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Precipitation of iron-hydroxy-phosphate of added ferric iron from domestic wastewater by an alternating aerobic–anoxic process

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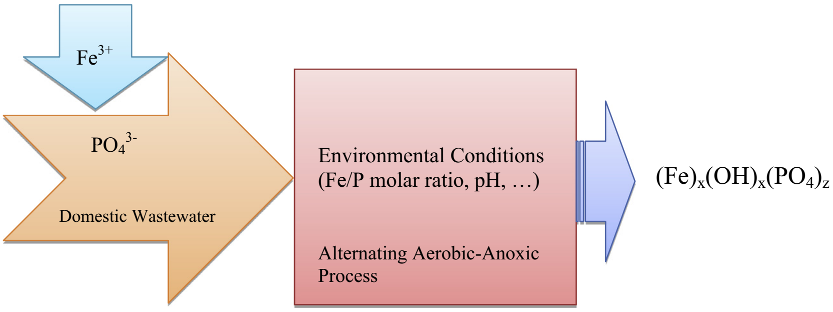
HIGHLIGHTS

- Precipitation of phosphate by an alternating aerobic anoxic process was assessed.
- The empirical formulas of iron-hydroxy-phosphate were defined.
- Physicochemical-biological phosphorus removal was investigated.
- Effects of Fe/P molar ratio and pH on phosphorus precipitation were verified.
- The optimum efficiencies to remove SRP and TP were verified.

GRAPHICAL ABSTRACT

Formation of iron-hydroxy-phosphate by an alternating aerobic–anoxic process is dependent on the environmental conditions.



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ABSTRACT

Removal of phosphorus from a municipal wastewater by simultaneous precipitation of iron-hydroxy-phosphate (IHP) was investigated. The addition of Fe^{3+} was performed to supplement biological excess phosphorus removal by a completely mixed alternating aerobic–anoxic (AAA) activated sludge process. The cycles of 3-h anoxic time and 3-h aerobic digestion were set to controlling a single-sludge nitrification–denitrification. In this study, attempt has been made to analyse the effects of initial dissolved Fe/P molar ratio and pH on IHP precipitation. The AAA treatment process to remove soluble reactive and total phosphorus from domestic wastewater had a moderate efficiency. The empirical formula of IHP that differs from different pH ranges was verified. Two types of $Fe_4(OH)_9PO_4$ and $Fe_5(OH)_6(PO_4)_3$ precipitate may occur in different conditions of the AAA process. The efficiency of phosphorus removal from domestic wastewater by an AAA process was verified to contribute to a working methodology for the application of technologies in the field of domestic wastewater treatment.

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1. Introduction

The design of secondary domestic wastewater treatment plants (WWTPs) is usually based on the need to reduce carbonaceous, nitrogenous and phosphorus matters loads to limit pollution of the environment. Most domestic wastewater treated in industrial-scale WWTP includes a variety of physical, chemical or biological treatment processes. This must take account of the efficient removal of both carbonaceous and nitrogenous matters achieved by different types of conventional biological WWTP; however, -phosphorus removal from a domestic wastewater to meet the effluent standards regulated by the law may be achieved either through chemical removal, advanced biological treatment or a combination of both [1,2]. Note that the target of phosphorus content in a treated wastewater effluent should be below than 1 mgP L^{-1}. A separate mixer setting up in both the anaerobic zone and anoxic zone and two other mixers equipped in the ditches has been used for the removal of phosphorus matter from domestic wastewater [3]. Multizone structure of anaerobic–aerobic–anoxic process favours the enhancement of denitrifying phosphorus removal and simultaneous nitrification–denitrification for domestic wastewater treatment systems [4].

The forms of phosphorus present in domestic wastewater can include organic, soluble or bound forms. Understanding the relationship among these forms of phosphorus is necessary to understand sources of phosphorus and the extent to which phosphorus can move within the environment. Soluble reactive phosphorus (SRP) or orthophosphates in a domestic sewage can range from 50% to 70%; the remainder should be in forms of polyphosphates and organic phosphorus [5]. Domestic sewage typically has total phosphorus levels ranging from 10 to 25 mgP L^{-1} corresponding to a load of 3.9–4.2 g per equivalent people per day [6]. Because of biotic hydrolysis of organic phosphorus occurred during passing period in a sewerage networks system and in a biological WWTP can transform polyphosphates and organophosphates into orthophosphates, approximately 90% of the SRP can be found in a treated wastewater effluent. The presence of phosphorus in an effluent of the WWTP can move into surface waters and causes water quality problems such as eutrophication [7].

Even the amount of chemical phosphorus precipitation of added Fe^{3+} can be calculated based on its stoichiometric reaction of $PO_4^{3-} + Fe^{3+} \rightarrow FePO_4$. The fact that a purely chemical precipitation can't be found due to classical culture media as domestic wastewater treated by biological processes have a complex composition [8]; however, -the removal of phosphorus from a domestic sewage can be described by other phenomena such as ion exchange, complexation and accumulation. Many assumptions have been made in defining the precipitation of phosphate from waters, i.e., (i) ferric phosphate ($FePO_4$) and ferric hydroxide ($Fe(OH)_3$) coexist in equilibrium [9,10], (ii) adsorption of phosphate on metal hydroxide [11,12] and (iii) precipitation of metal-hydroxy-phosphate [13,14].

Since previous studies have reported that the composition of iron-hydroxy-phosphate (IHP) precipitates can be represented by the empirical formulas of such as $Ca_kFe^{2+}_mFe^{3+}_n(H_2PO_4)_f(HCO_3)_e(OH)_h$ [15] and $Fe_{2.5}PO_4(OH)_{4.5}$ [16], do severe changes in environmental conditions of the experiment favour the formation of a wide variety of the IHP precipitates. It is well known that Fe^{3+} is a more stable ion than Fe^{2+} under normal conditions [17]; however, -the reduction of Fe^{3+} to Fe^{2+} at a neutral pH may not be evident in a domestic wastewater. Nevertheless, the reduction of Fe^{3+} to Fe^{2+} resulted in dissociation of ferric phosphate can be adapted for precipitation adjustment with a hypothetical Fe/P molar ratio [18]. A mass balance estimate of phosphorus adsorption and sedimentation has been made in modelling phosphorus removal from waters [19,20]. In the previous studies by Donnert and Selecker [21] and Hsu [22] have reported that the optimal phosphorus removal condition in a physicochemical and biological treatment process is dependent upon both molar ratio and quality of wastewater. The empirical formula of IHP formation of added Fe^{3+} can be proposed based on the loss of soluble iron and phosphorus from waters. Although the chemical composition of IHP precipitates has been interpreted by an empirical formula [15,16], the formation of IHP by simultaneous precipitation of $FePO_4$ and $Fe(OH)_3$ into a single-sludge nitrification–denitrification of the alternating aerobic–anoxic (AAA) process needs to be verified.

The objectives of this study are as follows: (1) to create a single-sludge nitrification–denitrification as biological and physicochemical media for simultaneous precipitations of $FePO_4$ and $Fe(OH)_3$, (2) to define the empirical formula for complex solids of IHP precipitates caused by simultaneous precipitations of $FePO_4$ and $Fe(OH)_3$ in different experimental conditions and (3) to assess the overall performance of the AAA process for the removal of phosphorus from domestic wastewater.

2. Materials and methods

2.1. Description of the treatment process and operating procedure

This study carried out in a single reactor of completely mixed AAA activated sludge process. As a biological fluidised bed system can be described by design and characterisation of long sludge retention time (SRT) of 15 days and low organic loading per unit of time, as shown in Fig. 1. The raw wastewater was stored in a storage tank at 4 °C and gently stirred until it was fed into the 10-L reactor. At a constant flow rate of 0.83 L h^{-1}, the hydraulic retention time (HRT) was kept constant at 12 h. The treated effluent was separated from the sludge in a settling tank. A return sludge pumping capacity of 200% of the wastewater flow rate was typical for the experiment. After the initial start-up process, which lasted about one month, a small amount of activated sludge was regularly extracted from the reactor to keep a constant SRT within close tolerances. However, it was difficult to control a constant amount of mix liquor suspended solids (MLSS) in the reactor due to the variability of the wastewater quality that fed the reactor. This study maintained the MLSS of the reactor at approximately 4 g L^{-1}. Even if a short anoxic phase was beneficial before an aerobic phase for effective nitrogenous and phosphorus matters removal [23], the cyclic conditions of 3-hour anoxic time and 3-hour aerobic period were set to guarantee an optimisation of nitrification–denitrification process during the experiment. The addition of ferric iron ($FeCl_3{\cdot}6H_2O$) with an average concentration of 26.33 mgFe L^{-1} was continuously fed into the reactor at a rate of one drop per second, even though intermittent chemical dose was recommendable for simultaneous chemical phosphorus removal [24]. The principle characteristics of the AAA process are depicted in Table 1.

2.2. Analytical methods

The sample concentrations of SRP were measured by ion chromatography with a conductivity measurement analyser (Dionex DX 100; Dionex Corporation, Sunnyvale, CA). Total phosphorus (TP) is a measure of all the forms of phosphorus (dissolved or particulate) that are found in a sample. The TP concentrations were analysed using the ascorbic acid method after mineralisation with potassium persulphate. The sample concentrations of soluble Fe were measured by atomic absorption spectrophotometry, and the same method was used for total Fe after mineralisation by aqua regia [25]. The pH, dissolved oxygen (DO), redox potential and temperature of the reactor were recorded automatically at 20-minute intervals using the CONSORT O_2/pH controller Model R301/R321.