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Effect of operating conditions on the chemical phosphorus removal using ferric chloride by evaluating orthophosphate precipitation and sedimentation of formed precipitates in batch and continuous systems

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HIGHLIGHTS

- Operational factors affected the process of phosphorus removal by ferric chloride.
- Activated sludge biomass and prolonged settling times favored the process efficiency.
- Fe(III)-treated bioreactor at a sludge age of 21 days showed the best performance.
- Higher sludge age produced the smallest flocs deteriorating the reactor performance.
- Floc size measurement using image analysis allowed monitoring these systems.

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ABSTRACT

Chemical phosphate removal by Fe(III) involves the precipitation of ferric phosphate and subsequent sedimentation of Fe–P particles. Physical–chemical factors that affect the phosphorus (P) precipitation are well known; however, the factors affecting the sedimentation of Fe–P precipitates have been poorly studied. The aims of this work were: (a) To study the effect of pH, presence of biomass (3.0 g TSS/L) and settling time on the orthophosphate precipitation by ferric chloride in a batch system. (b) To determine the effect of these factors on the sedimentation of the formed Fe–P particles. (c) To evaluate the performance of a laboratory-scale continuous activated sludge (AS) reactor operated with phosphorus simultaneous precipitation by ferric chloride under the optimum operating conditions determined from previous batch assays. Results from batch studies showed that presence of AS biomass and prolonged settling times favored the P removal. According to the proposed equation, in presence of biomass, the settling rate of the Fe–P precipitates was 3–7 times higher than that corresponding to phosphate buffer system. In the continuous system, Fe–P precipitates were gradually incorporated to the biomass, improving the reactor performance. However, a gradual shift of the size distribution from large to poorly settling small flocs was observed. The system operated at a sludge age of 21 days achieved more rapidly better performance than at 40 days. This last system showed bad flocculation exhibiting smaller flocs than the reactor with younger sludge. Simultaneous determination of the accumulation rate of fixed solids, and floc size distribution allows monitoring these systems.

1. Introduction

Municipal and industrial wastewaters containing high concentrations of phosphorous (P) should be treated before discharging to receiving water bodies. Phosphorous from wastewater can be present as orthophosphate, condensed inorganic phosphates and organophosphates. Chemical precipitation, enhanced biological phosphorus removal, or a combination of both are usually adopted to remove phosphorous from wastewaters. Chemical removal can be performed in different stages of the effluent treatment process. Simultaneous precipitation, which corresponds to the addition of coagulants on the aeration basin or after the secondary treatment, involves lowest cost and improved stability of activated sludge [1].

The process of phosphate chemical removal is complex and poorly understood, for the case of the salts of Fe(III), such as ferric chloride, it involves the following mechanisms: precipitation of ferric phosphate, ferric hydroxide and ferric-oxo-hydroxo-phosphate complex, phosphate adsorption on ferric hydroxide and

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Nomenclature

AS	activated sludge
COD	chemical oxygen demand (mg O_2/L)
DO	dissolved oxygen
DSVI	diluted sludge volume index (mL/g)
Fe_{TS}	total soluble Fe
Fe_T	total Fe
FSS	fixed suspended solids
Fe_{part}	particulated Fe
$[Fe_{part}]$	particulated Fe concentration
$[Fe_{part_o}]$	particulated Fe concentration at the start of the sedimentation period
F/M	food to microorganism ratio (kg COD/(kg VSS day))
HRT_C	hydraulic residence time in the clarifier (h)
HRT_T	total hydraulic residence time (h)
$[H^+]$	concentration of protons (mmol H^+/L)
IET	iron exposure time (day)
k	coefficient (L^{n+1} mmol Fe_{Part}^{-1} mmol H^{+-n} h^{-1})
k_1	second-order decay coefficient ((mmol Fe_{part}/L)$^{-1}$ h^{-1})
MMLAS	model mixed liquor of activated sludge
n	coefficient (dimensionless)
PB	phosphate buffer
PO_4^{3-}—P	orthophosphate
P_{part}	particulated P
SRT	solids residence time (day)
T	time (h)
TP	total phosphorus
TSS	total suspended solids
VSS	volatile suspended solids

coagulation and flocculation phenomena [2]. Fe salts form positively charged ferric-oxo-hydroxo-phosphate complexes that promote coagulation [2]. The chemical flocs formed are separated from the treated wastewater through a clarifier. It should be remarked that most of the studies are focused on the physical–chemical factors affecting the precipitation process of orthophosphate without considering the settling properties of the formed chemical precipitates. Fe:P molar ratio higher than 1.5:1 is commonly recommended for phosphate precipitation [3–5]; maximum efficiency of this process is achieved at pH values between 5.0 and 7.0 [4]. From studies of orthophosphate precipitation under uncontrolled pH conditions, it has been shown that activated sludge (AS) biomass does not affect the process performance [5]; however, it could facilitate the separation of the precipitates or Fe–P containing complexes, as was suggested by He et al. [6].

Small activated sludge flocs are generated by addition of metal salts on the secondary stage of wastewater treatment [7–9]. This constitutes a serious problem in activated sludge plants, since small flocs settle slowly affecting the system performance. Li [7] reported that adequate Fe(III) concentrations improved the bioflocculation and hence the sequencing batch reactor (SBR) performance; however, overdosage of Fe(III) reduced the fraction of the flocs with settleable sizes, deteriorating the final effluent quality. It is well known that a low sludge load (expressed as food/microorganism ratio) and a high sludge age promote bioflocculation; however, AS systems treated with Fe(III) under these operational conditions has been scarcely studied. In this context, it is interesting to operate an AS reactor exposed to Fe(III) at sludge age higher than 20 days in order to relate its performance to the changes in the floc size. Additional studies on the main factors that affect the process of chemical phosphate removal would be of great interest.

The aim of this study was to determine the most appropriate operating conditions for chemical phosphorus removal by ferric chloride in activated sludge systems (batch and continuous reactors). For this, the following specific objectives were proposed: (a) To study the effect of pH, presence of biomass and settling time on the orthophosphate precipitation in a batch system. (b) To determine the effect of pH, presence of biomass and settling time on the sedimentation of the Fe–P particles formed during the precipitation phase. (c) To evaluate the performance of a laboratory-scale AS reactor operated in continuous mode with simultaneous precipitation of phosphorus by ferric chloride under the optimum operating conditions determined from previous batch assays, testing different sludge ages.

2. Materials and methods

2.1. Biological and chemical materials

Activated sludge was obtained from an aerobic laboratory-scale (3.8 L) AS reactor with partial biomass recycle. The total hydraulic residence time (HRT_T) of the system was 29 h; the sludge age was maintained at 21 days by daily wasting 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 that was prepared twice a week; its composition was the following: cheese whey, 1.5 g/L as COD; $(NH_4)_2SO_4$, 0.94 g/L (7.12 mM); KH_2PO_4, 0.071 g/L (0.52 mM); $Na_2HPO_4{\cdot}7H_2O$, 0.213 g/L (0.80 mM); $NaHCO_3$, 1.0 g/L (12 mM); resulting nitrogen as ammonia (NH_3–N), 199.0 mg N/L; phosphorous as orthophosphate $\left(PO_4^{3-}\text{—}P\right)$, 40.0 mg P/L and total P (TP), 45.5 mg P/L. pH of the wastewater was adjusted to 7.0 adding a few drops of HCl (1 M). Cheese whey showed the following composition (% w/w): total lipid (3%), total protein (12%), lactose (75%), water (5%), and mineral salts (1%).

Assays of chemical phosphorus removal were performed in batch and continuous systems using ferric trichloride hexahydrate. 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. Assays of chemical phosphorus removal in batch systems

Chemical phosphorus removal by ferric chloride was studied in both systems: phosphate buffer (PB) solution and model mixed liquor of activated sludge (MMLAS). PB composition was: KH_2PO_4 0.071 g/L, $Na_2HPO_4{\cdot}7H_2O$ 0.213 g/L, $NaHCO_3$ 1 g/L. MMLAS system was obtained by sedimentation and then resuspension of activated sludge, from the aerobic reactor, in the PB solution previously described. The washing was performed to remove cellular debris and metabolic products. The biomass concentration of the MMLSA system expressed as total suspended solids (TSSs) was 3.0 ± 0.3 g/L.

All assays of chemical phosphorus removal were conducted in 500 mL glass vessels at room temperature (20 ± 2 °C) under constant pH conditions (pH = 5.0–8.0). PB or MMLAS (300 mL) and appropriate volumes of a stock solution of $FeCl_3{\cdot}6H_2O$ (74.0 mM) were mixed by magnetic stirring. Tested initial phosphorous concentrations ranged from 36 to 47 mg/L (1.16–1.51 mM), resulting