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Comparative analysis across four wastewater treatment facilities

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Release of phosphorus through pretreatment of waste activated sludge differs essentially from that of carbon and nitrogen resources: Comparative analysis across four wastewater treatment facilities

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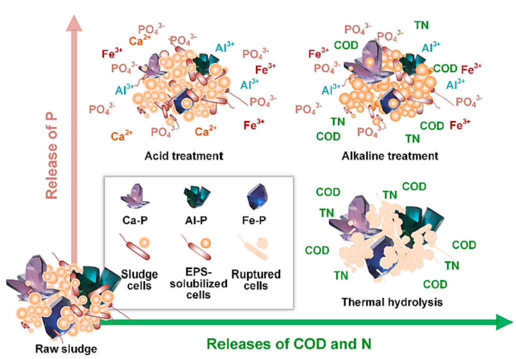
HIGHLIGHTS

- Sludge phosphorus efficiently released by pH modulation for various WWTPs.
- Release of phosphorus does not markedly correlate to those of organics and nitrogen.
- Alkaline treatment leads to simultaneous releases of phosphorus, COD and nitrogen.
- Added alkali can be utilized in the subsequent process of phosphate crystallization.

GRAPHICAL ABSTRACT



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ABSTRACT

The accumulation of phosphorus in activated sludge in wastewater treatment plants (WWTPs) provides potential for phosphorus recovery from sewage. This study delves into the potential for releasing phosphorus from waste activated sludge through two distinct treatment methods—thermal hydrolysis and pH adjustment. The investigation was conducted with activated sludge sourced from four WWTPs, each employing distinct phosphorus removal strategies. The findings underscore the notably superior efficacy of pH adjustment in solubilizing sludge phosphorus compared to the prevailing practice of thermal hydrolysis, widely adopted to enhance sludge digestion. The reversibility of phosphorus release within pH fluctuations spanning 2 to 12 implies that the release of sludge phosphorus can be attributed to the dissolution of phosphate precipitates. Alkaline sludge treatment induced the concurrent liberation of COD, nitrogen, and phosphorus through alkaline hydrolysis of sludge biomass and the dissolution of iron or aluminium phosphates, offering potential gains in resource recovery and energy efficiency.

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1. Introduction

The continuous rise of the world population requires a foreseeable increase in the global food supply, which would be inevitably dependent on the use of phosphorus fertilizers (Quist-Jensen et al., 2018). Excessive discharge of phosphorus after the consumption of phosphorus-containing products has, however, resulted in not only eutrophication of the receiving water bodies but also the loss of this essential element (Cordell et al., 2009). It has been reported that approximately 3.7 Mt of phosphorus from human activity ends up in sewage annually, accounting for 20 % of world demand of phosphate rock for fertilizer production (Kok et al., 2018).

The concentration of total phosphorus in sewage is approximately 6–8 mg/L (Wang et al., 2022; Zhou et al., 2017). In wastewater treatment plants (WWTPs), phosphorus is transferred from sewage to activated sludge through both biological and chemical processes. If this transfer is maximized, the waste activated sludge from the WWTPs can be a route for sewage phosphorus recovery. Enhanced biological phosphorus removal (EBPR) processes have been extensively employed in sewage treatment due to their notable advantage of not requiring chemical usage (Blackall et al., 2002). In this process, sewage phosphorus is transformed to polyphosphate in sludge cells and removed from the system through excess sludge wasting (Oehmen et al., 2007). Chemical phosphorus removal technologies using phosphate precipitants, such as Al and Fe salts, were adopted as early as the 1950′s and have become increasingly popular with stringent discharge limits of phosphorus being implemented in more countries and certain phosphorus-sensitive regions (Gebreeyessus and Jenicek, 2016). In many WWTPs, chemical dosing-assisted EBPR processes have been employed to enhance the removal efficiency at reasonable costs (Saoudi et al., 2022). For recovering phosphorus enriched in the waste activated sludge, its effective release to the aqueous phase is the first and critical step. Once the phosphorus is in a concentrated aqueous form (primarily as phosphate), it can be recovered through phosphate crystallization with struvite and hydroxyapatite as the prevalent products (Zhang et al., 2021).

The release of sludge phosphorus is found to be related to the distribution of phosphorus species in activated sludge. The speciation of phosphorus varies largely among WWTPs depending on factors such as the quality of raw sewage (particularly metal contents), the adopted process of sewage treatment, and the operating conditions (Yu et al., 2021). The content of phosphate in the sludge generated at a WWTP that received a mixed stream (including 15 %-20 % industrial wastewater) was reported to be 30 % higher than a WWTP dedicated solely to domestic wastewater (Wang et al., 2022). In two WWTPs where Fe salts were dosed, the sludge from the AO system was observed to contain 15 % more orthophosphate than the treatment system with only aerobic units. Li et al. (2020) reported that an increase in the sludge retention time (from 7 to 30 days) led to the transformation of phosphorus-bound Fe compounds from amorphous to densified phases with a significantly reduced surface area and reactivity and consequently an increasing difficulty of phosphorus release and recovery.

The release of phosphorus from activated sludge has been scattered studied using different treatment methods. He et al. (2016) reported that 49 % of the total phosphorus could be released from the waste activated sludge of an A^2/O WWTP when the sludge pH was adjusted to 4 whilst the number was 70 % at pH 12. A study with five WWTPs by Quist-Jensen et al. (2018) showed that *ortho*-P release at pH 2 was more efficient for digested sludge (70 % to 80 % of the total phosphorus) than for non-digested sludge (30 %). Xu et al., (2018a) reported that hydrothermal treatment at 200 °C, as an effective measure of sludge disintegration, released approximately 30 % of total phosphorus of the sludge from an A^2/O WWTP. In a study with Fe-rich activated sludge, Wang et al. (2021) increased the hydrothermal temperature from 175 to 225 °C, finding that the released phosphorus increased only marginally (from 7 to 7.5 mM). Zheng et al. (2020) reported that calcium dosing to the sludge decreased the efficiency of phosphorus release during hydrothermal treatment. Adding EDTA as a metal complexant into the sludge from chemical phosphorus removal processes was observed to enhance phosphorus release from Fe and Al-rich sludge during the anaerobic digestion by 497.8 % and 627.8 % (Ping et al., 2020). In a study of aerobic sludge digestion with pH controlled to exclude pH variation-induced dissolution/precipitation of phosphate, the release of phosphorus was observed to be inefficient ($<$ 60 mg/L in 8 d as associated with endogenous respiration of phosphorus accumulating organisms), in comparison to the high levels of total phosphorus of ~ 600 mg/L in the sludge. Liu et al. (2019) compared the efficiencies of phosphorus release from waste activated sludge by multiple methods, finding that alkaline treatment freed the highest amount of phosphorus (90 %) whilst acid treatment efficiently released orthophosphate (85 % of sludge phosphorus) for the studied sludge. Based on the above, it is evident that the effectiveness of sludge treatments in releasing phosphorus varies with the property of sewage sludge and the employed treatment methods, while the underlying mechanisms are still not well understood. In particular, for wastewater treatment plants with varying influent conditions and treatment processes, the appropriate selection of sludge treatment technologies for efficient phosphorus release warrants more research. At the same time, the incorporation of the sludge (pre) treatment step into the waste sludge management processes (e.g., digestion) and in a broader context to the entire system of water/sludge treatment and resource/energy recovery at an acceptable cost is also important.

In this study, a comparative investigation of two types of sludge treatment methods: hydrothermal treatment and pH adjustment was conducted, aiming to release phosphorus from waste activated sludge sourced from four WWTPs that employed distinct phosphorus elimination strategies. The correlations between the release of phosphorus and releases of COD and nitrogen, along with the pH-dependent nature of phosphorus release, were explored to unravel the intricate processes governing phosphorus mobilization. These investigations offer insights into effective strategies for liberating sludge-carrying phosphorus, contributing to the potential recovery of this valuable resource.

2. Materials and methods

2.1. Waste activated sludge

Waste activated sludge was collected from the sludge recirculation lines of four WWTPs in Beijing with different processes of phosphorus removal adopted (Table 1). The sludge samples were gravity thickened at room temperature for 12 h before use. Basic information of the WWTPs and properties of the thickened sludge are listed in Table 1.

2.2. Experiments of sludge treatment

Three methods of sludge treatment, i.e., thermal hydrolysis (TH), acid treatment (AC) and alkaline treatment (AK), were investigated to explore the effectiveness of these treatments in release sludge phosphorus. Thermal treatment was conducted by heating 200 mL of waste activated sludge in 250-mL closed vessels at 170 °C for 0.5 h (TH1), 1 h (TH2) and 2 h (TH3). For AC and AK treatments, 1 M HCl and 1 M NaOH were added dropwise to 100 mL of waste activated sludge to adjust the pH to 2 and 12, respectively. The pH was then maintained at the values for 30 min. The variations of phosphorus, COD and nitrogen in the aqueous phase were followed during the treatments. Additional sludge samples were used to analyze the transformation of phosphorus species during the treatments by the SMT method (Standards, Measurements and Testing protocol, the European Commission) and ^{31}P NMR (^{31}P nuclear magnetic resonance spectroscopy). Subsamples for inorganic phosphorus fractions from the SMT extraction were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) to determine the contents of metals in the sludge. Variation of the sludge morphology

Table 1
Basic information of the four WWTPs and properties of the thickened WAS. (A study on Qinghe sludge is presented in Liu et al., 2019).

	Qinghe	Xiaohongmen	Jinyuan	Yongfeng
WWTP				
Process	A^2/O	A^2/O	C-Tech SBR	Oxidation ditch
Capacity (m^3/d)	55,000	60,000	50,000	20,000
Chemical dosing	–	$Al_2(SO_4)_3$	$FeCl_3$	PAM
Thickened sludge				
TSS (g/L)	35.3 ± 0.8	22.8 ± 0.2	28.0 ± 0.6	37.9 ± 0.4
VSS (g/L)	27.3 ± 0.1	14.5 ± 0.1	16.7 ± 0.8	19.0 ± 0.5
VSS/TSS	77.1 %	63.4 %	59.4 %	50.2 %
COD_{mx} [a] (mg/L)	28848 ± 48	22407 ± 299	18272 ± 364	22530 ± 1729
COD_{aq} [b] (mg/L)	118 ± 3	98 ± 3	111 ± 20	40 ± 1
TP_{mx} [a] (mg/L)	938 ± 4	660 ± 8	883 ± 2	694 ± 2
TP_{aq} [b] (mg/L)	96.9 ± 0.9	-[c]	-[c]	25.0 ± 0.0
PO_4-P_{aq} [b] (mg/L)	96.1 ± 0.3	-[c]	-[c]	28.1 ± 0.0
TN_{mx} [a] (mg/L)	1523 ± 23	1194 ± 9	1614 ± 109	987 ± 24
TN_{aq} [b] (mg/L)	26.7 ± 0.3	17.4 ± 0.2	28.4 ± 1.5	10.4 ± 0.1
NH_4^+-N_{aq} [b] (mg/L)	19.2 ± 0.2	14.6 ± 0.1	24.2 ± 0.3	8.9 ± 0.3

[a] mx refers to sludge mixture;
[b] aq refers to aqueous fraction;
[c] below the detection limit.

was recorded by scanning electron microscopy (SEM).

The reversibility of sludge phosphorus release by pH adjustments was investigated with pH swings between 2 and 12. Two groups of waste activated sludge from Qinghe were used in this experiment. In Group A, 11 samples of 100-mL sludge were treated with HCl/NaOH to adjust the pH to different values ranging from 2 to 12. Each pH value was maintained for 30 min. In Group B, 300 mL of sludge was firstly alkali-treated to adjust the pH to 12 and then the sludge pH was lowered stepwise by adding HCl to 2 with a maintenance time of 30 min for each pH value. Soluble total phosphorus (TP_{aq}) and PO_4-P (PO_4-P_{aq}) were followed during the pH adjustment.

2.3. *Analyses of aqueous and solid phases of sludge*

pH was measured using a PHSJ-3F pH meter with an E-301F electrode (Leici, China). The concentrations of COD, TP, TN, PO_4-P and NH_4^+-N were determined using Hach testing reagents with a DR3900 spectrophotometer and a DRB-200 thermostat when digestion was required (Hach, USA). Prior to measuring the aqueous fractions, samples were filtered through polyethersulfone (PES) membranes with a pore size of 0.45-μm (Membrana, Germany). The concentrations of metals were determined by ICP-MS using an Agilent 7900 system (USA). The plasma was argon gas with a nebulizer gas flow of 0.69 L/min, a lens voltage of 7.8 V, and an RF power of 1600 W.

Microscopy imaging was performed by a Hitachi SU8000 field-emission scanning electron microscope (SEM). Sludge samples were fixed using 2.5 % glutaraldehyde and then dehydrated by a graded ethanol series as previously described (Cheng et al., 2017). The resulting samples were coated with gold prior to SEM examination.

2.4. *P speciation*

2.4.1. *SMT analysis*

The SMT harmonized protocol of the European Commission was employed to extract and determine different phosphorus fractions in waste activated sludge. The determined total phosphorus (TP) was divided into organic phosphorus (OP), apatite phosphorus (AP) and non-apatite inorganic phosphorus (NAIP) (Pardo et al., 2003).

2.4.2. *^{31}P NMR*

The procedure of sludge-phosphorus extraction for ^{31}P NMR analysis was modified from previous literature (Huang and Tang, 2015). Briefly, 0.1 g of freeze-dried (-60 °C) sludge sample was added to a 10-mL solution containing 0.25 M NaOH and 0.05 M EDTA and the mixture was agitated for 24 h at room temperature. The extract was centrifuged at 10,000 g for 30 min. The resulting supernatant was then filtered through 0.45-μm PES membranes (Membrana, Germany) and freeze-dried to powder. Prior to NMR examination, the powder sample was re-dissolved in 1 mL of 0.25 M NaOH. The NMR spectrum was acquired using a JNM-ECA600 spectrometer (JEOL, Japan) operated at 243 MHz at room temperature.

3. Results and discussion

3.1. *Species of P in the waste activated sludge*

The contents of total phosphorus in the sludges from the four sampled WWTPs were in the range of 18.5–25.9 mg/g SS (Fig. 1a). These values are similar to other values reported in the literature (Liu et al., 2020; Shi et al., 2019; Xu et al., 2015). The inorganic phosphorus accounted for 69.6 % −77.6 % of the sludge TP (according to SMT protocol) with non-apatite inorganic phosphorus being the major fraction of the inorganic phosphorus. Organic phosphorus in the sludge accounted for a minor proportion (17.2 %-26.8 %) of TP, comparable to the levels reported by Xie et al. (2011). Among the WWTPs, the contents of apatite-phosphorus in the sludge from Qinghe and Yongfeng were higher than in the other sludges. This is consistent with the relatively high proportion of calcium within the total metals in the sludges from these two WWTPs (Fig. 1b). The non-apatite inorganic phosphorus in the sludge from Xiaohongmen and Jinyuan accounted for a noticeably higher fraction of the total phosphorus because of the dosing of Al and Fe

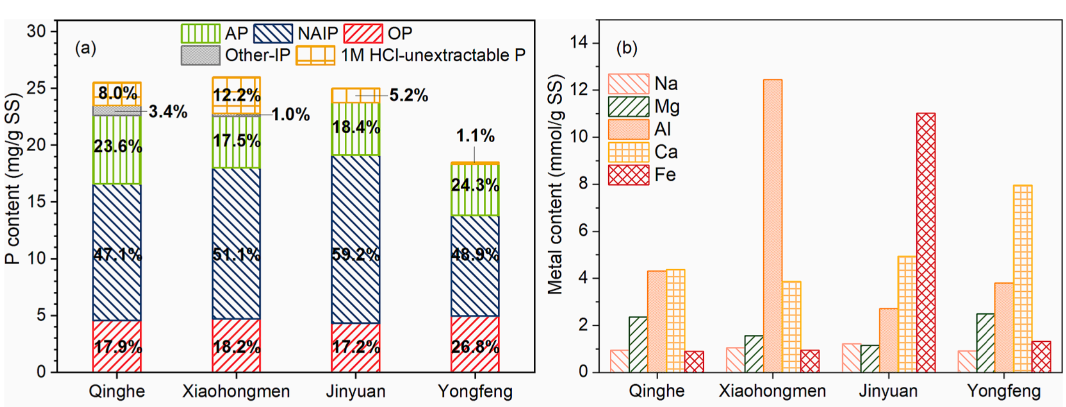

Fig. 1. Phosphorus fractions (a) and contents of metals (b) in the sludge from the investigated WWTPs. (A study on Qinghe sludge is presented in Liu et al., 2019).

Table 2
Results of ^{31}P NMR analysis of the sludge from the four WWTPs. (A study on Qinghe sludge is presented in Liu et al., 2019).

WWTPs	Phosphorus fraction (%)			
	Ortho-P	Monoester-P	Diester-P	Pyro-P
Qinghe	70.5	13.4	2.4	13.6
Xiaohongmen	80.5	10.4	3.1	6.0
Jinyuan	85.5	10.0	2.8	1.7
Yongfeng	84.5	9.4	2.7	3.5

salts as phosphorus precipitants. Indeed, the contents of these two metals were markedly increased in these sludges (Fig. 1b). Except Al and Fe that were dosed to the wastewater treatment systems for phosphorus elimination, the other major metals observed in the activated sludge were Ca^{2+}, Mg^{2+} and Al^{3+}. These are the common metal ions found in the sewage in the studied area of Beijing with high hardness of water (Zhai et al., 2015). In other words, sewage phosphorus can be, to different extent, immobilized via chemical precipitation regardless of whether external metals are dosed into the chemical phosphorus removal processes in WWTPs or into sewer systems (to control H_2S) (Wilfert et al., 2016). It is also worth mentioning that although the four WWTPs adopted distinct phosphorus removal strategies, the distribution of phosphorus species in the sludge did not differ significantly. Inorganic phosphorus remained the dominant form in all the WWTPs. This finding is important in evaluating the potential of sludge phosphorus release for its recovery and accordingly choosing appropriate methods and operating conditions.

Based on the results of ^{31}P NMR analysis (Table 2), *ortho*-P, mostly as phosphate precipitates according to the low fractions of aqueous forms shown in Table 1, was the dominant phosphorus species in all the sludge samples, accounting for 70.5 % to 85.5 % of TP_{mx}. The dominance of *ortho*-P agrees with the SMT results that inorganic phosphorus was the major fraction within the sludge-phosphorus pool. The content of pyro-P was noticeably higher in Qinghe sludge than those in the other three plants. Although no poly-P was observed (as indicated by the absence of detectable poly-P middle groups), the increased levels of pyro-P in Qinghe sludge show the activity of biological phosphorus immobilization in this EBPR-adopted WWTP considering that the 24-h extraction of sludge phosphorus using NaOH during the preparation of the NMR samples had induced the hydrolysis of polyphosphate to pyro-P (Ahlgren et al., 2005; Li et al., 2015). The results indicate that in WWTPs employing chemical phosphorus removal processes, an increased proportion of phosphorus becomes chemically immobilized as insoluble orthophosphate. This fact should be considered when seeking to release phosphorus for recovery purposes.

3.2. Effectiveness of sludge treatment on phosphorus release from waste activated sludge

3.2.1. Efficiencies of sludge phosphorus release by thermal hydrolysis and pH adjustments

Polyphosphate synthesized in activated sludge cells can be transformed and released as aqueous *ortho*-P under anaerobic conditions (Kroiss and Negm, 1994). For the non-treatment controls in this study, phosphorus release was observed in Qinghe and Yongfeng sludge after 12 h of thickening (Fig. 2). The released PO_4-P_{aq} approximated the released TP_{aq}, suggesting that the anaerobic release of phosphate by phosphorus accumulating organisms was responsible for the phosphorus release from the sludges of the two WWTPs where no metal salts (e.g., Al or Fe salts) was dosed (Li et al., 2015). No phosphorus release was observed in the sludge collected from Xiaohongmen and Jinyuan, indicating that the biologically released phosphorus, if any, had been effectively bound by the dosed chemical reagents. The results demonstrate that the majority of sludge phosphorus in chemical phosphorus removal systems remains stable during anoxic storage and additional treatment for phosphorus release would be required because direct separation of the fine and evenly distributed phosphate precipitates for phosphorus recovery is impossible (Wang et al., 2020).

As shown in Fig. 2, the release of phosphorus during thermal hydrolysis of waste activated sludge was inefficient for all the WWTPs although this technology has been successfully applied as a sludge disintegration measure to improve sludge digestion (Barber, 2016;

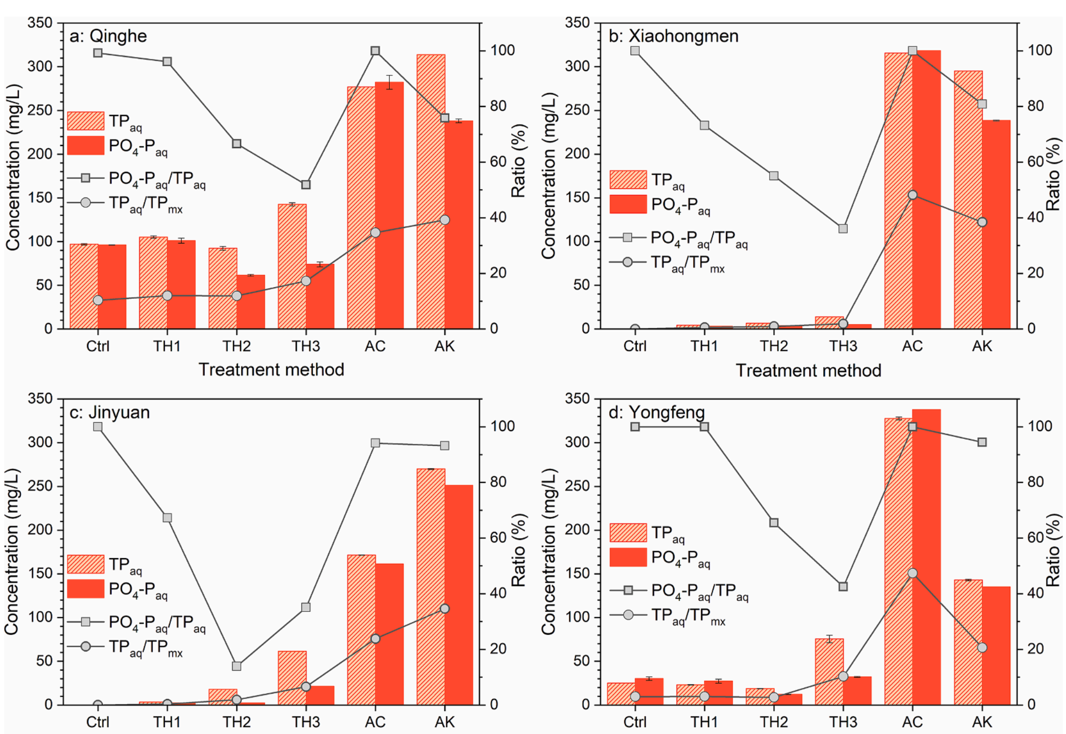

Fig. 2. Effectiveness of sludge treatment on P release for the four WWTPs. (A study on Qinghe sludge is presented in Liu et al., 2019).

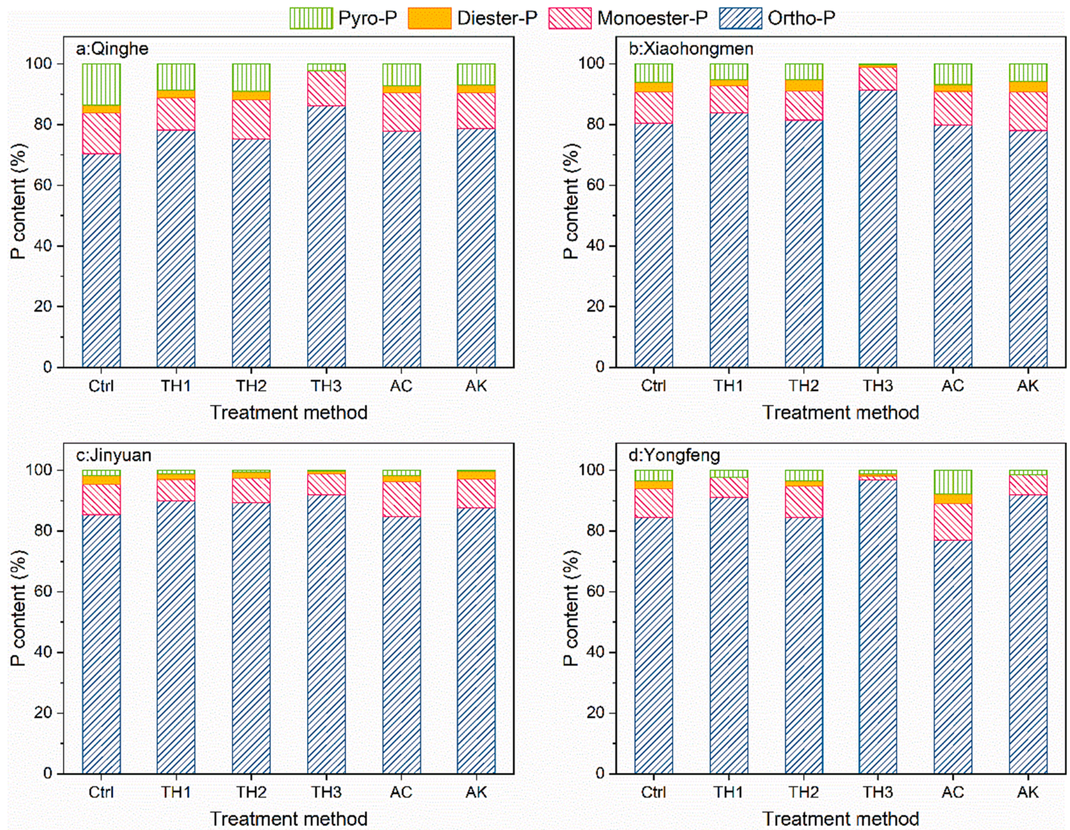

Fig. 3. Results of ^{31}P NMR analysis of the sludge from the four WWTPs after thermal hydrolysis (TH) and pH adjustments (AC: acid treatment; AK: alkaline treatment). (A study on Qinghe sludge is presented in Liu et al., 2019).

Gahlot et al., 2022). The extension of thermal treatment time from 0.5 to 2 h (TH1 → TH3) increased, to a small extent, the concentration of TP_{aq} whilst the increases in PO_4-P_{aq} were observed to be negligible, which led to a decrease in the PO_4-P_{aq}/TP_{aq} ratio. In the cases of Qinghe-TH2 and Yongfeng-TH2, the concentration of PO_4-P_{aq}, in fact, decreased after the thermal treatment. A similar decrease in liquid-phase phosphorus was observed by Deng et al. (2022) during TH treatment of excess sludge with a turning point temperature of 180 °C, above which the

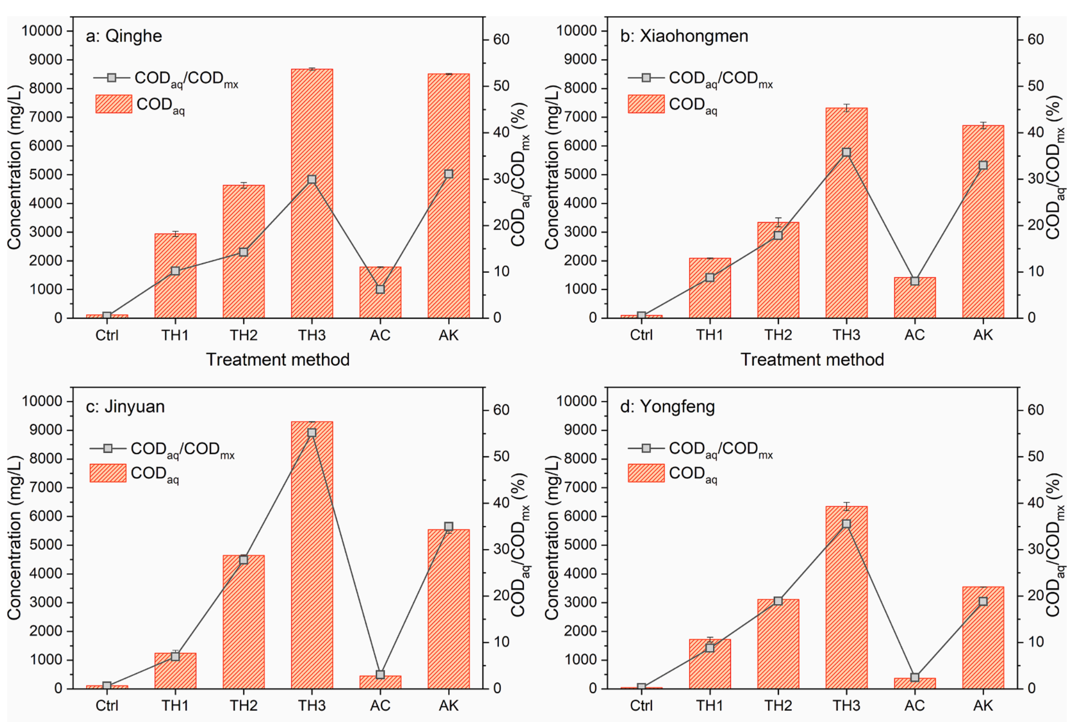

Fig. 4. Effectiveness of sludge treatment on COD release for the four WWTPs. (A study on Qinghe sludge is presented in Liu et al., 2019).

Table 3
Correlation among the releases of TP_{aq}, COD_{aq} and TN_{aq} from the sludge by different treatments.

WWTPs	COD_{aq}-TN_{aq} Pearson	Spearman	COD_{aq}-TP_{aq} Pearson	Spearman	TN_{aq}-TP_{aq} Pearson	Spearman
Qinghe	0.99	1.00	0.34	0.31	0.29	0.31
Xiaohongmen	0.94	0.94	0.06	0.37	−0.03	0.31
Jinyuan	1.00	1.00	0.19	0.54	0.19	0.54
Yongfeng	0.98	0.94	−0.24	0.03	−0.30	−0.2

precipitation of released soluble phosphate with metals in the sludge became evident. According to the NMR results (Fig. 3), the distribution of phosphorus species in the sludge did not change notably after TH1 and TH2 treatments with a minor increase in monoester-P due to the degradation of organic-P (Zhang et al., 2023). In contrast, the proportions of *ortho*-P increased notably when the time of thermal hydrolysis was extended to 2 h in TH3. The above results suggest that although *ortho*-P could be generated from the degradation of poly-/pyro-P and organic-P by the extended hydrothermal treatment, it remained or was immobilized in the sludge solids instead of being released. On the other hand, the organic-P tended to be solubilized through the disintegration of sludge cells by thermal hydrolysis (Fig. 2) though the total amount of organic-P decreased (Fig. 3) as a result of degradation/mineralization (Shi et al., 2019).

Compared with thermal hydrolysis, pH adjustment was found to be highly effective in releasing sludge phosphorus (Fig. 2). The released phosphorus by AC treatment was mainly *ortho*-P as revealed by the high PO_4-P/TP_{aq} ratios, suggesting that the phosphorus release was mainly via the acid-induced dissolution of phosphate minerals (Liu et al., 2020). Alkaline treatment was observed to be comparably effective in releasing phosphorus whilst the released PO_4-P_{aq} was, to different extents, less than the released TP_{aq} for the sludge from the four WWTPs (Fig. 2). This indicates that the elevated pH also induced the hydrolysis of cell materials, including the phosphorus-containing organic matter (Neyens et al., 2004; Xu et al., 2018b). Compared with the other WWTPs, the phosphorus release by AK treatment for Yongfeng sludge was less efficient because of the higher proportion of calcium-bound phosphorus in TP_{mx} (Fig. 1a and b), which is nearly insoluble at pH 12 (Xu et al., 2015). In other words, AK treatment may not be recommended for sludge in WWTPs where calcium-bound phosphorus is dominant although hydrolysis of cell materials under alkaline conditions can be an additional pathway of phosphorus release.

3.2.2. *Comparison of releases of phosphorus, COD and nitrogen from waste activated sludge*

Significant differences were observed in the release of COD and nitrogen in comparison to phosphorus throughout the course of different sludge treatments (Fig. 4). Evident solubilization of cellular organics occurred during both TH and AK treatments, reflected by the clear increase in COD_{aq} levels. Notably, acidification exhibited a low efficacy in COD release, particularly evident in the cases of Jinyuan and Yongfeng sludge, with only approximately 3 % of COD_{mx} being solubilized during the treatment. In contrast, TH and AK treatments both demonstrated a substantial capacity to solubilize over 30 % of the COD_{mx}, except for the alkaline treatment of Yongfeng sludge. The extension of thermal hydrolysis time from 0.5 h to 2 h exhibited a pronounced enhancement in the efficiency of COD solubilization. For Jinyuan sludge, a remarkable outcome was observed, with over 55 % of COD_{mx} being released as COD_{aq} by a 2-h TH treatment (Fig. 4c).

The pattern of TN release during the treatments was similar to that of COD (see supplementary material). The released TN_{aq} was mainly solubilized organic nitrogen from the cell materials because the increase in NH_4^+-N_{aq} was marginal and NO_x-N_{aq} was undetectable. This reveals that the solubilized nitrogen-containing organic molecules were not further degraded to produce NH_4^+-N via ammonification (Simsek et al., 2013).

According to the results of regression analysis for the concentrations of phosphorus, COD and nitrogen (Table 3), the releases of COD_{aq} and TN_{aq} were closely correlated during the treatments, while neither of which correlated notably with the release of TP_{aq}. This indicates that the released phosphorus was from an essentially different source compared to the observed COD_{aq} and TN_{aq}, which were likely same-sourced. Although carbon, nitrogen and phosphorus are all essential macronutrients for microorganisms, the predominant presence of *ortho*-P (rather than organic-P or intracellular poly-P) in the sludge suggests that phosphate mineralization and precipitation/immobilization are the main mechanisms of phosphorus transformation in the WWTPs. Therefore, effective release of phosphorus from sludge solids would rely on the re-dissolution of phosphate minerals. In contrast, the simultaneous increases in COD_{aq} and TN_{aq} during the sludge treatment indicate that carbon and nitrogen can be released via the disintegration and solubilization of sludge cell organics. Therefore, an ideal sludge treatment method for simultaneous release of phosphorus, carbon and nitrogen for nutrients recovery/reuse needs to be capable of both dissolving inorganic *ortho*-P and solubilizing sludge organics. Based on the results in this study, alkaline treatment could be considered as an option when a chemical phosphorus removal process using Fe or Al salts is adopted in the WWTP because it allows for the simultaneous hydrolysis of organic matter and dissolution of Fe/Al phosphates at a certain high pH (Bashir et al., 2019).

The effectiveness of the sludge treatments for phosphorus release was, to some extent, revealed by the variations in the sludge morphology as shown in the SEM images (see supplementary material). In comparison with the untreated control sludge with a highly rough surface, TH sludge was more homogenized due to the rupture of sludge flocs and cell disintegration, explaining the effective releases of COD and nitrogen (Foladori et al., 2010; Ruiz-Hernando et al., 2014). After AC treatment, the sludge flocs mostly remained intact. This is consistent with the inefficiency of COD and TN solubilization (Fig. 4 and supplementary material) and demonstrates that the efficient release of *ortho*-P was not from the sludge organics. The morphology of AK sludge, however, differed significantly from all the aforementioned sludge with naked cells clearly seen on the surface of the sludge flocs, suggesting that the extracellular polymeric substances (EPS) of the sludge cells were effectively solubilized/hydrolyzed during the AK treatment (Neyens et al., 2004). This is also evidenced by the 3D-EEM fluorescence spectra with intensive peaks for tryptophan-like species as soluble proteins observed after the treatment (see supplementary material). The released EPS had likely played a significant role in releasing CODaq during the AK treatment as EPS can account for up to 70 % of the sludge biomass (Liu and Fang, 2003).

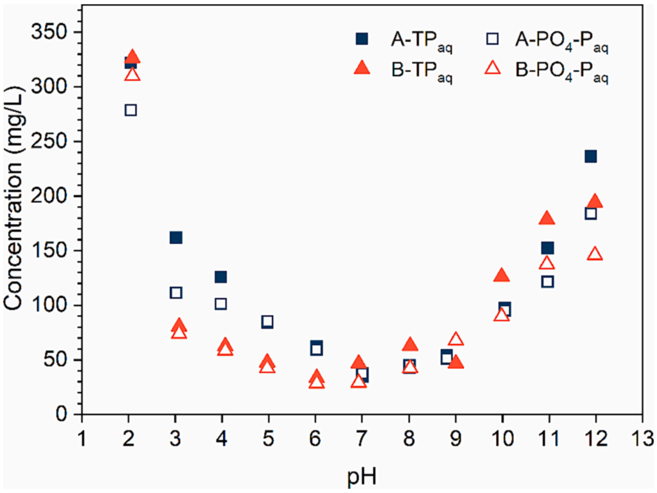

Fig. 5. Effect of pH variations on phosphorus release from waste activated sludge (A: adjustment of pH to values between 2 and 12; B: adjustment of pH firstly to 12 and then stepwise to 2).

3.2.3. Mechanisms of phosphorus release based on its reversibility with pH swings

The release of sludge phosphorus with pH adjustments in the range of 2–12 (Group A: sludge treatments for pH values from 2 to 12; Group B: adjusting sludge pH to 12 and then lowering stepwise to 2) clearly shows its reversibility, pH-dependence and the significant enhancement at pH extremes (Fig. 5). In Group B, the released non-orthophosphate was gradually transformed/hydrolyzed to *ortho*-P during the stepwise pH adjustments as the gap between the concentrations of TP_{aq} and PO_4-P_{aq} reduced from 48.3 mg/L at pH 12 to 16.5 mg/L at pH 2. The levels of TP_{aq} and PO_4-P_{aq} at pHs of 3–6 in Group B were noticeably lower than those in Group A, indicating that the generated PO_4-P through alkaline hydrolysis of organic phosphorus tended to be immobilized (Monhemius, 1977).

It is worth noting that after 24 h of sludge storage in Group A, the sludge pHs moved towards neutrality due to the buffering capacity of the activated sludge (Fig. 6a) (Xu et al., 2015). A highly acidic condition of pH 2 exceeded the buffering capacity of the sludge, leading to a significant increase in phosphorus release. As shown in Fig. 6b, the buffering capacity of the sludge, for the starting pH levels of 3–10, resulted in the re-immobilization of phosphorus with final concentrations of approximately 50 mg/L. This observation confirms the reversibility of phosphorus release induced by pH adjustments as stated above. With the starting pH values of 11 and 12, the reduction in concentration of aqueous organic phosphorus during the storage, as evidenced by the reduced concentration of TP_{aq} and the unchanged concentration of PO_4-P_{aq}, indicates the occurrence of alkaline hydrolysis of organic-P or poly/pyro-P. The unchanged concentration of PO_4-P_{aq}, however, suggests that the generated PO_4-P_{aq} was immobilized and/or had offset the drop in PO_4-P_{aq} concentration as a result of pH buffering.

The pH-dependence of phosphorus release is consistent with the fact that *ortho*-P was the major phosphorus species in the waste activated sludge as addressed in Section 3.1. Because of the reversibility of phosphorus release by pH adjustments, it is necessary to prioritize the step of phosphorus recovery as separable products before re-adjusting the pH to an appropriate value for subsequent processes, such as sludge digestion. Considering that both phosphate crystallization, as currently the most practical technology for phosphorus recovery (such as the production of struvite and vivianite), and anaerobic sludge digestion consume alkalinity under commonly adopted conditions, alkaline treatment of waste activated sludge would be a wise strategy to fully utilize the dosed chemicals. A proposed process is illustrated in supplementary material. As discussed earlier, the release of COD by alkaline treatment was comparable to that by thermal hydrolysis and significantly more efficient than that by acid treatment due to the effective hydrolysis of cell materials under alkaline conditions (Liu et al., 2017). The COD-rich stream, after stripping phosphorus, can be used as a carbon source to enhance denitrification especially when the C/N ratio of the sewage is low and/or stringent discharge limits of TN are implemented (see supplementary material). Therefore, to simultaneously solubilize carbon, nitrogen and phosphorus from waste activated sludge for resource and energy recovery, alkaline treatment can be a cost-effective alternative.

4. Conclusion

Adjustments of pH were effective in solubilizing phosphorus from the excess sludge because of the dominance of inorganic phosphate within the total phosphorus content of the sludge solids. The release of phosphorus through thermal hydrolysis, a commonly employed sludge treatment method, was negligible. Alkaline treatment led to simultaneous release of phosphorus, COD and TN as a result of phosphate solubilization and biomass hydrolysis. As such, it would become a promising alternative for sludge pretreatment considering the growing need for resource and energy recovery from sewage whilst the process integration with a minimal operating cost is to be studied.

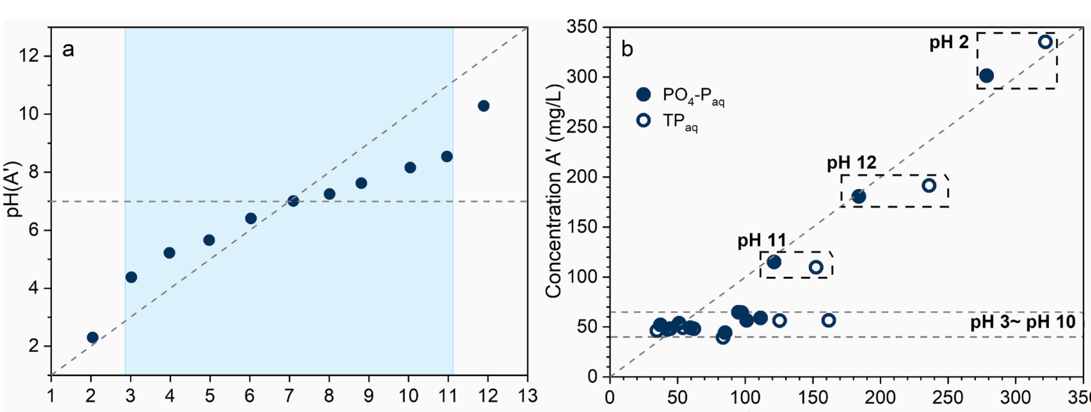

Fig. 6. Variations of pH (a) and phosphorus concentrations (b) in 24 h after pH adjustment (A and A' denote the value/concentration before and after the 24-h storage, respectively).

CRediT authorship contribution statement

Shaoyu Deng: Writing – original draft, Investigation. **Jiaqi Liu:** Writing – review & editing, Investigation. **Xiaofan Yang:** Investigation. **Dezhi Sun:** Methodology, Conceptualization. **Aijie Wang:** Conceptualization. **Mark C.M. van Loosdrecht:** Writing – review & editing, Conceptualization. **Xiang Cheng:** Writing – review & editing, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Xiang Cheng reports financial support was provided by Ministry of Science and Technology of the People's Republic of China. Xiang Cheng reports financial support was provided by National Natural Science Foundation of China. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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