

Revealing the Roles of Microplastics and Dissolved Organic Matter in Phosphorus Recovery via Struvite Crystallization in Batch and Fluidized-Bed Reactors

Junna Yan[†], Mengyu Ma[†], and Feihu Li^{†,‡,*}

[†] School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, 219 Ningliu Road, Nanjing 210044, China

[‡] NUIST Reading Academy, Nanjing University of Information Science and Technology, 219 Ningliu Road, Nanjing 210044, China

*E-mail: fhli@nuist.edu.cn ORCID: <https://orcid.org/0000-0002-2969-8276>

Abstract: Struvite crystallization, a promising technology for nutrient recovery from wastewater, is ever more encountering challenges due to the presence of emerging contaminants such as microplastics, which are ubiquitous in wastewater. In this study, we investigate the roles of microplastics and humic acid in struvite crystallization in batch and fluidized bed reactors, with emphasis on crystallization kinetics and physicochemical properties of struvite crystals. Batch crystallization kinetic experiments were conducted with synthetic wastewater with varying concentrations of microplastics and humic acid. The results showed that microplastics expedited the nucleation and growth rates of struvite (e.g., 1.43 times the blank suspension in the presence of 30 mg L⁻¹ of zinc loaded polyethylene terephthalate particulates), while humic acid hindered the formation of struvite. Besides, X-ray diffraction analysis and the Rietveld refinement revealed that the presence of microplastics and/or humic acid can result in quite many changes in phase compositions of the reclaimed precipitates in batch and fluidized bed reactors. The characterization analysis demonstrated that microplastics act as seeds of struvite nucleation, spurring the formation of well-defined struvite, while humic acid favors the formation of newberyite rather than struvite in both the batch and the fluidized bed reactors. These findings highlight the need for a more comprehensive understanding of the interactions between emerging contaminants and struvite crystallization processes to optimize nutrient recovery strategies for mitigating their adverse impact on the quality and yield of struvite-based fertilizers.

1. Introduction

Phosphorus (P) is an essential element for the survival of all living organisms on our planet. Over 90% of P in all the living beings on earth originated from ores, non-renewable resources [1, 2]. The world population has been about 8.1 billion so far according to the most recent United Nations estimates, which will spur a growing demand for more mineral fertilizers for food production. This will no doubt accelerate the depletion of global phosphate rock reserves since more than 90% of P ores were consumed in the production of fertilizers [3-5]. Moreover, quite much of P fertilizers are lost from the croplands or forestlands into waterways due to soil erosion [2] and find their way to the ocean eventually [6]. Such a one-way phosphorus flow (i.e., P flux from rock to ocean) is unsustainable considering the limitation in the supply of accessible phosphate rocks, and the impossibility of geologically replenishing these ores by natural phosphorus cycle [7]. It is therefore pressing to develop efficient P recovery and recycling strategies for reclaiming this valuable element from P-rich streams and effluents (viz. secondary P resources), thus implementing a closed P cycle in the context of the circular economy.

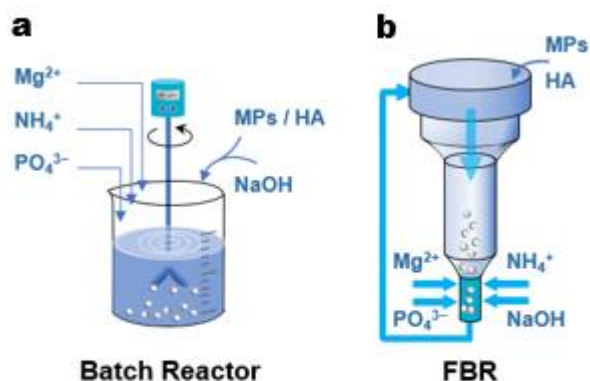
Chemical precipitation has been demonstrated as one of the most promising approaches for P recovery from waste streams [8-11]. Over the past decades, struvite crystallization via chemical precipitation, in particular, has gained much more attention as the route strategy for P recovery and recycling due to its practical value to the fertilizer industry [1, 12]. Historically, struvite formation and accumulation in municipal wastewater treatment plants (MWTPs) often cause operational issues, especially leading to the clogging of pipelines conveying supernatant from sludge digestion systems [13, 14]. Nevertheless, a heap of benefits accompanied by P recovery through struvite crystallization have been identified, viz. the reduction in P and nitrogen load of side-stream and sludge liquors within pipelines of MWTPs, the decline of total sludge volumes, and more importantly the additional value for the MWTPs by commercializing the reclaimed struvite

(MgNH₄PO₄·6H₂O) as fertilizers [14-16]. Thereafter, extensive laboratory-scale investigations have been carried out worldwide [9, 10, 14, 17-19], which have significantly advanced the practical application of this technology at the industrial scale [20, 21].

Generally, both the P recovery efficiency through struvite crystallization and the quality of reclaimed struvite are usually determined by the water compositional chemistry of the parent solutions [14, 22]. Specifically, solution pH, the molar ratio of Mg:NH₄⁺:PO₄³⁻, and the co-occurred foreign species or impurities collectively play a critical role in defining the efficiency of phosphorus recovery as well as the quality of reclaimed struvite [12, 23, 24]. It was reported that the presence of sulfate ions can remarkably reduce the P recovery efficiency in a fluidized-bed reactor (FBR), while the copresence of sulfate and fluoride ions did not impact the P recovery efficiency but lowered the quality of the reclaimed struvite, viz. reducing its crystallization ratio [23]. Kofina *et al.* observed that the presence of citrate and phosphocitrate can depress struvite precipitation up to 75-80% in batch reactors (BRs) at pH 8.5 and 25 °C [25]. Similarly, the inhibiting impacts of humic acid (HA) [26, 27], alginate acid [28], and phenolic organics [29] on struvite formation were demonstrated respectively. Interestingly, glucose [26], and some volatile fatty acids (VFAs), e.g., acetate, propionate, and butyrate [30] were believed to improve and facilitate the crystallization process of struvite, and hence the crystallization ratio. In addition to the struvite crystallization ratio, and more importantly, the cooccurring of toxic impurities such as heavy metals, antibiotics, and antibiotic resistance genes (ARGs), can pose a biosecurity issue to the croplands where the reclaimed struvite was applied [27, 31-34]. Moreover, recent studies indicated that microplastics (MPs) are omnipresent in environmental media, including nutrient-rich waste streams [35, 36]. MPs can act as a vector of toxic pollutants [37]. Such MPs are likely to be encapsulated into calcium carbonate in the chemical precipitation process when exposing to dissolved organic matter (DOM) [38]. However, little is known on the effects of MPs along with HA on the struvite formation kinetic

as well as the quality of the resulting struvite precipitates, especially in the context of P recovery from nutrient-rich waste streams via struvite crystallization. It is also not known whether MPs can act as a deposition platform or nucleation seed for struvite.

This study aims to identify how aged MPs and DOM molecules influence the crystallization kinetics and the quality of struvite in BRs and FBRs (Scheme 1) under ambient conditions. HA was selected as the model DOM molecule, while aged polyethylene (PE) and polyethylene terephthalate (PET) pellets were chosen to represent MPs. Trace heavy metals such as copper and zinc ions are likely to be found in nutrient-rich streams (e.g., swine wastewater) and bound to the surface of MPs [39, 40]. Two aged MP suspensions were dispersed and loaded with dissolved Cu^{2+} or Zn^{2+} individually before applying in the struvite crystallization experiments. The suspension pH and the dissolved phosphate concentration were monitored to study the crystallization kinetics. X-ray diffraction (XRD), X-ray fluorescence (XRF) analysis, and Fourier-transform infrared (FTIR) spectroscopy were used to investigate the quality of reclaimed struvite.



Scheme 1. (a) Batch reactor (BR), and (b) fluidized bed reactor (FBR) for struvite crystallization.

2. Materials and methods

2.1 Materials

All chemicals used for struvite crystallization are of analytical pure grade. Monopotassium phosphate (KH_2PO_4 , $\geq 99.0\%$), magnesium chloride (MgCl_2 , $\geq 98.0\%$), sodium hydroxide (NaOH , $\geq 99.0\%$), and ammonium magnesium phosphate hexahydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, 98.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ammonium chloride (NH_4Cl , 99.5%) was obtained from Macklin Biochemical Co., Ltd. (Shanghai, China). Humic acid (HA) was provided by Shanghai Yuanye Bio-Technology Co., Ltd (Shanghai, China). The microplastics (MPs), polyethylene (PE), and polyethylene terephthalate (PET) of *ca.* 50 μm in size were purchased from Wangda Plastic Material Co., Ltd (Dongguan, China), and artificially aged over 20 days using a heat persulfate oxidation method. After loading with copper or zinc ions in a set of adsorption experiments [40], the metal-loaded MPs (denoted by PE-Cu, PE-Zn, PET-Cu, and PET-Zn, respectively) were used as impurities in the struvite crystallization experiments. Ultrapure deionized (DI) water ($18.2 \text{ M}\Omega\text{-cm}$, 25°C) was employed for preparing solutions.

2.2 Struvite crystallization in a batch reactor (BR)

The batch crystallization kinetic experiments were carried out with a constant Mg:N:P molar ratio of 1:3:1 in a 1000-mL beaker (Figure S1a, Supporting Information) at standard atmospheric pressure and temperature (*ca.* 25°C). In brief, solution A was prepared by dissolving 0.83 mmol of KH_2PO_4 into 493 mL of DI water, to which a dilute NaOH solution was added to adjust the pH to 11 ± 0.2 . Likewise, solution B was synthesized by combining 0.83 mmol of MgCl_2 and 2.5 mmol of NH_4Cl with 7 mL of DI water, which was then quickly poured into the beaker with solution A and mixed moderately over a magnetic stirrer (INTLLAB, Shenzhen, China). The pH of the resulting suspension (denoted by the impurities inside or blank) was monitored using a pH meter (PHS-25, Rex Electric Chemical) and recorded every minute for 60 min, while the concentration of remaining soluble phosphate ($\text{PO}_4^{3-}\text{-P}$) was measured every 5 min following the ascorbic acid method as described elsewhere [41]. Five mL of suspension was sampled at 5-minute intervals and immediately forced through a $0.45\text{-}\mu\text{m}$ mixed cellulose ester membrane filter mounted with a syringe. The filtrate was then acidized with 20 μL of 6M HCl to stop the crystallization reaction [42]. Next, the concentration of soluble phosphate was determined using a JH723PC visible spectrophotometer (Shanghai, China). The effects of aged MPs and HA on the crystallization kinetics were studied following the same protocols with the addition of a certain amount of such specific impurities.

All the precipitate samples were collected centrifugally after the termination of each batch reaction (i.e., 60 min), followed by rinsing twice with DI water and drying in an oven at 80°C overnight. The crystallization kinetic rate constant was determined by fitting the data to a first-order kinetic model that was formulated as follows [42],

$$-\frac{dC}{dt} = k(C_0 - C_e) \quad (1)$$

$$\ln(C - C_e) = -kt + \ln(C_0 - C_e) \quad (2)$$

Where k is the rate constant (h^{-1}), C is the soluble phosphate (reactant) concentration (mg L^{-1}) at time t , C_0 and C_e are the phosphate ($\text{PO}_4^{3-}\text{-P}$) concentration at initial and equilibrium state ($\text{mmol}\cdot\text{L}^{-1}$).

2.3 Struvite crystallization in an FBR

Struvite formation kinetic experiments were also performed in a customer-made FBR (Figure S1b, Supporting Information) [43]. The phosphate-enriched effluents were from a set of rapid adsorption-desorption enrichment operations as described in our earlier works [44, 45]. The FBR feed solution ($\sim 5 \text{ L}$) was prepared by combining the phosphate-enriched effluents with certain amounts of MgCl_2 and NH_4Cl to achieve a final Mg:N:P molar ratio of 1.3:4:1 [23]. Sodium hydroxide solution (0.1 M) was used as the alkaline solution to adjust the initial pH of the feed solution to above 11 within the FBR setup. To start with, the feed solution was fed into the FBR at a flow rate of 5 mL min^{-1} for 5 min using a peristaltic pump (BT-100, Longer Pump Co., China). Next, the NaOH solution was fed at a flow rate of 3 mL min^{-1} using another pump, while the third pump linking the bottom and the upper top of the FBR setup was launched meanwhile at 10 mL min^{-1} to circulate the mixture and keep a fluidization state.

After circulating for 6 days, the experiment was terminated and the struvite precipitates were reclaimed from the FBR bottom (Figure S1b), followed by centrifugal separating, rinsing thrice with DI water, and air drying over 24 h before further characterization. The effects of seed ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, 98.0%), and PET impurity on struvite formation in FBRs were investigated.

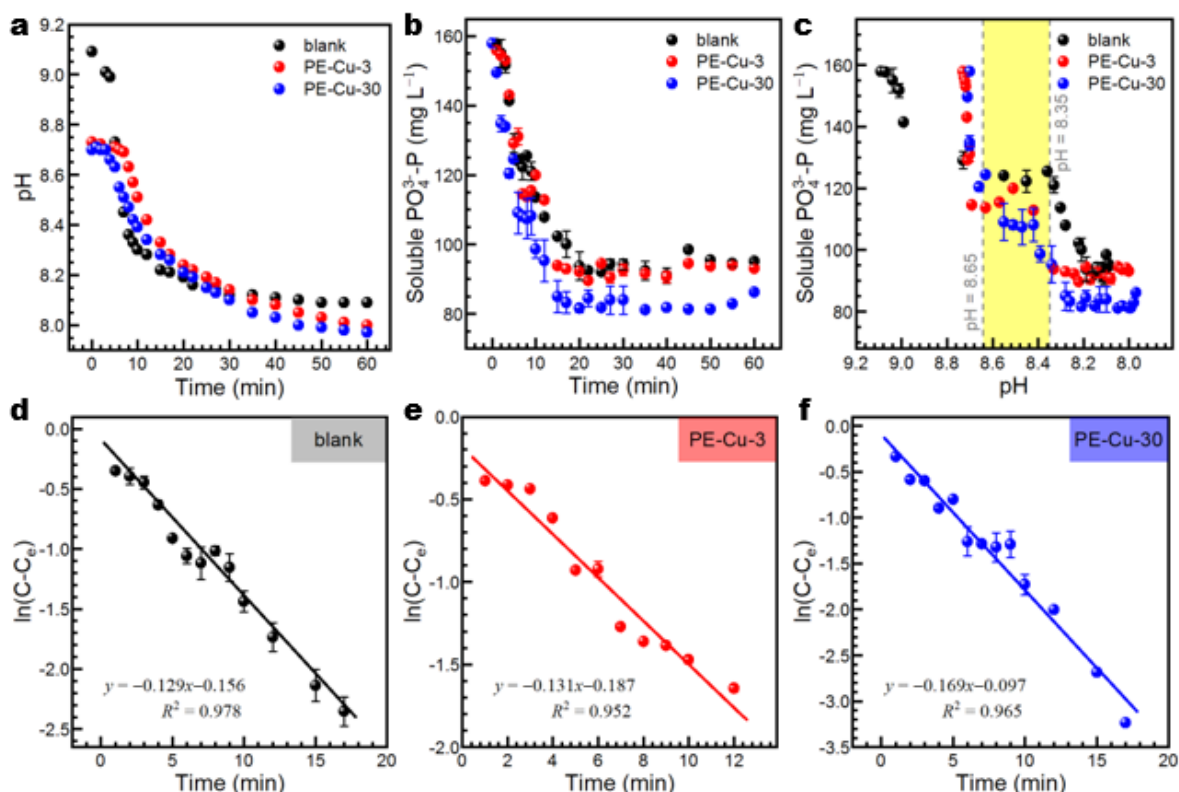


Figure 1. (a) The suspension pH profiles, (b) Plots of soluble $\text{PO}_4^{3-}\text{-P}$ versus reaction time Plots of soluble $\text{PO}_4\text{-P}$ versus pH, (c) Plots of soluble $\text{PO}_4\text{-P}$ versus pH during the struvite crystallization in batch reactors with varying contents of PE-Cu (Note: blank, PE-Cu-3 and PE-Cu-30 stand for 0, 3, and 30 ppm, respectively; the yellow shaded region in panel c represents a lag phase of struvite formation at pH 8.35 – 8.65 possibly due to nucleation kinetics); (d-f) Kinetic linear fitting plots of soluble phosphate concentration versus time in suspensions with (d) 0, (e) 3, and (f) 30 ppm of PE-Cu.

Actual wastewater (WW) from a local sewage treatment plant (Table S1) was used to explore the effect of natural DOM on struvite formation.

2.4 Characterization of the reclaimed precipitates

X-ray diffraction (XRD) analysis was conducted on a Shimadzu XRD-6100 diffractometer with Cu-K radiation ($\lambda = 1.54178 \text{ \AA}$). Mass percentages of mineral phase in the reclaimed precipitates were calculated by the whole-pattern fitting (WPF) module embedded in Jade software (MDI, USA). Using the soil mode, the elemental composites of the reclaimed precipitates were recorded using a handheld X-ray fluorescence (XRF) spectrometer of the DELTA series DC-4000 (Olympus, USA). A Nicolet iS5 spectrometer (Thermo Fisher, USA) was used for Fourier transform infrared (FTIR) spectroscopy acquisition. Scanning electron microscopy (SEM) was performed using an SU1510 electron microscope (Hitachi, Japan) at an accelerating voltage of 1.5 kV.

3. Results and Discussions

3.1 Effect of MPs on the kinetics of struvite formation in BRs

Apart from Mg^{2+} , there are no other species (e.g., Ca^{2+} or DOM) in the suspensions that can form precipitates or complexes with phosphate, so the likelihood of struvite formation can be verified by monitoring the decrease in $\text{PO}_4^{3-}\text{-P}$ concentration and the pH, thereby determining the kinetics of struvite crystallization indirectly. As shown in Figure 1a-b, both the pH and the soluble

$\text{PO}_4^{3-}\text{-P}$ in the suspension denoted blank decreased rapidly with reaction time, approaching to equilibrium state at about 40, and 20 min, respectively. The struvite formation reaction would consume a large amount of PO_4^{3-} , which shifts the equilibrium of orthophosphate species to the right-hand side (i.e., $\text{H}_3\text{PO}_4 \leftrightarrow \text{H}_2\text{PO}_4^- + \text{H}^+ \leftrightarrow \text{HPO}_4^{2-} + 2\text{H}^+ \leftrightarrow \text{PO}_4^{3-} + 3\text{H}^+$), releasing a lot of protons to the suspension and thereby lowering its pH eventually. It was found that the initial nucleation rate of struvite is extremely fast when the suspension pH is > 9 [42]. Note that a distinct lag phase developed as the suspension pH fell from above 9 to the range of 8.65–8.35 (the yellow-shaded region in Figure 1c), which is likely attributed to the reduced nucleation kinetics by the decrease in pH [42]. With an assumption that the inverse reaction of struvite formation is minimal and negligible, the data recorded in the initial metastable stage before achieving an equilibrium state (0–16 min) was chosen to fit with the first-order kinetic model (eq. 2), and the best-fit kinetic equations and corresponding parameters are tabulated in Table 1. The fit coefficient (R^2) is as high as 0.978 for the suspension blank, indicating the first-order kinetic model is reasonable enough to describe and predict the changes in soluble $\text{PO}_4^{3-}\text{-P}$ concentration (Figure 1d). The rate constant of 7.74 h^{-1} is less than that reported earlier at pH 9 (i.e., 12.3 h^{-1}) [42], which is likely due to the difference of the struvite-forming ion concentration and ratios applied that defines the supersaturation of the resulting solutions. Supersaturation is believed to be the primary influence on the struvite formation induction time provided that mixing is sufficient [46]. Moreover, the induction

time has been included in our case while it seems to be excluded by Nelson *et al.* [42], as evidenced by the difference in the time range selected (0–16 min versus 2–9 min). This also contributed to the relatively less kinetic rate constant in the current study.

When the aged MP impurities were introduced into the suspensions, for instance, PE-Cu pellets (i.e., PE-Cu-3, and PE-Cu-30), the initial pH dropped from 9.1 to ~8.7 (Figure 1a), possibly since all the MP pellets were aged by the heat persulfate oxidation (HPO) and preloaded copper or zinc ions in suspension at pH 6 [40]. Similar plots of $\text{PO}_4^{3-}\text{-P}$ versus time in the presence of PE-Cu as that of blank demonstrates that struvite was formed in a similar way (Figure 1b). More importantly, note that the more the PE-Cu impurities are introduced, the faster the soluble $\text{PO}_4^{3-}\text{-P}$ concentration reaches a steady state in the initial 20 min (Figure 1b), suggesting that the introduction of PE-Cu can facilitate the struvite formation. Likewise, the lag phases appeared once again in the plots of $\text{PO}_4^{3-}\text{-P}$ versus pH in suspension with PE-Cu impurities as pH fell within the range of 8.65–8.35 (Figure 1c), but the pH span is narrower than that of the blank sample, indicating that the presence of PE-Cu also enhances the nucleation kinetics. In addition, the linearities of both experimental data with PE-Cu impurities show a good fit ($R^2 > 0.95$, Figure 1e–f), demonstrating that the first-order kinetic model is reasonable in predicting the decrease in the logarithmic concentration of soluble $\text{PO}_4^{3-}\text{-P}$ in suspensions with PE-Cu impurities. The kinetic rate constants are 7.86, and 10.14 h^{-1} for PE-Cu-3, and PE-Cu-30, respectively (Table 1), both greater than that for the blank suspension, confirming the positive effect of PE-Cu in promoting struvite formation in BRs.

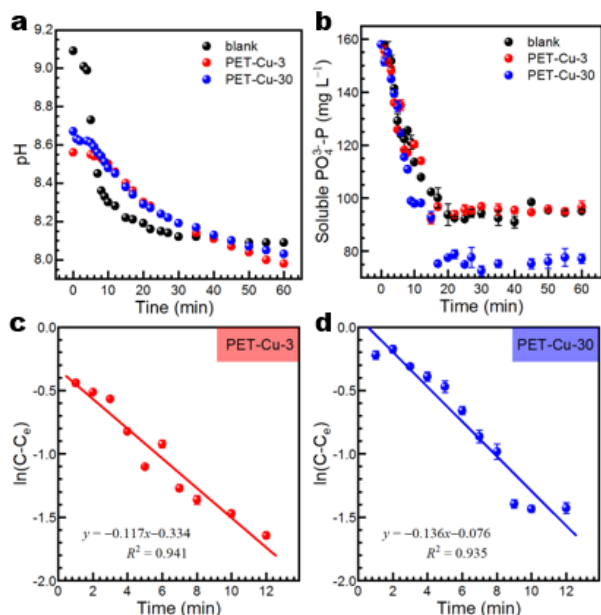


Figure 2. (a) The suspension pH profiles, (b) Plots of soluble $\text{PO}_4^{3-}\text{-P}$ versus reaction time in suspensions with varying contents of PET-Cu; (c) Kinetic linear fitting plots of soluble $\text{PO}_4^{3-}\text{-P}$ in suspensions with (c) 3 ppm and (d) 30 ppm of PET-Cu.

Similarly, the same trends of pH and soluble $\text{PO}_4^{3-}\text{-P}$ concentration with time have also been observed in the cases of suspensions with other impurities including PET-Cu (Figure 2a–b),

PE-Zn (Figure S2a–b), and PET-Zn (Figure S3a–b). The kinetic fitting results (Table 1) demonstrated high linearity (Figure 2c–d, Figure S2c–d, Figure S3c–d) as well, confirming the generalized applicability of the first-order model in describing the change of soluble $\text{PO}_4^{3-}\text{-P}$ in these suspensions with varying impurities during the struvite formation process. For instance, the presence of 30 ppm of PET-Zn demonstrated the rapidest crystallization kinetic rate, 1.43 times of the blank (Table 1). Recall that the introduction of these MP impurities can somewhat decrease the initial pH (Figure 1b, 2b), thereby increase the induction time by depressing the nucleation kinetics [42, 47]. This speculation is evidenced by the slightly lower rate constants of suspensions with 3 mg L^{-1} of MP impurities than that of the blank suspension (Table 1). However, the addition of more MP impurities into these suspensions (i.e., up to 30 mg L^{-1}) can distinctly offset the reduced nucleation kinetics caused by the decline in pH, as revealed by the higher rate constants compared to that of the blank suspension (i.e., $k_{\text{PE-Zn-30}} > k_{\text{PE-Cu-30}} > k_{\text{PET-Cu-30}} > k_{\text{PET-Zn-30}} > k_{\text{blank}}$, see Table 1).

3.2 Effect of HA and MPs on the kinetics of struvite formation in BRs

Recall that HA is believed to inhibit the crystallization of struvite [26, 27]. As shown in Figure 3a–b, the decreases in both the suspension pH and the soluble $\text{PO}_4^{3-}\text{-P}$ concentration with time are slower in the presence of HA relative to those of blank, indicating the inhibitory impact of HA on the formation of struvite. Using in situ liquid-cell atomic force microscopy, Ge *et al* observed that HA can greatly stabilize amorphous calcium phosphate by the formation of molecular organo-mineral bonding, thereby delaying the crystallization of thermodynamically stable calcium phosphate [48]. It was found that HA preferentially binds divalent or trivalent cations by forming humic-metal complexes of medium to high stability, which is likely to further bind P and form humic-metal-P complexes in aqueous solutions [49]. Interestingly, the initial pH of these suspensions with HA has been increased by 0.2 and 0.5 units for the suspension HA-10 and HA-100, respectively, possibly due to the higher affinity of HA toward protons [50]. Preceding reports suspected that organic acids are likely to complex with Mg^{2+} and NH_4^+ to form complexes of high thermodynamical stability and release protons meanwhile, leading to the gradual decrease in solution supersaturation and the significant increase in free energy barrier for nucleation and thus the induction time [26, 51]. Besides, these organic acids may be sorbed over the active sites of the nuclei, yielding molecular organo-mineral complexes of high stability and thus blocking the struvite crystal growth [26, 48].

Note that the linear fitting and description of the logarithmic concentration of soluble $\text{PO}_4^{3-}\text{-P}$ versus time using the first-order model (eq. 2) failed in suspensions of HA over the range of 0–10 min (Figure 3c–d). However, the logarithmic concentration of soluble $\text{PO}_4^{3-}\text{-P}$ showed excellent linearity against time in the range of 0–4 min, with rate constants (k) as high as 20.16, and 27.42 h^{-1} for suspension HA-10, and HA-100, respectively (Table 1). Such higher k values would not contribute to the struvite formation reaction based on the above explanation, but probably to the formation of HA-metal-phosphate complexes of high thermodynamical stability [48, 49]. Interestingly, when co-introducing 10 mg L^{-1} of HA and 30 mg L^{-1} of PET-Cu into the blank suspension (i.e., the HA+PET-Cu suspension), the plot of pH versus time changed slightly whereas the plot of soluble $\text{PO}_4^{3-}\text{-P}$ versus time varied remarkably (Figure 3a–b). This observation

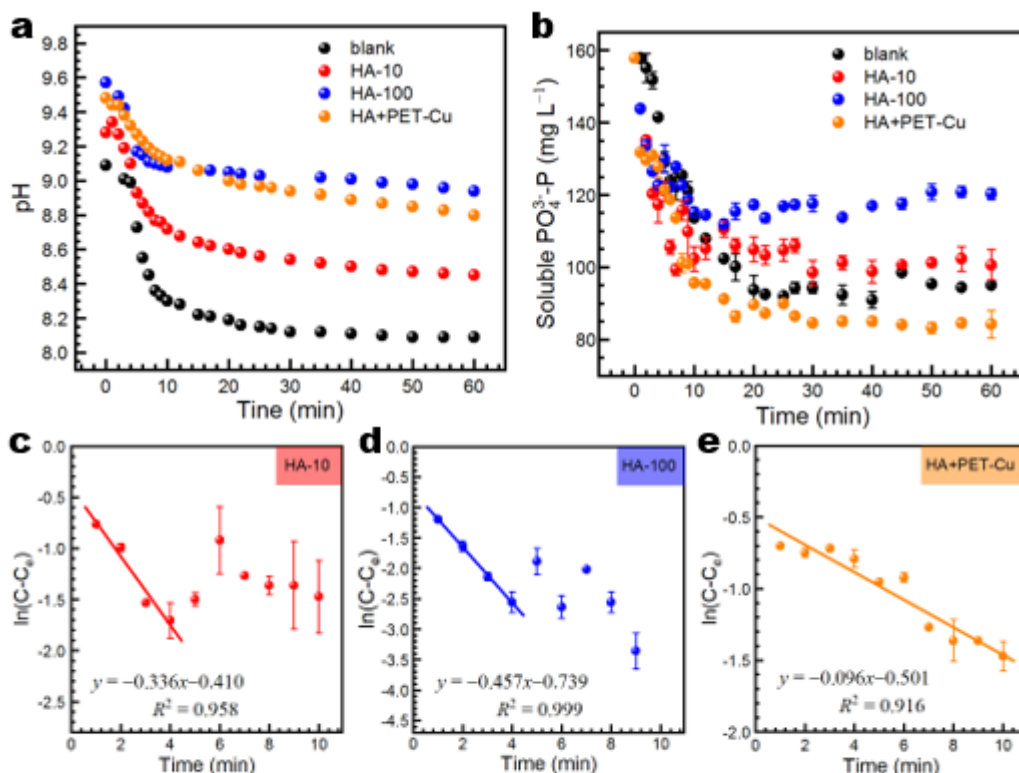


Figure 3. (a) The suspension pH profiles, (b) Plots of soluble $\text{PO}_4^{3-}\text{-P}$ versus reaction time in suspensions with varying contents of HA and/or PET-Cu; (c) Kinetic linear fitting plots of soluble $\text{PO}_4^{3-}\text{-P}$ in suspensions with (c) 10 ppm of HA, (d) 100 ppm of HA, and (e) 10 ppm of HA + 30 ppm of PET-Cu (denoted by HA+PET-Cu).

indicates that the pH values are primarily governed by the HA, while the induction time is dominated by PET-Cu. Note that the first-order model demonstrates a good fit in describing the logarithmic concentration of soluble $\text{PO}_4^{3-}\text{-P}$ against time in suspension HA+PET-Cu (Figure 3c), with a rate constant of 5.76 h^{-1} (Table 1). In comparison with suspensions blank and PET-Cu-30, the rate constants follow the order $k_{\text{PET-Cu-30}} > k_{\text{blank}} > k_{\text{HA+PET-Cu}}$, indicating that PET-Cu and HA played exactly opposite roles in struvite formation. Collectively, HA molecules appear to inhibit struvite formation by a set of complexation reactions even at a low content (e.g., 10 mg L^{-1}), and MPs are likely to compensate for this inhibitory influence of HA by reducing the induction time and thereof facilitate the crystallization of struvite in the complex suspensions.

3.3 Effect of MPs on the precipitates reclaimed from BRs

Apart from the influence on the kinetic of struvite formation, both MPs and HA also played different roles in regulating the physiochemical properties (e.g., morphologies, chemical, and phase compositions) of the resulting precipitates in BRs. In the absence of any impurities (i.e., the blank suspension), for instance, the precipitate (denoted as blank) demonstrated a well-defined XRD pattern (Figure 4a). By using the Rietveld refinement algorithm (i.e., the WPF refinement module in Jade version 6.5, MDI), we calculated that the phase compositions of the precipitate blank are 16.6 wt% newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, JCPDS #75-1714), 32 wt% halite (NaCl , JCPDS #70-2509), and 51.4 wt% sal-ammoniac (NH_4Cl , JCPDS #73-0365) (Figure 4b). XRF and FTIR spectra revealed that its major chemical compositions (P, K, Cl, etc.,

Figures S4c) and functional groups (VP-O , VN-H , and VO-H , Figure 4c), are highly identical to the XRD results (Figure 4a-b). Moreover, the SEM images showed that the blank precipitate is composed of well-defined microcrystal mixtures (Figure 4d1), with cubic halite (marked by a yellow arrow, Figure 4d2), newberyite microrods (marked by a blue arrow, Figure 4d2), and irregular-shaped sal-ammoniac.

Interestingly, there were clear changes in the XRD pattern of the reclaimed precipitate when 3 mg L^{-1} (ppm) of PE-Cu was introduced (red line labeled as PE-Cu-3, Figure 4a), with increasing intensities of newberyite and disappearing of other phases. Similar changes were also observed in the XRD pattern of precipitate reclaimed from BRs with 3 ppm of PE-Zn ((red line, Figure S4a). The WPF refinement results indicated that there are 96.7 wt% of newberyite, 2.9 wt% of $\text{MgHPO}_4 \cdot x\text{H}_2\text{O}$ (JCPDS #46-0375), and trace magnesite (MgCO_3 , JCPDS #80-0101) in precipitate PE-Cu-3 (Figure 4b), while PE-Zn-3 is composed of 95.8 wt% newberyite and 4.2 wt% struvite (JCPDS #71-2089, Figure S4b). These observations suggest that the presence of PE impurities, irrespective of the metal ions loaded, can facilitate the formation of newberyite. This is evidenced by the corresponding FTIR spectra with greater intensities of VP-O vibrations (e.g., P-O stretching at 1004 cm^{-1}) and less intensities of VN-H vibration at 1427 cm^{-1} compared to those observed in the blank precipitate (Figures 4c, S4d). Besides, SEM images show that rod-like newberyite embedded in PE surface dominates in precipitate PE-Cu-3 (Figure 4e), whereas PE-Zn-3 is predominant by irregular scale-like newberyite grew over the surface of PE particulates (Figure S5b). Therefore, it's reasonable to speculate that PE

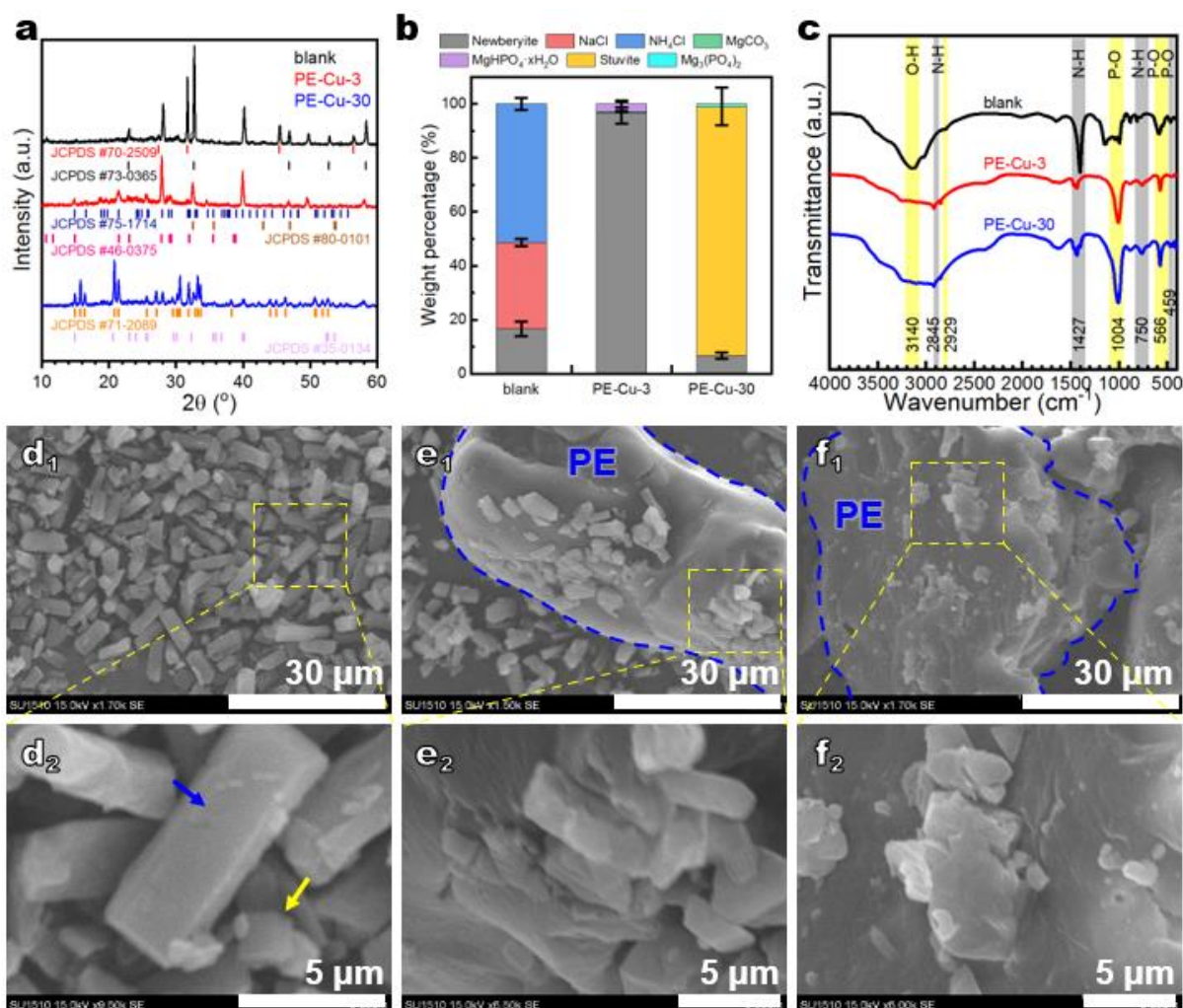


Figure 4. Characterizations of precipitates from batch reactors in the absence or presence of PE-Cu impurities. (a) XRD patterns, (b) phase compositions, (c) FTIR spectra; SEM images of (d) the control sample (i.e., precipitate from the blank suspension), (e) the reclaimed samples with 3 mg L^{-1} PE-Cu, and (f) 30 mg L^{-1} PE-Cu.

particulates (highlighted with PE in Figure 4) govern the phase transformation while the metal ions loaded on PE (viz. Cu^{2+} , Zn^{2+}) regulate the morphology of the resulting newberyite. It is worth noting that both precipitates were dominated by struvite when 30 ppm of PE-Cu or PE-Zn were added into the BRs, with 92.3 wt% and 80 wt% struvite in PE-Cu-30 and PE-Zn-30, respectively (Figures 4a-b, S4a-b). Molecular spectrum results (Figures 4c, S4c-d) also demonstrate the above observations. Note that the surfaces of PE particulates were embedded by many irregular struvite microcrystals (Figure 4f, S5c), implying PE impurities, in particular the cracked or defective domains, can serve as centers for nucleation and crystallization of struvite and newberyite [12, 47]. Given the fact that the presence of 3 ppm PE-Cu or PE-Zn favored the formation of newberyite while the addition of 30 ppm of PE facilitated the transformation from newberyite to struvite (Figures 4b, S4b), we can conclude that newberyite is less thermodynamically stable in the pH region studied but struvite is more sensitive to co-occurring impurities [52].

Notably, no newberyite was found in the precipitates in the presence of PET impurities, regardless of the metals loaded and

their contents in the reaction suspensions (Figures 5, S6). Only rod-like struvite and amorphous components were identified in these precipitates (i.e., PET-Cu(Zn)-3(30), Figures 5, S6, S7). The more PET impurities presented, the more struvite crystals were formed, with up to 83.3 wt% and 97.8 wt% of struvite found in PET-Cu-30 and PET-Zn-30, respectively (Figures 5b, S6b). These struvite crystals were embedded in PET surfaces (Figures 5d-e) or coated over these impurities (Figures S7b-c). In comparison to PE impurities, PET particulates are more likely to induce the formation of struvite under the same conditions, which may contribute to their much more oxygen-containing functional groups relative to PE particulates [40].

3.4 Effect of HA on the precipitates reclaimed from BRs

In contrast to the above MP impurities, the presence of HA impurities cannot fully suppress the formation of halite crystals even if its content is as high as 100 ppm (Figures S8, S9). However, as observed in the presence of low doses of PE impurities (viz. PE-Cu(Zn)-3), the introduction of HA significantly promotes the formation of newberyite (Figure S8). Specifically, the more HA

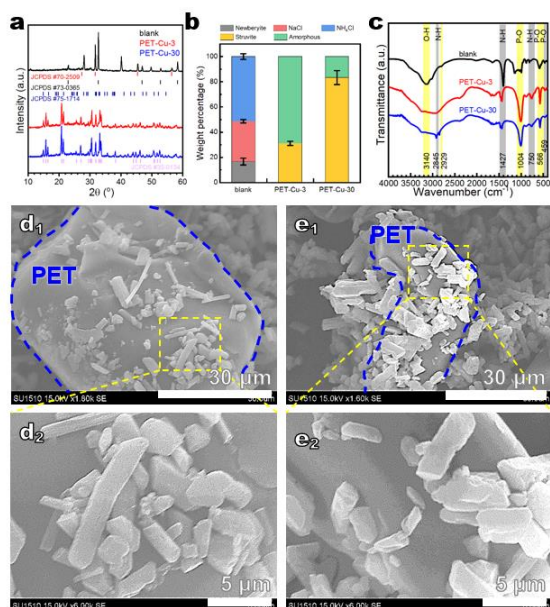


Figure 5. Characterizations of precipitates from batch reactors with varying contents of PET-Cu. (a) XRD patterns, (b) phase compositions, (c) FTIR spectra; SEM images of (d) the reclaimed precipitate with 3 mg L⁻¹ PET-Cu, and (e) 30 mg L⁻¹ PET-Cu.

was added in the reactant mixtures, the more newberyite crystals were yielded, with a mass ratio as high as 95.4 wt% in the precipitate HA-100, 5.7 times the ratio in the blank sample (Figure S8b). This might be attributed to the massive deprotonated carboxylic groups within HA molecules especially in alkaline solutions, which often show greater affinity towards ammonia than magnesium ions [53], thereby facilitating the formation of newberyite rather than struvite.

Interestingly, when 100 ppm of HA and 30 ppm of PET-Cu were added simultaneously in the reactant mixtures, the resulting precipitate (i.e., HA+PET-Cu) is featured by a small amount of rod-like newberyite and a large amount of needle-like struvite crystals (Figure S9). WPF refinement results indicate that it has a phase composition of 18.5 wt% newberyite and 81.5 wt% struvite (Figure S8). These results are identical to the aforementioned observations that demonstrate the preference of PET impurities in inducing the formation of struvite (Figures 5b, S6b), implying the potential seeding effect of such impurities during the struvite crystallization in BRs.

3.5 Effect of MPs and HA on the precipitates reclaimed from FBRs

As shown in Figure 6, no newberyite crystals were found in all precipitates reclaimed from FBRs. A possible explanation would be that newberyite is less thermodynamically stable than farringtonite (Mg₃(PO₄)₂, JCPDS #88-0413) in solutions at 25 °C and 1 bar [54], which may lead to phase transformations from newberyite to farringtonite and struvite during the 6-day operation in FBRs. Different from the phase composition of the blank in BRs (Figure 4b), the blank precipitate in FBRs is composed of 16.7 wt% struvite, 71.2 wt% farringtonite, and 12.1 wt% of amorphous phase (Figures 6a-b). When 1 g L⁻¹ of pure MgNH₄PO₄·6H₂O was introduced as seeds in the feed solutions, the amorphous component disappeared and the amount of struvite was increased to 31.7 wt% in the resulting precipitate denoted as seed (Figure 6b). This phenomenon is as expected and indicates that seeds could enhance the transformation of amorphous components to struvite

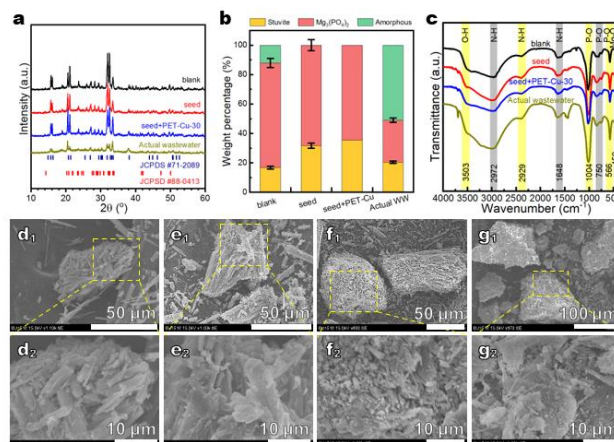


Figure 6. Characterizations of precipitates in FBRs in the absence or presence of PE-Cu impurities. (a) XRD patterns, (b) phase compositions, (c) FTIR spectra; SEM images of (d) the control sample (i.e., sample from the blank suspension), (e) sample with 1 g L⁻¹ seed, (f) 1 g L⁻¹ seed + 30 mg L⁻¹ PET-Cu, and (g) sample using the actual wastewater (sludge dewatering liquid) as influents.

but not to farringtonite. Noticeably, the copresence of seed (1 g L⁻¹) and PET-Cu (30 ppm) impurities in the feed solution can further spur the formation of struvite, with 35.4 wt% of struvite found in the corresponding precipitate seed+PET-Cu (Figure 6b). This observation verifies the seeding effect of PET particulates in FBR once again, as noted above in BRs (Figure 5b).

In the case of using actual wastewater as the feed solution, its phosphate concentration has been pre-adjusted up to 474 ppm, three times the P concentration in other feed solutions in FBRs. A preliminary experiment indicated that no precipitates were gained when using actual wastewater as the feed solution containing 158 ppm of P. It can be speculated that, based on the high COD concentration in the actual wastewater (Table S1), it is likely due to the high content of DOM in the feed solution which somewhat inhibited the formation of struvite [26, 29]. A large increase in the P concentration of the feed solution can effectively compensate for the inhibitory effect of DOM on struvite formation, yielding a precipitate with a phase composition of 20.4 wt% struvite (versus 16.7 wt% struvite in the blank), 28.6 wt% farringtonite, and 51 wt% amorphous components (Figure 6b). The corresponding FTIR spectra with a group of typical infrared bands also confirmed the phase evolutions of these precipitates (Figure 6c). SEM images indicate that all the precipitates in FBRs are featured by many irregular and compact agglomerates composed of numerous rod-like crystals (Figure 6d-g). Note that the more the seed and/or PET impurities presented, the more compact the resulting precipitates were (Figure 6f), in good agreement with earlier reports [1, 21].

3.6 Roles of MPs and HA on struvite crystallization

The crystallization process can generally proceed in either heterogeneous or homogenous manners according to the classical nucleation theory [55]. Providing similar precursor elements and the same conditions, heterogeneous nucleation occurs more preferentially than homogenous nucleation as the free energy barrier for nucleation may be significantly reduced in the presence of colloidal or solid impurities [56]. Based on the above kinetic and characterization results, it is clear that MP and HA exerted quite different influences on the crystallization reactions irrespective of the type of reactors where the reactions took place. Note that the MP impurities used are indiscernible PE and PET particulates of ~ 50 μm in diameter (Figures 4c, 5d). Therefore,

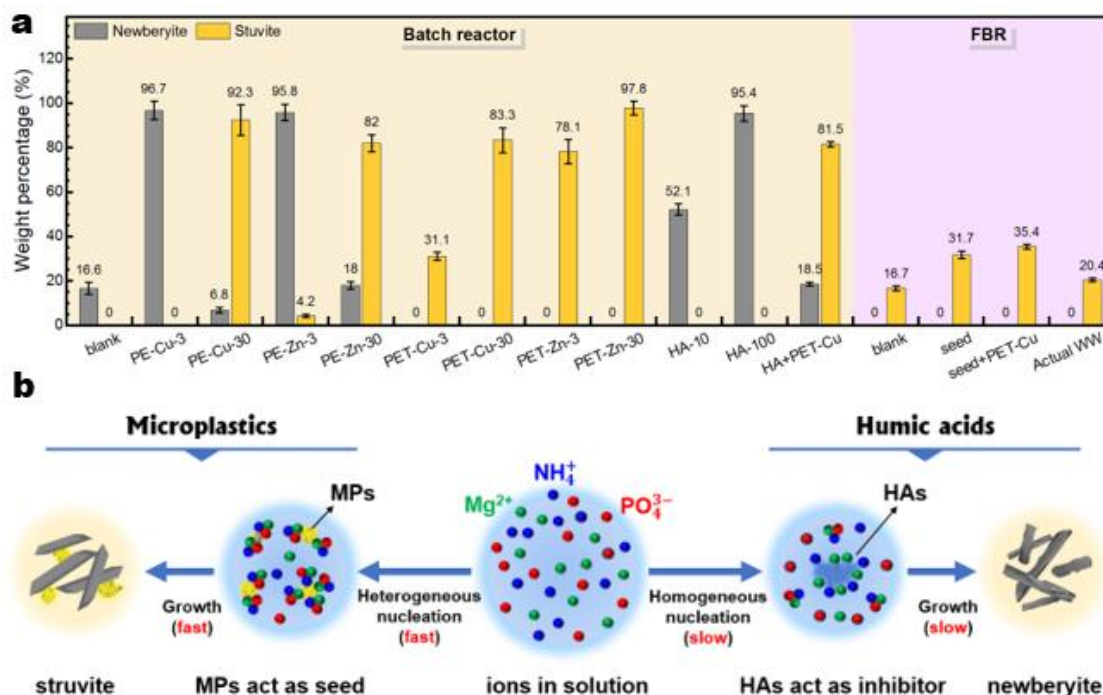


Figure 7. (a) Weight percentage of newberyite and struvite in precipitates reclaimed from BRs and FBRs as a function of co-occurring impurities. (b) Schematic illustration of the roles of MPs and HA in struvite formation in BRs and FBRs.

the presence of either PE or PET renders the reaction system a heterogeneous one due to their large surfaces that are favorable for nucleation. The less in diameter and the rougher in surface, the more the free energy barrier of nucleation of phosphate crystals (e.g., struvite, newberyite, and farringtonite) would be reduced as the MP surface can stabilize the newly formed nuclei. Specifically, there are many defective domains as well as oxygen functional groups over the surface of aged PE and PET particulates [40], both of which are believed the most active binding centers for crystal-forming ions and/or monomers, thereby facilitating the following nucleation and crystallization of phosphate crystals [57]. Indeed, the presence of either PE or PET has induced faster nucleation and crystallization rates (Table 1), and a greater proportion of struvite in the reclaimed precipitates (Figure 7a), verifying the seeding role of such impurities in struvite crystallization in BRs and/or FBRs [58, 59].

On the contrary, HA is a group of soluble macromolecules rich in carboxyl and carbonyl groups, which are likely to bind struvite-forming cations, and nuclei in aqueous solutions [49]. This interaction appears to reduce the solution supersaturation and increase the energy barrier of nucleation, prolonging the induction time of nucleation and subsequent crystallization (Table 1) [26, 51]. Besides, as discussed above, the presence of HA appears to create a favorable environment for newberyite formation (Figure 7a), yielding a much higher proportion of rod-shaped newberyite crystals in the presence of 100 ppm HA as impurities (Figures S8, S9). This observation is in good agreement with previous reports [26, 27]. In light of the above results, the roles of MPs and HA in struvite formation have been rationally proposed and illustrated schematically in Figure 7b. Specifically, MPs can lower the free energy barrier of struvite formation by providing quite large defective surfaces that serve as nucleation sites even though both

MP surface and struvite nuclei are negatively charged (Figure S10). However, HA plays an inhibitory role in mediating the formation of struvite, probably through a complex of interactions including bridge complexation, static Coulomb interaction, and so on. Collectively, both PE and PET particulates serve as seeding materials spurring nucleation and subsequent crystallization of struvite crystals in BRs and/or FBRs, while HA seems to inhibit the formation of struvite but facilitate newberyite formation due to complex interactions [60]. To this end, more investigations are needed to elucidate the mechanism for this extraordinary role of HA impurities on the molecular level.

4. Conclusions

This study has comprehensively elucidated the roles of aged microplastic and humic acid impurities in the struvite crystallization process in batch and fluidized bed reactors. The crystallization kinetic results reveal that the presence of aged microplastics significantly increases the nucleation and growth rate of such crystals, primarily because the large surfaces of MP can serve as reactive sites for newly formed nuclei, reducing the free energy barrier of nucleation and thereby expediting the growth of struvite in solutions. Humic acid, on the other hand, inhibits the nucleation and growth of struvite crystals but favors the formation of newberyite crystals. Interestingly, the co-presence of microplastics and humic acid can significantly compensate for the inhibitory effects of humic acid on the formation rate of struvite, yielding a precipitate dominated by struvite. Moreover, it also showed that the presence of microplastics and/or humic acid can significantly impact the quality of the resulting precipitates from struvite crystallization, leading to complex changes in both the phase compositions and the morphology. From an environmental perspective, these findings provide crucial insights into a

previously underexplored interaction between microplastics, humic substances, and crystal-forming ions during P recovery processes in BRs and FBRs. Given the ubiquitous presence of microplastics and humic substances in wastewater, our study underscores the importance of considering the impact of microplastics on nutrient recovery technologies and highlights the necessity of tailored approaches to mitigate their adverse effects on the efficiency of recovering nutrients in the form of struvite and the quality of the reclaimed struvite, with significant implications for wastewater treatment and sustainable agriculture.

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Appendix A. Supporting Information

Supporting information to this article can be found online.

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Table 1. Best-fit kinetic equations and corresponding parameters of struvite crystallization in batch reactors with varying contents of impurities derived from the first-order model (Eq. 2).

Suspension code	Impurity	Content (ppm)	First-order kinetic equation	k (h ⁻¹)	Time Range	R^2
blank	none	0	$y = -0.129x - 0.156$	7.74 ± 0.44	0 – 16 min	0.978
PE-Cu-3	PE-Cu	3	$y = -0.131x - 0.187$	7.86 ± 0.59	0 – 12 min	0.952
PE-Cu-30	PE-Cu	30	$y = -0.169x - 0.097$	10.14 ± 0.58	0 – 16 min	0.965
PET-Cu-3	PET-Cu	3	$y = -0.117x - 0.334$	7.02 ± 0.62	0 – 12 min	0.941
PET-Cu-30	PET-Cu	30	$y = -0.136x - 0.076$	8.16 ± 0.72	0 – 12 min	0.935
PE-Zn-3	PE-Zn	3	$y = -0.120x - 0.279$	7.20 ± 0.61	0 – 12 min	0.939
PE-Zn-30	PE-Zn	30	$y = -0.184x - 0.136$	11.04 ± 1.16	0 – 12 min	0.919
PET-Zn-3	PET-Zn	3	$y = -0.118x - 0.337$	7.08 ± 0.51	0 – 10 min	0.960
PET-Zn-30	PET-Zn	30	$y = -0.133x - 0.187$	7.98 ± 0.43	0 – 10 min	0.977
HA-10	HA	10	$y = -0.336x - 0.410$	20.16 ± 2.97^a	0 – 4 min	0.958
HA-100	HA	100	$y = -0.457x - 0.739$	27.42 ± 0.60^a	0 – 4 min	0.999
HA+PET-Cu	HA, PET-Cu	10, 30	$y = -0.096x - 0.501$	5.76 ± 0.62	0 – 10 min	0.916

^a These high k values would not contribute to the struvite formation reaction but to the complexation reactions between HA, metal ions, and phosphate [48, 49].