the precipitation of orthophosphate using ferric chloride in the presence of activated sludge in order to represent conditions of simultaneous precipitation, and in exhausted wastewater to simulate conditions of post-precipitation, (b) to compare the experimental results with predictions from a chemical equilibrium model, and (c) to propose

a mechanistic model to determine the coagulant dose required to achieve a given orthophosphate removal degree at constant pH in activated sludge batch reactors.

2. Materials and methods

2.1. Biological and chemical materials

Activated sludges were obtained from an aerobic laboratory-scale (4.5 L) activated sludge reactor with partial biomass recycle. The hydraulic residence time was 25 h; the sludge age was maintained at 21 d by daily wasting of mixed liquor directly from the reactor. Aeration and mixing were supplied by aerators; air was introduced through porous diffusers at the bottom of the aeration basin. The reactor was fed with a model wastewater of a dairy industry (inlet stream) that was prepared twice a week; its composition was the following: cheese whey, $1.5 g L^{-1}$; $(NH_4)_2SO_4$, $0.94 g L^{-1}$ (7.12 mM); KH_2PO_4 , $0.071 g L^{-1}$ (0.52 mM); $Na_2HPO_4 \cdot 7H_2O$, $0.213 g L^{-1}$ (0.80 mM). In order to obtain different alkalinity levels, $0.5 g L^{-1}$ (6 mM) or $1 g L^{-1}$ (12 mM) of $NaHCO_3$ was added to the feeding wastewater. In all cases, pH of the wastewater was adjusted to 7.0 by adding a few drops of HCl (1 M). Under steady-state conditions dissolved oxygen (DO) concentration was above $4 mg L^{-1}$, pH was 7.5 ± 0.4 , total suspended solid (TSS) concentration ranged between 2300 and 2700 $mg TSS L^{-1}$ and soluble chemical oxygen demand (COD_S) of the effluent ranged between 30 and 80 $mg L^{-1}$.

Ferric trichloride hexahydrate was used in all the orthophosphate precipitation assays. All inorganic salts used in the present work were commercial products of reagent grade from Anedra (San Fernando, Argentina). Dehydrated cheese whey was from Food S.A. (Villa Maipú, Argentina).

2.2. Orthophosphate precipitation assays

All orthophosphate precipitation assays using ferric chloride were conducted in 200 mL glass vessels at room temperature ($20 \pm 2^\circ C$).

2.2.1. Kinetic assays

These studies were conducted to determine the time scale required to achieve a significant degree of precipitation. In order to avoid interferences from soluble or particulate organic compounds that could be present in the exhausted wastewater from the activated sludge system, all the assays were performed in a model solution with the following composition: $(NH_4)_2SO_4$, $0.75 g L^{-1}$; KH_2PO_4 , $0.071 g L^{-1}$; $Na_2HPO_4 \cdot 7H_2O$, $0.213 g L^{-1}$. This model solution represents the exhausted wastewater from the activated sludge reactor (outlet stream) in order to reproduce phosphorous removal by post-precipitation.

Precipitation kinetics of orthophosphate were determined by mixing 150 mL of the model solution and appropriate volumes of a stock solution of ferric chloride (62.9 mM). Tested Fe(III) concentrations ranged from 0 to 2.47 mM; in all cases, the initial orthophosphate concentration (P_0) was 1.33 ± 0.02 mM. The mixtures were gently stirred (50–60 rpm) during different contact times (0–95 h), then, samples were withdrawn to determine pH and soluble orthophosphate concentration (P). Tested initial Fe:P molar ratio ($Fe_0:P_0$) ranged between 0 and 1.85; results were reported as the ratio between P and its initial value (P/P_0) as a function of the contact time.

2.2.2. Effect of the presence of biomass on orthophosphate precipitation

Orthophosphate precipitation was studied in the mixed liquor samples from the activated sludge reactor to represent conditions

of simultaneous removal of phosphorous; in this case, the biomass concentration was $2400 \pm 100 \text{ mgTSS L}^{-1}$. For comparison purposes, precipitation experiments in the effluent of the activated sludge reactor (exhausted wastewater without biomass) were also conducted to simulate post-precipitation. In all cases, ferric chloride concentrations up to 3.64 mM were tested; initial soluble orthophosphate concentrations ranged between 1.26 and 1.37 mM . Each mixture was gently stirred (50 – 60 rpm) for 30 min , and then the agitation was stopped to allow a 45 min sedimentation phase. After that, samples were withdrawn to determine pH and orthophosphate concentration.

2.2.3. Orthophosphate precipitation in mixed liquor samples from the activated sludge reactor: effect of the inlet stream alkalinity level

Different wastewaters with three alkalinity levels, named low (without carbonate added), medium ($0.5 \text{ g L}^{-1} \text{ NaHCO}_3$), or high ($1 \text{ g L}^{-1} \text{ NaHCO}_3$) were fed to the activated sludge reactor. Once the steady state was reached, mixed liquor samples were withdrawn to perform orthophosphate precipitation experiments in a similar way to those described in the previous section (30 min agitation and 45 min sedimentation phases). After the sedimentation phase, pH and orthophosphate concentration in the supernatant were measured.

2.2.4. Orthophosphate precipitation in the presence of biomass under constant pH

In these experiments pH values of the tested samples of mixed liquor and ferric chloride were maintained constant ($\pm 0.1 \text{ pH}$ units) by adding a few drops of NaOH or HCl stock solutions (1 M) during the agitation and sedimentation phases. Tested pH values ranged from 5.0 to 9.0 ; in all cases biomass concentration was $2400 \pm 100 \text{ mgTSS L}^{-1}$. After the sedimentation phase, orthophosphate (P) and total soluble iron (Fe_{TS}) concentrations in the supernatant were measured. From these data, composition of the precipitate in terms of Fe:P molar ratio was calculated as follows:

$$(\text{Fe} : \text{P})_{\text{prec}} = \frac{\text{Fe}_0 - \text{Fe}_{\text{TS}}}{\text{P}_0 - \text{P}} \quad (1)$$

where Fe_0 (mM) is the added ferric iron concentration, Fe_{TS} (mM) is the total soluble ferric iron concentration, P_0 (mM) the initial orthophosphate concentration, and P (mM) the orthophosphate concentration.

2.3. Analytical methods

Activated sludge biomass concentration was measured as chemical oxygen demand (COD) and transformed into total suspended solids (TSS) using a calibration curve previously determined [16]. COD was measured using a commercial reagent (Hach Company, Loveland, CO).

The samples from orthophosphate precipitation experiments were centrifuged for 5 min at $13,000 \text{ rpm}$ (Eppendorf centrifuge model 5415C); then, the supernatant was filtered through $0.45 \mu\text{m}$ cellulose acetate membranes (GE Osmonics). The centrifugation step was used to minimize the obstruction of the membranes, which were selected due to their extremely low binding characteristics. Orthophosphate and total soluble ferric iron concentrations in the filtrate were determined using commercial reagents (Hach Company, Loveland, CO). pH was measured using a polymer body pH probe (Broadley-James Corp., USA) connected to a pH monitor (Masstek, Argentina). Before each experiment, the pH meter was calibrated using standard buffers provided by Anedra. For measurement of pH 5.0 , 6.0 , and 7.0 , the electrode was calibrated using

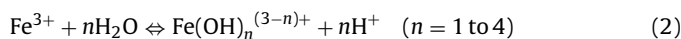
pH 4.01 and 7.01 buffers. For measurement of pH 8.0 , and 9.0 , the electrode was calibrated using pH 7.01 and 10.01 buffers.

All results presented in this paper are average values of at least two experiments.

3. Results and discussion

3.1. Orthophosphate precipitation kinetics

Fig. 1 shows orthophosphate precipitation and pH values as a function of time corresponding to different initial Fe:P molar ratios in model solutions. For all the tested conditions most of the composition changes occurred within the first 2 h ; in fact, the orthophosphate precipitation at this contact time was more than 97% of that obtained at $t = 95 \text{ h}$. In addition, from 2 to 95 h pH values were constant, confirming that orthophosphate precipitation reaction was fast enough to be almost complete within the first 2 h . As the initial Fe:P molar ratio increased, orthophosphate removal increased and pH decreased. An orthophosphate removal of 95% was obtained when the highest initial Fe:P molar ratio was tested. Although acceptable phosphate removals were achieved, final pH values were very low, ranging between 2 and 3 when the initial Fe:P molar ratios were higher than 0.71 . This drop of pH was due to hydrolysis reactions of Fe(III) such as the following [17]:



For this reason, if ferric chloride is added directly to the aeration basin of the activated sludge reactor, the resulting pH values (about 2 – 3) are not compatible with the normal metabolic activity of most microorganisms that are present in such systems.

The degree of pH change is a function of several parameters such as the initial pH, the presence of buffer systems (mainly carbonate and phosphate) and the amount of Fe(III) added, among others. The addition of Fe(III) has a double effect on pH; a direct effect due to the hydrolysis reactions (Eq. (2)) and an indirect effect by decreasing the buffer capacity due to phosphate precipitation.

3.2. Effect of the presence of biomass and alkalinity of the medium on orthophosphate precipitation

Orthophosphate precipitation in mixed liquor samples from the activated sludge reactor was analyzed to reproduce simultaneous precipitation. These results can be compared to the post-precipitation procedure using the exhausted wastewater of the reactor (outlet stream) in the absence of biomass. Fig. 2a shows that orthophosphate precipitation with ferric chloride in both media was similar; thus, the presence of biomass did not affect the performance of the precipitation process. In both cases, precipitation efficiencies of about 90% were obtained when the initial Fe:P molar ratio was higher than 1.4 . Although slightly higher pH values were obtained in the presence of biomass (Fig. 2b), the resulting pH was below 3 , which is not compatible with the biological activity of activated sludges [18].

With regard to the effect of biomass on the removal of phosphates using ferric chloride, He et al. [19] suggested that most P-Fe containing particles are trapped by meshes of biological fibrils, some of which are attached to extracellular organics, and others adhere directly to the surface of the cells. As a result, the presence of biomass may improve the sedimentation of P-Fe containing particles, so they are likely to settle readily in the secondary clarifier [19]. The analytical techniques used in our work allowed evaluation of the formation of non-soluble phosphate species in the presence of activated sludge; further research is necessary to assess the effect of biomass on the sedimentation properties of P-Fe containing particles.

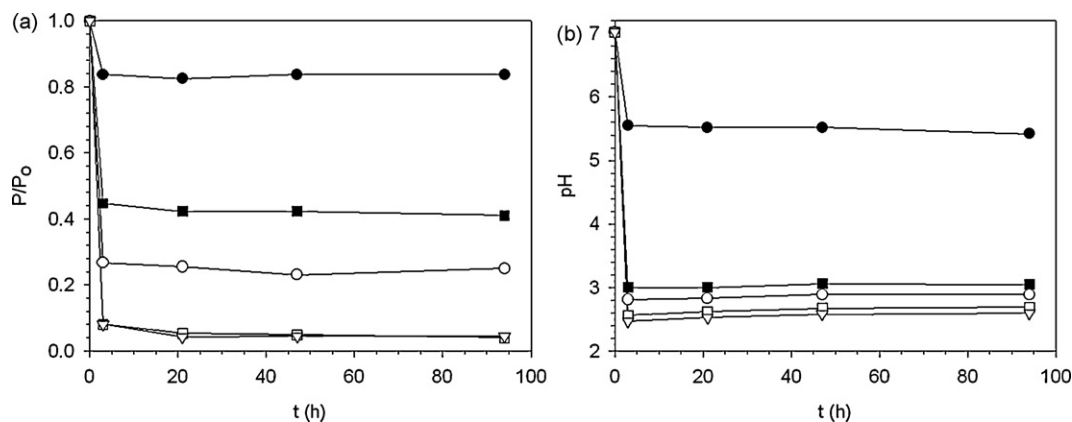


Fig. 1. Effect of contact time on: (a) precipitation of orthophosphate, and (b) pH in model solutions using different initial $Fe_0:P_0$ molar ratios ($Fe_0:P_0$): (●) 0.23, (■) 0.71, (○) 0.95, (□) 1.42, (▽) 1.89.

In order to determine the minimum amount of $NaHCO_3$ that was necessary to maintain the $pH > 6$, wastewaters with three different alkalinity levels were fed to the activated sludge reactor. Fig. 2a shows that the alkalinity level did not affect orthophosphate precipitation. However, the change of pH was less with higher carbonate concentrations (Fig. 2b). The best results were obtained by adding $1 \text{ g L}^{-1} NaHCO_3$ (12 mM) to the inlet stream with an initial $Fe:P$ molar ratio = 1.9; in these conditions pH was maintained above 6.2 and orthophosphate removal was higher than $97 \pm 2\%$. However, if lower orthophosphate removals are necessary to attain the orthophosphate discharge limit, lower $NaHCO_3$ concentrations may be used. For example, Fig. 2 shows that an orthophosphate removal higher than 94%, with a final pH value above 5.7, can be obtained by using $Fe_0:P_0 = 1.8$, adding $0.5 \text{ g L}^{-1} NaHCO_3$ (6 mM) to the inlet stream.

3.3. Orthophosphate precipitation in the presence of biomass under constant pH

To study the orthophosphate precipitation using ferric chloride under constant pH conditions, the buffer capacity of the wastewater was increased by supplementing the feeding wastewater of the activated sludge reactor with $1 \text{ g L}^{-1} NaHCO_3$. Tested pH values ranged from 5.0 to 9.0, the typical pH operational range of activated sludge systems [18].

Fig. 3a shows that orthophosphate precipitation in the presence of biomass was similar for initial $Fe:P$ molar ratios up to about 1.5 and pH values between 5 and 8. When the initial $Fe:P$ molar ratio

was higher than 1.5, orthophosphate precipitation increased as pH decreased (insert in Fig. 3a). Orthophosphate precipitation at pH 9 was less effective than precipitation at the other tested pH values. At the highest initial $Fe:P$ molar ratio tested ($Fe_0:P_0 = 3$), the orthophosphate precipitation was close to 90%; however, when the tested pH ranged from 5 to 8, orthophosphate removals higher than 98% were obtained. Obtained results indicate that a large excess of $Fe(III)$ (up to three times the stoichiometric value, $Fe:P = 1$) was necessary to achieve acceptable orthophosphate removals to meet effluent discharge requirements in most countries.

Fig. 3b shows the total soluble $Fe(III)$ (Fe_{TS}) as a function of the initial $Fe:P$ ratio for the different tested pH. In all cases, Fe_{TS} concentration was lower than 0.02 mM; indeed, Fe_{TS} concentrations as low as 0.001 mM were obtained for pH values ranging between 7 and 9; however, higher Fe_{TS} concentrations were obtained at lower pH values. Considering the $Fe(III)$ hydrolysis reactions (Eq. (2)), it is clear that low pH values shift these reactions to the left, increasing $Fe(III)$ solubility. For this reason, although orthophosphate removal efficiency is favored at low pH, this condition also increases the $Fe(III)$ solubility.

$Fe(III)$ hydrolysis and $FePO_4$ precipitation reactions always compete with each other; as a result, only a fraction of the added $Fe(III)$ is actually used to form $FePO_4(s)$. In order to evaluate the efficiency of $Fe(III)$ to precipitate phosphorous, the fractions of $Fe(III)$ that formed $FePO_4(s)$ and $Fe(OH)_3(s)$ were calculated from the mass balances for Fe and P as follows:

$$Fe_0 = Fe_{TS} + FePO_4(s) + Fe(OH)_3(s) \quad (3)$$

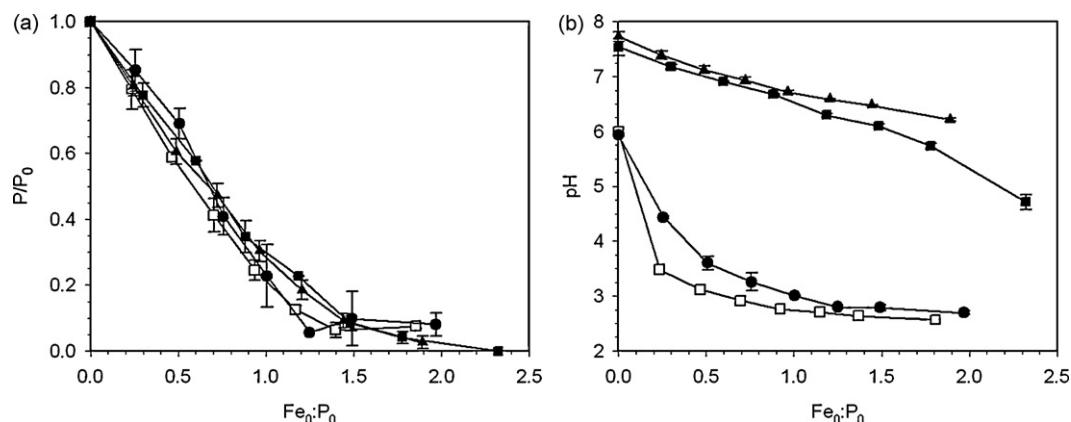


Fig. 2. Effect of the initial $Fe:P$ molar ratio ($Fe_0:P_0$) on: (a) precipitation of orthophosphate, and (b) pH values corresponding to the following systems: (□) exhausted model wastewater without biomass, and activated sludge mixed liquor with different alkalinity levels: (●) low (no $NaHCO_3$ addition), (■) medium (6 mM $NaHCO_3$), (▲) high (12 mM $NaHCO_3$). The biomass concentration in the activated sludge mixed liquor was $2400 \pm 100 \text{ mgTSS L}^{-1}$.

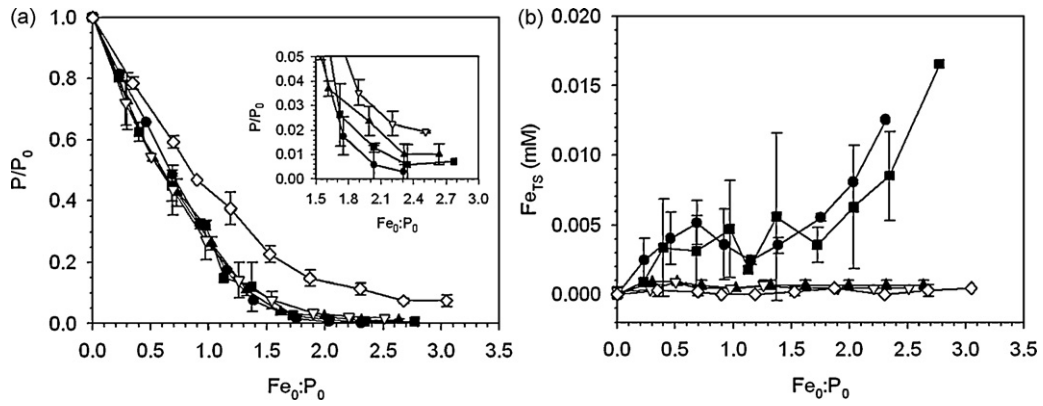


Fig. 3. Effect of the initial Fe:P molar ratio ($Fe_0:P_0$) on: (a) the precipitation of orthophosphate, and (b) the corresponding total soluble Fe(III) (Fe_{TS}) at constant pH in the presence of biomass ($2400 \pm 100 \text{ mgTSS L}^{-1}$). pH values: (●) 5.0, (■) 6.0, (▲) 7.0 (▽) 8.0, and (◇) 9.0.

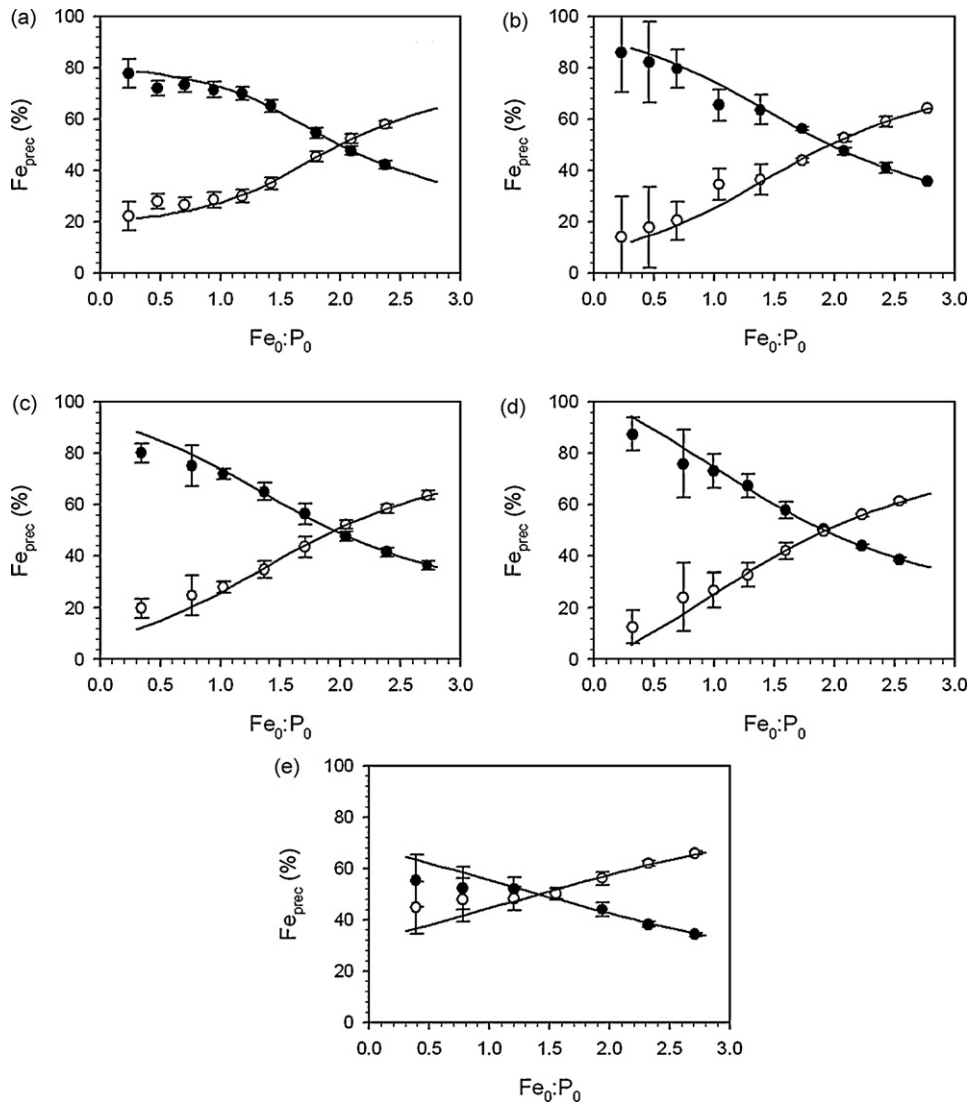


Fig. 4. Fraction of Fe(III) precipitated (Fe_{prec} , %) as $FePO_4$ (●) or $Fe(OH)_3$ (○) as a function of the initial Fe:P molar ratio ($Fe_0:P_0$) for different pH values: (a) 5.0, (b) 6.0, (c) 7.0, (d) 8.0, and (e) 9.0. Lines indicate the results obtained with the proposed mechanistic model (Eqs. (11) and (12)) using the coefficients shown in Table 2.

Table 1

Ferric iron and phosphate species that are present in the medium used in the precipitation experiments predicted by the software CHEAQS [25].

Soluble species containing			Solid species
Phosphate only	Ferric iron only	Ferric iron and phosphate	
PO ₄ ³⁻	Fe ³⁺	FeHPO ₄ ⁺	Fe(OH) ₃ (s)
H ₂ PO ₄ NH ₃ ⁻	Fe(OH) ²⁺	FeH ₂ PO ₄ ²⁺	FePO ₄ (s)
H ₃ PO ₄ NH ₃ ⁰	Fe(OH) ₂ ⁺	FeH ₃ PO ₄ ³⁺	KFe ₃ (SO ₄) ₂ (OH) ₆ (s)
HPO ₄ ²⁻	Fe(OH) ₃ ⁰	FeH ₄ PO ₄ ⁴⁺	
H ₂ PO ₄ ⁻	Fe(OH) ₄ ⁻	FeH ₆ (PO ₄) ₃ ⁰	
H ₃ PO ₄ ⁰	Fe ₂ (OH) ₂ ⁴⁺		
H ₄ PO ₄ ⁺	Fe ₃ (OH) ₄ ⁵⁺		
NaPO ₄ ²⁻	FeCO ₃ ⁺		
NaHPO ₄ ⁻	Fe(OH)CO ₃ ⁰		
NaH ₂ PO ₄ ⁰	Fe(CO ₃) ₂ ⁻		
Na ₂ PO ₄ ⁻	FeSO ₄ ⁺		
Na ₂ HPO ₄ ⁰	Fe(SO ₄) ₂ ⁻		
KPO ₄ ²⁻	FeCl ₂ ⁺		
KHPO ₄ ⁻	FeCl ₃ ⁰		
KH ₂ PO ₄ ⁰			
K ₂ PO ₄ ⁻			
K ₂ HPO ₄ ⁰			

$$P_0 = P + \text{FePO}_4(s) \quad (4)$$

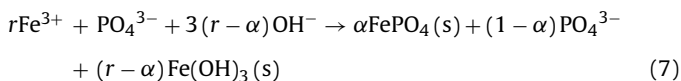
where Fe_{TS} and P are total soluble Fe(III) and orthophosphate concentrations respectively. Combining Eqs. (3) and (4), the following expressions were obtained:

$$\frac{\text{FePO}_4}{\text{Fe}_0} = \frac{P_0 - P}{\text{Fe}_0} \quad (5)$$

$$\frac{\text{Fe(OH)}_3}{\text{Fe}_0} = \frac{\text{Fe}_0 - \text{Fe}_{\text{TS}} - P_0 + P}{\text{Fe}_0} \quad (6)$$

Eqs. (5) and (6) were used to calculate the fractions of Fe(III) forming FePO₄(s) and Fe(OH)₃(s), respectively. Fig. 4 shows that the fraction of Fe(III) precipitated as FePO₄(s) decreased from 80–90% to 35–40%, as the initial Fe:P molar ratio increased. For pH values between 5 and 8, no effect of pH was observed; however, lower efficiencies of Fe(III) to form FePO₄(s) were obtained at pH 9, due to the formation of higher amounts of Fe(OH)₃(s).

The overall stoichiometry of ferric phosphate precipitation using ferric chloride can be represented by means of the following simplified expression:



where r is the initial Fe:P molar ratio (Fe₀:P₀), and α is the total phosphorous fraction precipitated as FePO₄(s). Taking into account the mass balances for Fe and P (Eqs. (3) and (4)), the following constraints between coefficients r and α can be derived: if $0 \leq r \leq 1$, then $\alpha \leq r$; for $r > 1$, $\alpha \leq 1$. If $\alpha = 0$, all phosphorous remains dissolved as PO₄³⁻ and no FePO₄(s) is formed. On the contrary, $\alpha = r \leq 1$ represents the optimum condition in which all ferric iron is precipitated as FePO₄(s). In all cases, the excess of Fe(III), represented by the coefficient $(r - \alpha)$, precipitates as Fe(OH)₃(s); other hydrolysis species were neglected. Eq. (7) assumes that both FePO₄(s) and Fe(OH)₃(s) were completely insoluble, thus, total soluble Fe(III) concentration is also neglected. It must be pointed out that the latter assumption is in accordance to the very low values of total soluble Fe(III) concentrations (less than 0.02 mM) observed experimentally within the tested conditions.

From Eq. (7), the Fe:P molar ratio of the precipitate, (Fe:P)_{prec}, can be calculated as follows:

$$(\text{Fe} : \text{P})_{\text{prec}} = \frac{r}{\alpha} \quad (8)$$

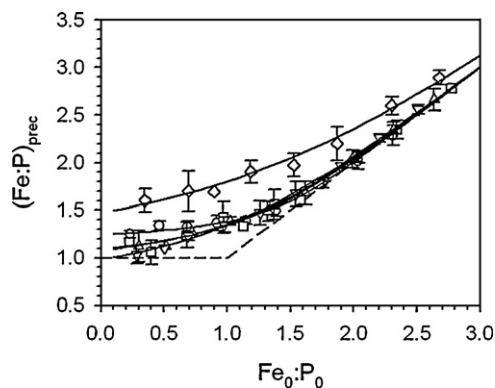


Fig. 5. Fe:P molar ratio of the precipitate, (Fe:P)_{prec}, as a function of the initial Fe:P molar ratio (Fe₀:P₀) corresponding to the following pH values: (○) 5.0, (□) 6.0, (△) 7.0 (▽) 8.0, (◇) 9.0. Dotted line represents the ratio (Fe:P)_{TPrec} (Eq. (8)) assuming the optimum condition ($\alpha = r \leq 1$). Continuous lines represent the proposed mechanistic model (Eqs. (11) and (12)) using the coefficients shown in Table 2.

Fig. 5 shows the experimental Fe:P molar ratio of the precipitate, (Fe:P)_{prec}, calculated by using Eq. (1) as a function of the initial Fe:P molar ratio ($r = \text{Fe}_0:\text{P}_0$) for the different tested pH values; in addition, the dotted line represents the ratio (Fe:P)_{TPrec} assuming the optimum condition ($\alpha = r \leq 1$). Fig. 5 shows that for all the tested pH values, experimental (Fe:P)_{prec} ratios were higher than the ratio (Fe:P)_{TPrec} calculated using Eq. (8) that assumes the optimum condition. This result indicates that the co-precipitation of FePO₄(s) and Fe(OH)₃(s) may occur even at a pH value as low as 5.

3.4. Analysis of orthophosphate precipitation experiments at a constant pH using a chemical equilibrium model (CHEAQS)

Precipitation experiments at a constant pH were performed in a medium containing ammonium sulphate, sodium and potassium

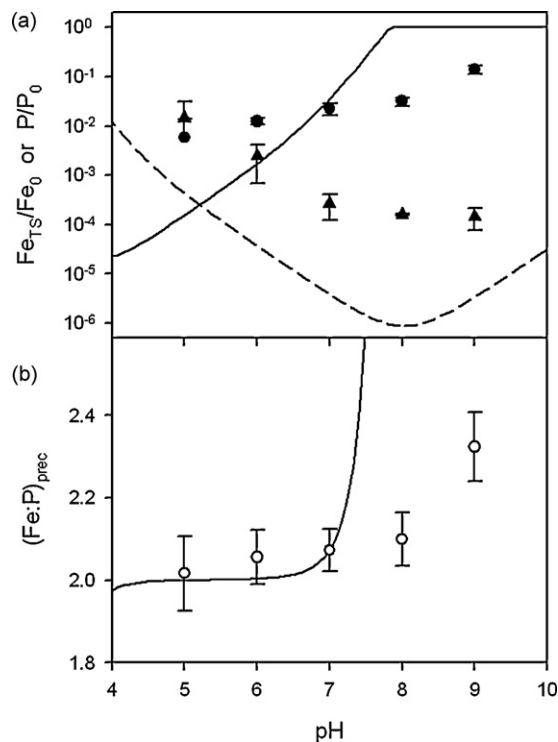


Fig. 6. Effect of pH (a) on P/P₀ (●) and Fe_{TS}/Fe₀ (▲) ratios, and (b) on the Fe:P molar ratio of the precipitate, (Fe:P)_{prec} (○). In all cases the initial Fe:P molar ratio was 2. Lines represent the predictions using a chemical equilibrium model (CHEAQS).

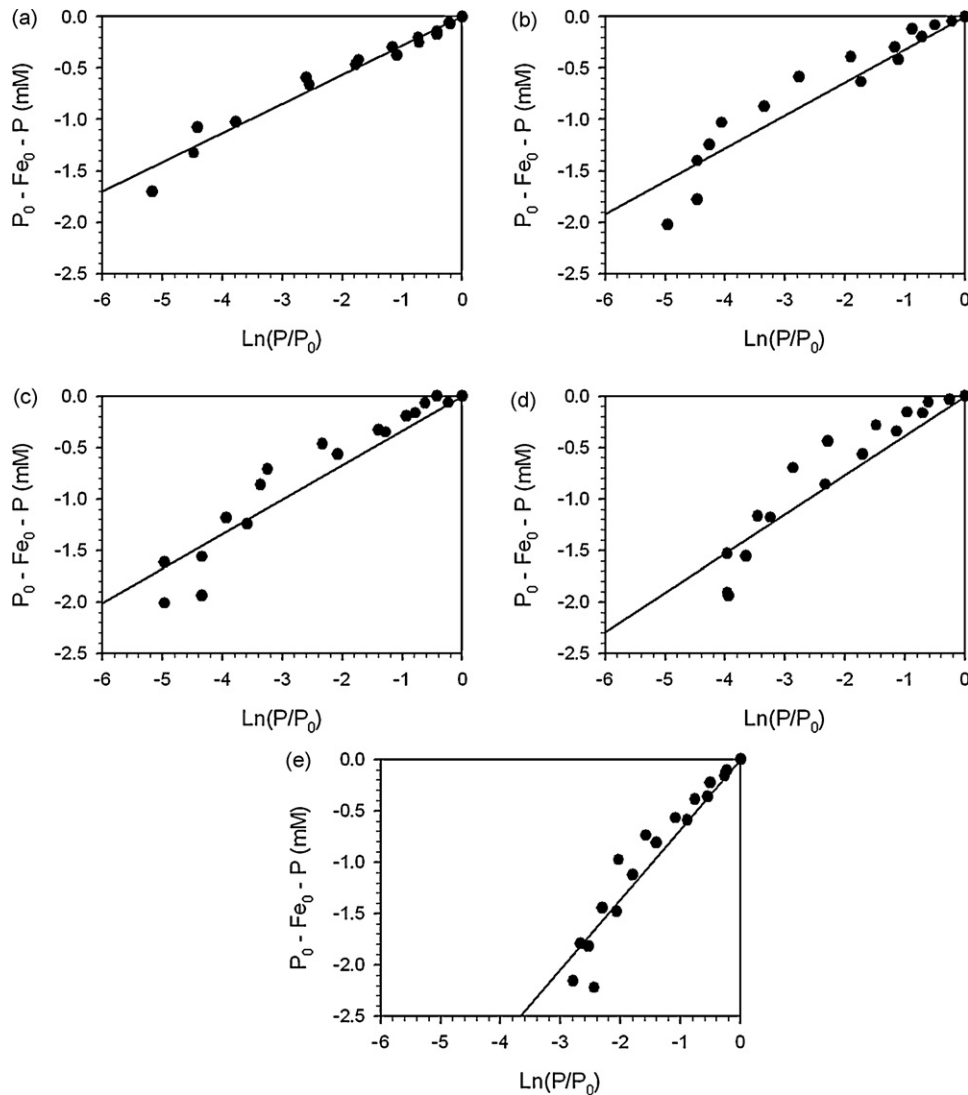
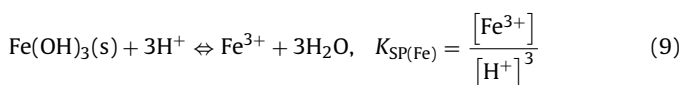


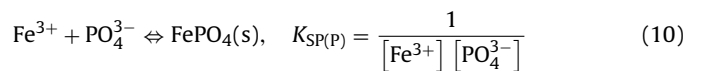
Fig. 7. Plot of $Y = P_0 - Fe_0 - P$ as a function of $X = \ln(P/P_0)$ (Eq. (15)) corresponding to the different tested pH values: (a) 5.0, (b) 6.0, (c) 7.0, (d) 8.0, and (e) 9.0.

phosphates, sodium bicarbonate, and ferric chloride as precipitant. The software CHEAQS was applied to identify all the species that were potentially present in the medium used in the precipitation experiments; by applying this software, 37 soluble and 3 solid species were identified (Table 1). Two of the identified solids were $Fe(OH)_3(s)$ and $FePO_4(s)$ as expected; the third solid phase, $KFe_3(SO_4)_2(OH)_6(s)$, is known as jarosite. This mineral is formed at low pH (about 1–2.5) during biochelating of iron-containing sulphides, for example; thus, it is commonly found in sediments of acid mine drainage-impacted environments [20]. High temperatures (about 70 °C) or long times (several weeks) are usually necessary to form this mineral from aqueous solutions [21,22]. In addition, there are no reports concerning the formation of jarosite during the phosphorous removal from wastewaters using ferric iron. For these reasons, the formation of jarosite was neglected in the present work.

The solubility of amorphous $Fe(OH)_3(s)$ can be represented by the following reaction:



where $K_{SP(Fe)}$ (M^{-2}) is the solubility constant of amorphous $Fe(OH)_3(s)$. The value corresponding to $\log[K_{SP(Fe)}]$, at infinite dilution and 298 K, ranges between 3 and 5 [17]. Reaction (9) competes with the orthophosphate precipitation reaction:



Literature data concerning $\log[K_{SP(P)}]$ range from 23 (for amorphous $FePO_4$) to 28.7 (for strengite) [23,24]; the default value for $\log[K_{SP(P)}]$ in CHEAQS is 26.4 [25].

Within the range reported in the literature, the most favourable combination of K_{SP} values to precipitate orthophosphate with ferric chloride corresponds to $\log[K_{SP(Fe)}] = 5$ (the highest solubility for $Fe(OH)_3(s)$) and $\log[K_{SP(P)}] = 28.7$ (the lowest $FePO_4(s)$ solubility). Assuming these K_{SP} values, the ratios Fe_{TS}/Fe_0 , P/P_0 , and $(Fe:P)_{prec}$ corresponding to an initial Fe:P molar ratio of 2.0 were calculated as a function of pH using the software CHEAQS. Fig. 6a shows that the calculated ratio Fe_{TS}/Fe_0 as a function of pH was lower than the experimental data; in addition, a strong deviation was also obtained for the ratio P/P_0 . Theoretical calculations using software CHEAQS showed that even under the most favourable combination of K_{SP} values, ferric phosphate precipitation should not take place if pH

is higher than about 7.8. For this reason, as pH tends to 7.8 a sharp increase of the calculated $(\text{Fe:P})_{\text{prec}}$ ratio was obtained (Fig. 6b). However, experimental results show that ferric phosphate precipitation occurred even at pH 9 and $(\text{Fe:P})_{\text{prec}}$ ratios were lower than 2.4. The differences between the software predictions and experimental results concerning the precipitation of ferric phosphate may be due to kinetic features of the precipitation process that equilibrium calculations do not take into account. Aqueous phase reactions (such as acid/base equilibria) are generally faster than precipitation/dissolution reactions; while time scale for the former is about seconds, days to months are usual for the latter to achieve the thermodynamic equilibrium. Other authors also demonstrated that equilibrium chemistry is not always fully applicable to the precipitation of phosphorus using ferric chloride. In most cases authors are forced to postulate new ferric phosphate species [24], adsorption [23] or complexation mechanisms [26] to better represent their results.

3.5. Analysis of orthophosphate precipitation experiments in the presence of biomass at a constant pH using a kinetic approach

The above mentioned analysis demonstrates that equilibrium chemistry cannot explain the precipitation of $\text{FePO}_4(\text{s})$ at pH values higher than 8 (Fig. 6). In addition, for all the tested conditions of pH and initial $\text{Fe}_0:\text{P}_0$ ratios (r), $\text{Fe}(\text{III})$ hydrolysis and FePO_4 precipitation reactions compete with each other (Figs. 4 and 5). For this reason, a kinetic approach was applied to analyze the phosphorous precipitation process using ferric chloride in the presence of biomass at different pH values ranging between 5 and 9.

Both $\text{Fe}(\text{III})$ hydrolysis and ferric phosphate precipitation kinetics have been studied extensively [27–30]. During the addition of ferric chloride, besides the precipitation of $\text{FePO}_4(\text{s})$, $\text{Fe}(\text{III})$ also reacts with water to form soluble mononuclear $(\text{Fe}(\text{OH})_n)^{3-n}$, $n=1-4$ or multinuclear hydrolysis species $(\text{Fe}_2(\text{OH})_2^{4+}$, $\text{Fe}_3(\text{OH})_4^{5+}$), and amorphous $\text{Fe}(\text{OH})_3(\text{s})$ precipitate [17]. The term total soluble $\text{Fe}(\text{III})$ (Fe_{TS}) in Eq. (3) represents the sum of all the soluble species that contain ferric iron (Table 1). The simplest kinetic expressions to represent the co-precipitation of FePO_4 and $\text{Fe}(\text{OH})_3$ can be obtained assuming that reaction rates are of the first order with respect to each reactant. Therefore, for a given pH value, $\text{Fe}(\text{III})$ hydrolysis rate is proportional to the total soluble $\text{Fe}(\text{III})$ concentration (Fe_{TS}); in addition, FePO_4 precipitation rate is proportional to Fe_{TS} and to the soluble phosphate concentration (P). Thus, proposed kinetic expressions are the following:

$$\frac{dP}{dt} = -k_p \text{Fe}_{\text{TS}} P \quad (11)$$

$$\frac{d\text{Fe}_{\text{TS}}}{dt} = -k_p \text{Fe}_{\text{TS}} P - k_{\text{Fe}} \text{Fe}_{\text{TS}} \quad (12)$$

where k_p ($\text{mM}^{-1} \text{s}^{-1}$) and k_{Fe} (s^{-1}) are conditional rate constants, that is, rate constants that may depend on pH. Dividing Eq. (12) by Eq. (11) gives:

$$\frac{d\text{Fe}_{\text{TS}}}{dP} = 1 + \frac{k_{\text{Fe}}}{k_p} \frac{1}{P} \quad (13)$$

The initial conditions are $\text{Fe}_{\text{TS}, t=0} = \text{Fe}_0$ and $P_{t=0} = P_0$. Rearranging Eq. (13) and integrating both sides the following expression was obtained:

$$\text{Fe}_{\text{TS}} - \text{Fe}_0 - P + P_0 = \frac{k_{\text{Fe}}}{k_p} \ln \left(\frac{P}{P_0} \right) \quad (14)$$

As $t \rightarrow \infty$, $\text{Fe}_{\text{TS}} = 0$ and $P = P_\infty$, therefore

$$P_0 - \text{Fe}_0 - P_\infty = \frac{k_{\text{Fe}}}{k_p} \ln \left(\frac{P_\infty}{P_0} \right) \quad (15)$$

Table 2

Effect of pH on the calculated values of k_{Fe}/k_p from the linear regression of Eq. (15).

pH	k_{Fe}/k_p (mM)	r^2
5.0	0.283 ± 0.028	0.9615
6.0	0.320 ± 0.047	0.9174
7.0	0.335 ± 0.045	0.9225
8.0	0.381 ± 0.066	0.9103
9.0	0.682 ± 0.063	0.9271

Eq. (15) can be applied if, within the time intervals studied in precipitation experiments, both $\text{Fe}(\text{III})$ hydrolysis and FePO_4 precipitation rates are fast enough to assume that $P \cong P_\infty$. This approximation was valid under the experimental conditions tested in the present work because most of the composition changes occurred within the first 2 h (see Section 3.1). From Eq. (15), a plot of $Y = P_0 - \text{Fe}_0 - P$ as a function of $X = \ln(P/P_0)$ should be a straight line with the slope k_{Fe}/k_p (Fig. 7). Calculated ratios k_{Fe}/k_p and r^2 values for the linear regressions at different pH values obtained from Fig. 7 are shown in Table 2. Taking into account the number of data corresponding to each regression ($n = 18$ data/exp), r^2 values above 0.91 demonstrate a good agreement between the proposed mechanistic model and experimental data. Although there were systematic deviations from linearity in the plots of Fig. 6 at low P/P_0 values, these conditions corresponded to initial Fe:P molar ratios higher than 2, which were outside the operational range for technological purposes. Table 2 shows that as pH increased, higher k_{Fe}/k_p ratios were obtained, indicating that a higher proportion of $\text{Fe}(\text{III})$ precipitated as amorphous ferric hydroxide.

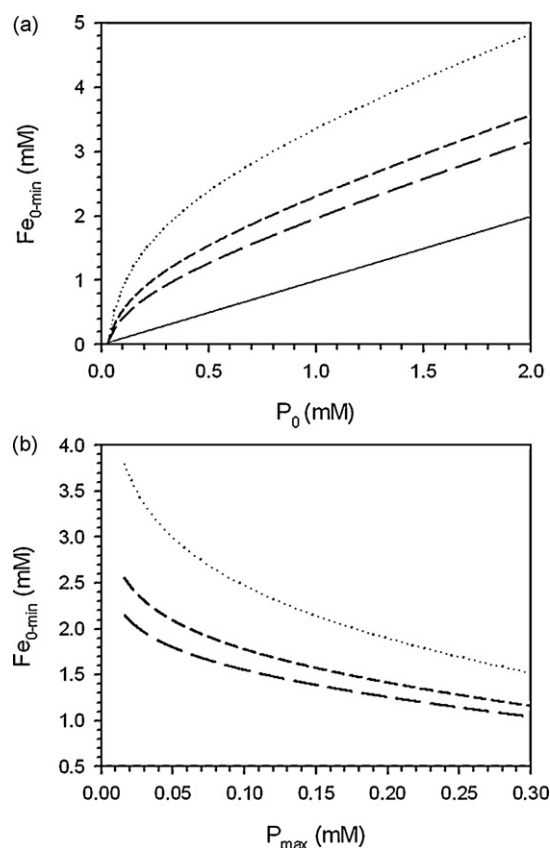


Fig. 8. a) Minimum ferric chloride concentration ($\text{Fe}_{0\text{min}}$) required to achieve a discharge limit for orthophosphate concentration of $P_{\text{max}} = 0.03$ mM as a function of initial orthophosphate concentration (P_0); (b) effect of P_{max} on $\text{Fe}_{0\text{min}}$ corresponding to an initial orthophosphate concentration $P_0 = 1$ mM. In (a) and (b), pH values are the following: 5.0 (—), 8.0 (---), 9.0 (.....). Continuous line represents the stoichiometric ratio 1:1.

For each tested pH value and initial phosphate concentration, the proposed mechanistic model was used to calculate the soluble phosphate concentration as a function of the $Fe_0:P_0$ ratio; then, the fraction of Fe(III) forming $FePO_4(s)$ and $Fe(OH)_3(s)$ was calculated by means of Eqs. (5) and (6), respectively. Continuous lines in Figs. 4 and 5 representing the proposed model agree with the obtained experimental data, confirming its validity.

Eq. (15) may be useful to determine the minimum initial ferric chloride concentration (Fe_{0min}) required to achieve a given discharge limit concentration for orthophosphate (P_{max}) as a function of the initial orthophosphate concentration (P_0) and pH. Fig. 8a shows that for all tested pH values, Fe_{0min} is higher than the value calculated assuming a stoichiometric ratio 1:1 because a fraction of the added Fe(III) precipitates as $Fe(OH)_3(s)$. For example, if $P_0 = 1$ mM then a Fe_{0min} concentration ranging between 1.9 (pH 5) and 3.4 mM (pH 9) is necessary to achieve a discharge limit for orthophosphate concentration of 0.03 mM (Fig. 8a). In addition, Fig. 8a shows that as P_0 increases, the difference between the coagulant dose at pH 5 and at pH 9 also increases. The discharge limit concentration for orthophosphate (P_{max}) also affects Fe_{0min} ; however, an increment of tenfold in P_{max} (from 0.03 to 0.3 mM) only reduces twofold the required Fe_{0min} (Fig. 8b). In several countries, regulations indicate that P_{max} depends on the receiving body water; thus, Eq. (15) can help not only to calculate Fe_{0min} for a given pH and P_0 values, but also to choose the optimal receiving body water in order to minimize operating costs of orthophosphate precipitation using ferric chloride in activated sludge reactors.

4. Conclusions

In this work the effect of the presence of activated sludge, alkalinity, pH (5 to 9), and initial Fe:P molar ratio ($Fe_0:P_0$, 0 to 3) on the precipitation of orthophosphates using ferric chloride was analyzed.

The presence of biomass did not affect the performance of orthophosphate precipitation; however, the addition of ferric chloride caused a drop of pH to values below 3.0 not compatible with the normal metabolic activity of activated sludges.

When 1 g L^{-1} $NaHCO_3$ (12 mM) was added, orthophosphate removals higher than $97 \pm 2\%$ and pH levels above 6.2 (compatible with the biomass activity) were obtained using an initial Fe:P molar ratio = 1.9.

Precipitation experiments at constant pH (5–9) showed that although orthophosphate removal efficiency is favored at low pH, this condition also increases the Fe(III) solubility. Besides, for all the tested pH values, co-precipitation of $FePO_4(s)$ and $Fe(OH)_3(s)$ occurred.

Calculations using a chemical equilibrium model (CHEAQS) predicted that ferric phosphate precipitation should not take place if $pH > 7.8$. However, experimental results show that ferric phosphate precipitation occurred even at pH 9. The differences between the software predictions and the experimental results may be due to kinetic features that equilibrium calculations do not take into account.

A mechanistic model was proposed to predict the soluble orthophosphate concentration as a function of the initial Fe:P molar ratio for different pH values. The model assumes that reaction rates for hydrolysis of Fe(III) and $FePO_4(s)$ precipitation are first order with respect to orthophosphate and total soluble ferric iron. For initial Fe:P molar ratios lower than 2, which is the operational range for technological purposes, the proposed model adequately predicted the soluble orthophosphate concentration, and the composition of the precipitate in terms of the fraction of coagulant Fe(III) that formed $FePO_4(s)$ and $Fe(OH)_3(s)$.

The proposed model can be applied to calculate the minimum ferric chloride concentration required to achieve a given discharge limit concentration for orthophosphate as a function of the initial orthophosphate concentration and pH in an activated sludge reactor with simultaneous precipitation.

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