Evolution of phosphorus with the promotion of KOH in supercritical water gasification of dewatered cyanobacteria from ion perspective

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Abstract

Phosphorus is a very important resource, and dewatered cyanobacteria contains a large amount of it. Basic additives, such as KOH, are often used to promote hydrogen production during supercritical water gasification (SCWG) of biomass, but their effects phosphorus transformation have rarely been investigated. In this study, SCWG of dewatered cyanobacteria with potassium salt and KOH was conducted in autoclave at 400°C for 10 min, to investigate the effect of K^+ on the transformation of phosphorus under neutral and alkaline conditions. Results showed that K^+ increased the proportion of phosphorus in the solid phase from 88.4% to 90.8–98.3%. Furthermore, K^+ could promote the transformation of iron-combined phosphorus to calcium-combined phosphorus and occluded phosphate. Only when the reaction environment was alkaline, the proportion of phosphorus in the solid phase was significantly reduced to a minimum of 26.1%. When the amount of OH^- was sufficient, can this part of phosphorus and organic phosphorus, which was decomposed and transformed by the promotion of OH^-, be transferred to the liquid products. Results from this study laid a foundation simultaneously for hydrogen production and phosphorus recovery more environmentally and high-effectively.

Keywords

Dewatered cyanobacteria; Supercritical water gasification; Phosphorus; KOH ; Additive

1. Introduction

Phosphorus is an important element in the life activities of human beings, animals, and plants (Hao et al., 2013; Law et al., 2019). However, phosphate resources are limited and non-renewable worldwide. Based on current demand and development rate, the global phosphate stock should be depleted in 50–100 years (Zhu et al., 2023). Therefore, it is essential to recover phosphorus from various wastes sources. Dewatered cyanobacteria came from cyanobacterial blooms and enriched a large amount of phosphorus in eutrophic water, which are potential raw materials for phosphorus recovery (Heilmann et al., 2014). In recent years, cyanobacterial blooms frequently occur in lakes, such as Lake Taihu, Lake Chaohu, and Lake Dianchi in China, owing to eutrophication. For example, the cyanobacterial slurry (with a solid content of 0.5%) recovered alone in Lake Taihu reached 13.43 million tons, including 896 tons of phosphorus between 2007 and 2018 (data from the Wuxi Cyanobacteria Control Office). A cyanobacterial slurry can enter water–algae separation stations and precipitate sludge-like solid matters after flocculation and dehydration, which are called dewatered cyanobacteria. Dewatered cyanobacteria typically contain 85%−95% moisture content and is difficult to fully dehydrate due to its strong hydrophilicity and extracellular polymeric substance content (Li et al., 2021), thus the production of dewatered cyanobacteria still huge. Moreever, dewatered cyanobacteria consist mainly of unstable biological cells, making them difficult to treat and utilize.

Supercritical water gasification (SCWG) is a promising technology for treating various wastes that contain high-moisture compounds, such as sewage sludge (Yildirir & Ballice, 2019), algae (Samiee-Zafarghandi et al., 2019), and animal manures (Tavasoli et al., 2018) in recent years. This technology takes advantage of the large amount of water in wet feedstock as a reaction medium, eliminating the energy-intensive feedstock drying step, and can be used to decompose the organic pollutants in feedstock. At same time, clean energy such as syngas can be obtained to reduce the cost of waste treatment. However, the gasification efficiency of SCWG of biomass waste is usually not high, and so many studies use additives to improve hydrogen production (Guo et al., 2010; Pairojpiriyakul et al., 2014; Zhai et al., 2013; Li et al., 2023). Carbon additives, metal and metal oxide additives, and alkali metal additives are the commonly used additives, with KOH being one of the most common alkali metal additive. The effects of KOH on hydrogen production and coke inhibition were studied in SCWG of different biomass (Xu et al., 2013; Su et al., 2022; Zhang et al., 2021), while the effects on phosphorus conversion attracted few attention. Zhu et al. (2011) studied dewatered sludge from the aspect of phosphorus conversion during SCWG. They found that phosphorus mostly exists in solid products in calcium-combined forms, and this trend has been observed in most other studies (Bircan et al., 2011; Yanagida et al., 2009). Therefore, many researchers studied how to recover phosphorus from solid products after SCWG of different wastes. Acid/alkaline extracting is typically performed to release phosphorus from solid products into the extraction solution, which is then used to recover phosphorus (Acelas et al., 2014; Zhai et al., 2014). However, this method is relatively complex because phosphorus mainly forms solid products after the reaction. In previous work, a one-step recovery method was proposed to solve this problem by enriching phosphorus in liquid products after SCWG using KOH (Chen et al., 2019). The one-step recovery method can effectively convert phosphorus into a liquid phase, and the conversion rate can reach more than 70% the effects of other types of basic additives (NaOH, Na_2CO_3 and K_2CO_3) have also been tested, but their effects on the distribution of phosphorus in the solid/liquid products were less obvious than that of KOH. Wang et al. (2019) also found that the addition of a KOH additive in the SCWG of dewatered sludge could transform phosphorus into a liquid phase. In addition to dewatered cyanobacteria or sludge, waste biomass, which can produce hydrogen by SCWG, such as chicken manure and cow manure also have a rich phosphorus content. If phosphorus can be transferred to a liquid phase for further one-step recovery while promoting hydrogen production, it will lead to important resource recovery benefits. However, it is not clear whether the anions or cations of KOH play a major role, and furthermore, the reaction pathways that these inducing ions adopt and their roles are still unknown.

Therefore, it is very important to understand the basic principle and transformation trend of a KOH additive in the promotion of the distribution and transformation of phosphorus between a solid and liquid phase. In this study, various K^+-containing additives were used to study the effects of KOH additive on the transformation of phosphorus in the solid–liquid two-phase system firstly from an ionic perspective of the anions and cations. Futhermore, the reaction mechanism of KOH-promotion of phosphorus into a liquid phase was also discussed.

2. Materials and methods

2.1 Materials

In this study, dewatered cyanobacteria biomass was collected from a water–algae separation station called Yang Wan at Lake Taihu, China, the primary dehydration of cyanobacteria biomass was performed by mechanical pressure filtration with flocculant in the water−algae separation station. It was taken back to the laboratory and stored in a refrigerator at about 4 °C for subsequent experiments. In the process of the SCWG experiment, no pretreatment such as drying is needed, and direct wet sample loading is sufficient. The basic properties of dewatered cyanobacteria are detailed in Table 1. The used reagents, i.e., KCl, K_2SO_4, and KOH, were all analytically pure powder particles and purchased from Aladdin Chemistry Co., Ltd, Shanghai, China.

2.2 Experimental procedures

The experiments were performed in a 316 L stainless-steel batch autoclave purchased from Songling Chemical Instrument Co. (Yantai, China)., which was heated by a salt bath furnace. They have been described in detail in a previous study (Gong et al., 2014). 36.5 g dewatered cyanobacteria (i.e. 33 g water and 3.5 g dried matter) and a certain proportion of the additives were jointly added in the autoclave, and the temperature was raised to 400 °C (when the water volume in the reactor reached 33 mL, the pressure could reach 23 MPa (Chen et al., 2019)), the reaction residence time was 10 min. The above reaction parameters were determined by previous study of other scholars on dewatered cyanobacteria (Zhang and Zhang, 2017), which can ensure that the feedstock react fully in supercritical water. After the reaction, the reactor was taken out of the salt bath furnace and rapidly cooled to room temperature by a fan. After cooling, the products were separated and collected as described above (Xu et al., 2012).

The total molar amount of K^+ when adding 6 wt.% KOH was taken as the total molar amount of K^+ in the mixed additive. KCl, K_2SO_4, and KOH are added after mixing in different proportions, two different potassium salts are selected for this study, which makes the comparison between neutral conditions and alkaline conditions more comprehensive and universal. The molar concentration of potassium ions in each group is consistent, and the specific mixtures are listed in Table 2.

2.3 Analytical methods

The inorganic elements (Ca, Al, Fe, Mg, K, Na, and Si) in the dewatered cyanobacterial samples were determined by an inductively coupled plasma optical emission spectrometer (Optima 8000, PerkinElmer, America). C, H, N, and S contents were determined by an elemental analyzer (ElementarVario EL III, Elementar, Germany). The total phosphorus and dissolved reactive phosphorus (DRP) in the liquid products were measured by an ultraviolet spectrophotometer (UV2450, Shimadzu, Japan) based on Water and Wastewater Monitoring and Analysis Methods (Ministry of Environmental Protection of the People's Republic of China, 2002). The continuous chemical extraction method (Zhang & Zhang, 2017) was used to determine the phosphorus forms and contents in the solid products, including total phosphorus (TP), organic phosphorus (Org-P), exchangeable phosphorus (Ex-P), aluminum-combined phosphorus (Al-P), iron-combined phosphorus (Fe-P), occluded phosphate (Oc-P), and calcium-combined phosphorus (Ca-P), which consisted of self-ecological phosphorite and debris phosphorus.

3. Results and discussions

3.1 Mass and phosphorus balance

Figure 1 shows the mass and phosphorus balance without the addition of additives. After SCWG reaction, most of the mass is distributed in the liquid product, only 2.97% of the mass is distributed in the solid product, which is related to the high moisture content of dewatered cyanobacteria, and some of the organic matter is transformed from solid phase into the aqueous phase after the SCWG, so the proportion of the solid phase is further lower than that of the raw material. However, the distribution of phosphorus is not proportional to the mass distribution, 88.43% of phosphorus is enriched in the solid product, similar result was also corroborated in the research of other scholars (Acelas et al.,2014; Yan et al., 2023). Due to its binding with Fe^{3+}, Al^{3+} and Ca^{2+}, most of the phosphorus tends to exist in the solid state.3.1 Effects of K^+ on the distribution and form of phosphorus in the solid and liquid products

3.1.1 Effects of K^+ on the distribution of phosphorus in the solid and liquid products

Neutral potassium salts KCl and K_2SO_4 were added as additives to represent K^+ in a certain proportion under the reaction conditions of 400 °C and 10 min. Figure 2(a) depicts the effects of K^+ on the distribution of phosphorus in the solid and liquid products. The results show that only added K^+ inhibits the transfer of phosphorus from solid products to liquid products. Compared with the reaction without additives, the proportion of phosphorus in the liquid products decreases. The proportion of phosphorus in the liquid product is 11.56% without additives, 1.68% and 2.58% when KCl and K_2SO_4 added alone, respectively. When KCl and K_2SO_4 are mixed at the molar ratio of K^+ to 1:1, the 9.15%. These results indicate that anions affect the distribution of phosphorus in the solid and liquid products during the SCWG of dewatered cyanobacteria. The proportion of phosphorus in the liquid products when K_2SO_4 added alone is higher than that when KCl added alone. This may be because SO_4^{2-} can easily combine with Ca^{2+}, Al^{3+}, Fe^{3+}, and other metal ions to undergo partial precipitation, thus releasing a small amount of the phosphate radicals bound to those metal ions. The released phosphate radicals could be combined with K^+ to form liquid products. Furthermore, the difference in the solubility between KCl and K_2SO_4 in supercritical water can also affect the distribution of phosphorus in the solid and liquid products. Interestingly, compared with KCl and K_2SO_4 added alone respectively, the proportion of phosphorus in the liquid products is the largest when KCl and K_2SO_4 mixed at the molar ratio of K^+ to 1:1. The coexistence of KCl and K_2SO_4 in supercritical water may interact with each other and produce a special impact on the reaction. However, the specific reaction process still needs further study to explain clearly, while which is not the focus of this paper.

3.1.2 Effects of K^+ on the form of phosphorus in the liquid products

Figure 2(b) illustrates the effects of K^+ on the concentration and form of phosphorus in the liquid products. As observed, the concentration of TP in the liquid products decreases when K^+ is added alone. Specifically, the concentration of TP in the liquid products after adding KCl alone and K_2SO_4 alone is 10.6 mg/L and 10.54 mg/L, respectively; these values are closely similar. Notably, when KCl and K_2SO_4 are mixed in the molar ratio of K^+ of 1:1, the concentration of TP in the liquid products increases to 31.02 mg/L, which is close to that in the liquid products after the reaction without additives. When KCl and K_2SO_4 are added separately, the concentration of TP in the liquid products is similar, but the proportion of phosphorus in the solid and liquid products is different. This is related to the distribution of the product mass, recovery rate of the products, and loss of some phosphorus elements (such as adherence to the wall of the centrifugal tube with very few oil products). In addition, only the added K^+ has little effect on the DRP in the liquid products, and the proportion of the DRP in the liquid products fluctuates slightly around 50%.

3.1.3 Effects of K^+ on the form of phosphorus in solid products

As shown in Figure 3, K^+ mainly affects the distribution of Fe-P and Org-P in the solid products. After SCWG reaction, Al-P and Fe-P in raw feedstocks decreased significantly while Ca-P increased significantly. Compared with the products from the reaction without additives, the proportion of Fe-P in the solid products decreases significantly after K^+ addition, whereas the proportion of Ca-P and Oc-P increases slightly. This indicates that the reduced Fe-P has converted to some Ca-P and Oc-P instead. And the increased Org-P in the solid products may be released from cyanobacteria cells in dewatered cyanobacteria under the promotion of K^+. The proportion of Al-P and Oc-P in the solid products can reach 3.12% and 2.47%, respectively, when KCl and K_2SO_4 are added in the molar ratio of 1:1. However, the content and proportion of Al-P and Oc-P in the solid products are very low when KCl is added alone, which might be owing to the influence of Cl^- on the extractants used to extract Al-P and Oc-P, resulting in their insufficient and incomplete extraction. The addition of K^+ does not increase the proportion of Ex-P in the solid products, which indicates that the only K^+ cannot promote the formation of Ex-P.

3.2 Effects of OH^- on the distribution and form of phosphorus in the solid and liquid products

3.2.1 Effects of OH^- on the distribution of phosphorus in the solid and liquid products

Figure 4 illustrates that the proportion of phosphorus in the liquid products increases gradually with the addition of OH^-. Figure 4 (a) displays that the proportion of phosphorus in the liquid products is 16.27% when the K^+ molar ratio of KCl and KOH is 1:1, while Figure 4 (b) shows that is 23.95 when the K^+ molar ratio of K_2SO_4 and KOH is 1:1. Hence, when the molar ratio of OH^- reaches half of the total anion molar ratio of the additives, the proportion of phosphorus in the liquid products begins to gradually exceed that in the liquiproducts after the reaction without additives (i.e. 11.56%). This indicates that mixed additives can promote the transfer of phosphorus from solid products to liquid products. OH^- has a tremendous influence on the distribution of phosphorus in the solid and liquid products, and it is beneficial to the transfer phosphorus from solid products to liquid products. Since phosphorus are usually distributed in solid products, subsequent utilization of phosphorus elements still needs to be transferred to the liquid phase by acid leaching. Gorazda et al. (2018) leached the solid product with 2.7 mol/L nitric acid, the leaching rate of phosphorus element was 81.52%, so it is meaningful to promote the distribution of phosphorus element in the liquid phase by KOH in this article, which can effectively reduce the amount of subsequent leaching solution. Compared with Figure 4 (a) and Figure 4 (b), the distribution of phosphorus in the solid and liquid products is very similar, which shows that differences between Cl^- and SO_4^{2-} anions have less influence on the distribution of phosphorus in the solid and liquid products when OH^- existing. Overall, OH- anions have more influence on the distribution of phosphorus in the solid and liquid products than the other anions.

3.2.2 Effects of OH^- on the form of phosphorus in the liquid products

As can be seen from Figure 5, with the increase in the KOH content in the mixed additives, the concentration of TP in the liquid products increases, whereas the addition of OH^- obviously promotes the conversion of the non-dissolved reactive phosphorus (NDRP) into DRP in the liquid products to a certain degree. Therefore, the proportion of the DRP in the liquid product would increase rapidly when adding OH^-. In Figure 5 (a), at a molar ratio of 1:1 of K^+ in the KCl and KOH mixtures, the concentration of TP in the liquid products is 88.13 mg/L. In Figure 5 (b), at a molar ratio of 1:1 of K^+ in the K_2SO_4 and KOH mixtures, the concentration of TP in the liquid products is 112.94 mg/L. This indicates that the concentration of phosphorus in the liquid products gradually exceeds that in the reaction without additives (i.e. 35.13 mg/L) when the molar ratio of OH^- reaches half of the total anion molar ratio of the additives. Comparing Figures 5(a) and 5(b), it can be found that although the neutral potassium salts in the mixed additives are different, the concentration of TP in the liquid products is very similar This is was similar to the results of adding KCl and K_2SO_4 separately. Thus, the distribution of phosphorus in the solid and liquid products is different, but the concentration of TP in the liquid products is not very different.

3.2.3 Effects of OH^- on the form of phosphorus in the solid products

It can be seen from Figure 6 that with the increase in the KOH content in the mixed additives, Ex-P in the solid products clearly increases after adding OH^-. Together with Figure 3, it can be seen that only the coexistence of K^+ and OH^- is conducive to the formation of Ex-P. Compared with the condition without OH^- added, Fe-P decreases further and Oc-P increases further, which indicates that OH^- can also help convert some Fe-P to Oc-P. Obviously, Org-P decreases gradually with the increase in OH^- in the mixed additives, indicating that alkaline environment is beneficial to the decomposition and transformation of Org-P, similar result were observed under weakly alkaline conditions (Gong et al., 2020). Combining Figure 5 and Figure 6, it can be seen that the reduced Fe-P and Org-P forms in the solid products mainly transfer into the liquid products. K^+ can promote the transformation of Fe-P into other forms of phosphorus in the solid products, and when there is a certain amount of OH^- in the reaction environment, the formed alkaline atmosphere could promote the gasification efficiency of dewatered cyanobacteria, which greatly promote the transformation of Fe-P from solid products into the liquid products. The change in the Al-P and Ca-P in the solid products is relatively small, indicating that they are relatively less affected by the increasing OH^- in the mixed additives, this may be related to the stronger binding of Ca^{2+}, Al^{3+} and phosphorus (Zhang et al., 2020). In addition, it can be seen from Figures 6(a) and 6(b) that although the neutral potassium salts in the mixed additives are different, the overall distribution of phosphorus in the solid products is very similar. Figure 7 presents the XRD patterns of the dewatered cyanobacteria and solid products, allowing for the determination of the solid phase crystalline changes before and after the SCWG. Although Al-P and Fe-P were detected in dewatered cyanobacteria, XRD results indicated that no phosphorus-containing crystalline compound was formed. Meanwhile, in the solid-phase products, the use of additives did not affect the crystalline morphology of the phosphorus, as hydroxyapatite, whitlockite, and $AlPO_4$ were detected. Acelas et al. (2014) also found the existence forms of phosphorus of the same type in the XRD analysis of the solid residue from SCWG of sewage sludge.

3.3 Mechanism analysis of the effect of the KOH additive on the distribution and conversion of the solid and liquid phosphorus from ion perspective

Figure 8 shows the possible reaction pathway of phosphorus under the condition of KOH additive addition. From Figure 3 it is evident that Al-P and Fe-P are dominant in the dewatered cyanobacteria, and Org-P is partly present in the cyanobacteria cells. After SCWG reaction, Ca^{2+} present on the cyanobacteria cell wall is gradually released and binds with phosphorus to form a large amount of Ca-P in the solid products (Chen et al., 2019), Based on the analysis of sections 3.1 and 3.2, it can be inferred that the K^{+} in the KOH additive mainly promote the transformation of Fe-P to other forms of phosphorus such as Ca-P and Oc-P in solid products in the SCWG of dewatered cyanobacteria. It also promotes the release of a portion of Org-P from the cyanobacteria cells into the solid products. The presence of OH^{-} promotes the conversion from Fe-P to Ex-P and Oc-P in solid products. It also promotes part of phosphorus transformed from Fe-P, and part of phosphorus from the decomposition and transformation of Org-P both from the cyanobacteria cells and solid products into liquid products. Simultaneously, the presence of OH^{-} makes the reaction environment alkaline, and there is also a small amount of mutual transformation between Ca-P and Al-P, which is similar to previous research results (Zhu et al., 2011; Zhang & Zhang, 2019).

Obviously, to promote the transformation of phosphorus into liquid products, not only K^+, which can change the form of solid phosphorus and combine with phosphorus to form soluble cations, but also OH^-, which can provide an alkaline environment to promote the gasification efficiency of dewatered cyanobacteria and replace the metal ions bound with phosphorus in the solid products, can promote the maximal transfer of phosphorus from solid to liquid products.

4. Conclusions

This study elucidates the effect of alkali metal additives on the distribution and transfer of phosphorus in the SCWG products of dewatered cyanobacteria under neutral and alkaline conditions. Without additives, 88.43% of the phosphorus in the dewatered cyanobacteria was distributed in the solid products after SCWG, mainly in the form of aluminum-bound and iron-bound phosphorus. The anion, OH^-, and cation, K^+, of the additive jointly affect the transformation of phosphorus during the reaction. Under neutral conditions, the potassium ion promoted the proportion of phosphorus in the solid products to increase from 88.4% to 90.8%-98.3%, and facilitated the conversion of some Fe-P into other forms of phosphorus in the solid products.In comparison, the anions mainly affect the transformation between the solid and liquid phosphorus. When the reaction environment was alkaline and the OH- concentration was sufficient, a large amount of phosphorus was transferred to the liquid products, and the proportion of phosphorus in the solid products decreased to a minimum of 26.1%. In conclusion, the anions in the KOH additive mainly displace the phosphorus bound to the metal ions and promote the decomposition of organic phosphorus. Contrastingly, the cations mainly change the form of some phosphorus in the solid products and combine with the released phosphorus to form a soluble phosphate in the liquid products. Further characterization of the products and intermediates is needed to explore the mechanism of the effect of basic additives on phosphorus transfer and transformation.

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Figure Captions

Figure 1 Investigation of the mass and phosphorus balance without additive.

Figure 2 Effects of K^+ on the (a) distribution of phosphorus in the solid and liquid products and (b) form of phosphorus in the liquid products.

Figure 3 Effects of K^+ on the form of phosphorus in the solid products.

Figure 4 Effects of OH^- on the distribution of phosphorus in the solid and liquid products with (a) KCl and (b) K_2SO_4.

Figure 5 Effects of OH^- on the form of phosphorus in the liquid products with (a) KCl and (b) K_2SO_4..

Figure 6 Effects of OH^- on the form of phosphorus in the solid products with (a) KCl and (b) K_2SO_4..

Figure 7 XRD patterns of (1) raw dewatered cyanobacteria and solid residue, (2)without additive, (3) with KOH.

Figure 8 Possible reaction pathways of phosphorus under the condition of KOH additive addition.

Table

Table 1 Properties of the studied dewatered cyanobacteria

Moisture content (wt%)[a]	Proximate analysis (wt%)[b]			Ultimate analysis (wt%)[b]					HHV (MJ/kg)[d]
	OM	FC	Ash	C	H	N	S	O[c]	
90.63 ±0.35	74.67 ±0.62	1.69 ±0.53	23.64 ±0.53	34.87 ±0.28	5.64 ±0.13	7.12 ±0.03	0.84 ±0.20	27.89 ±0.38	15.09 ±0.01

Inorganic elements (wt%)[b]	P	Ca	Al	Fe	Mg	K	Na	Si
	0.48 ±0.02	0.29 ±0.01	3.04 ±0.02	0.77 ±0.04	0.19 ±0.01	0.48 ±0.11	0.05 ±0.01	0.10 ±0.01

[a]: On a wet basis.

[b]: On a dry basis.

[c]: By difference (O% = 100% - Ash% - C% - N% - S% - H%);

[d]: High heating value (HHV) calculated by the Dulong formula: HHV (MJ/kg) = $0.3383C + 1.443 (H – O/8) + 0.0927S + 0.01494N$.

Table 2 Molar ratios of the $KCl/K_2SO_4/KOH$ mixed additives

	Additive	**K^+ molar percentage (%)**				
K^+ group	KCl	0	100	0	50	
	K_2SO_4	0	0	100	50	
OH^- group	**Additive**	**K^+ molar percentage (%)**				
	KCl/K_2SO_4	100	66.67	50	33.33	0
	KOH	0	33.33	50	66.67	100

Figure

Figure 1

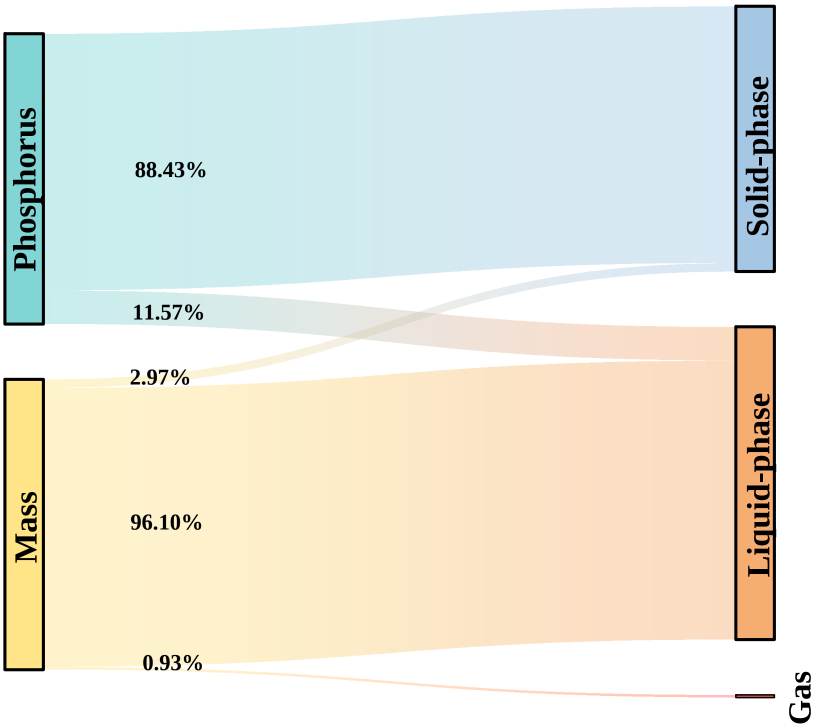
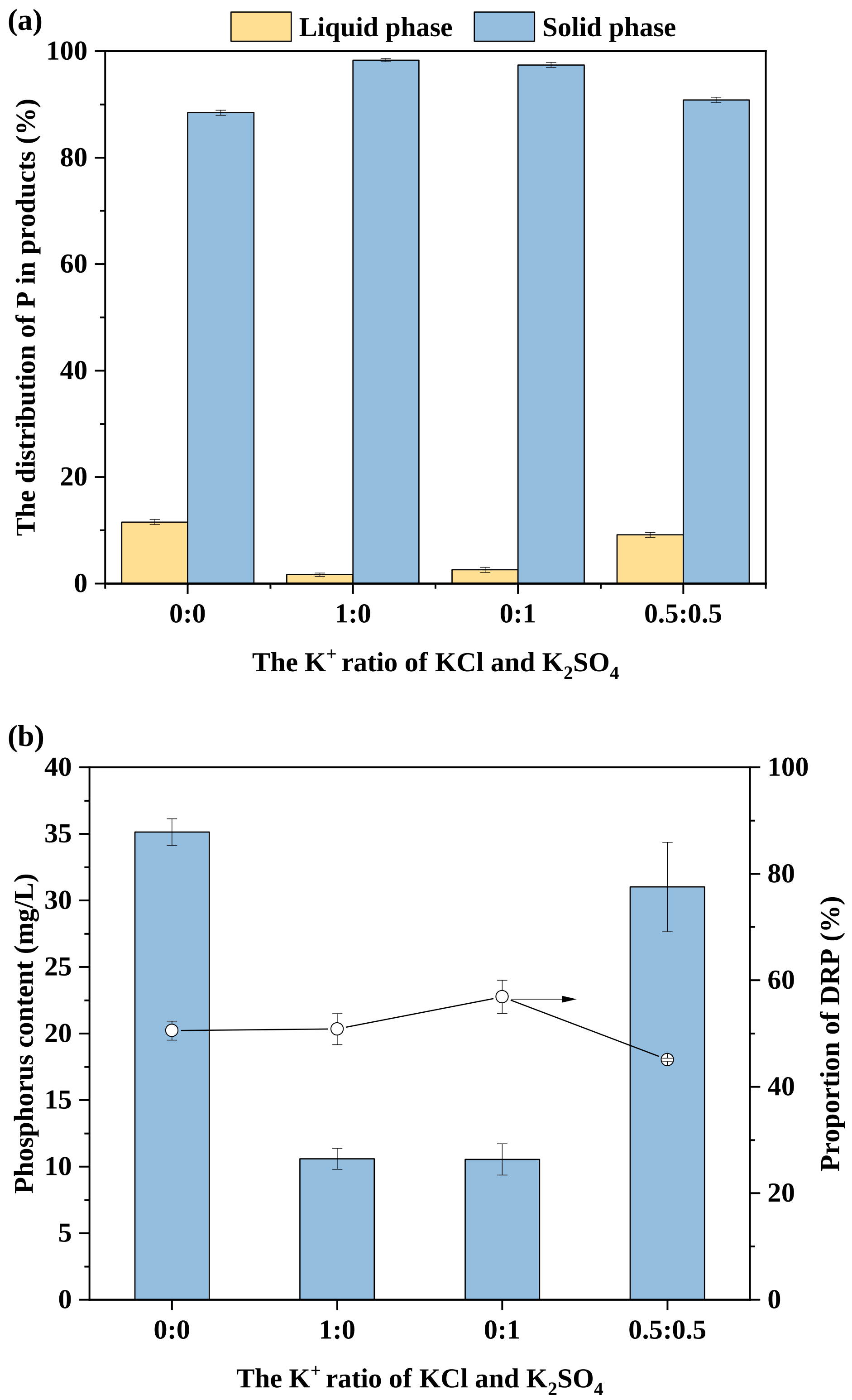


Figure 2



(a)
Liquid phase
Solid phase
The distribution of P in products (%)
100
80
60
40
20
0
0:0
1:0
0:1
0.5:0.5
The K+ ratio of KCl and K2SO4
(b)
Phosphorus content (mg/L)
40
35
30
25
20
15
10
5
0
Proportion of DRP (%)
100
80
60
40
20
0
0:0
1:0
0:1
0.5:0.5
The K+ ratio of KCl and K2SO4

Figure 3

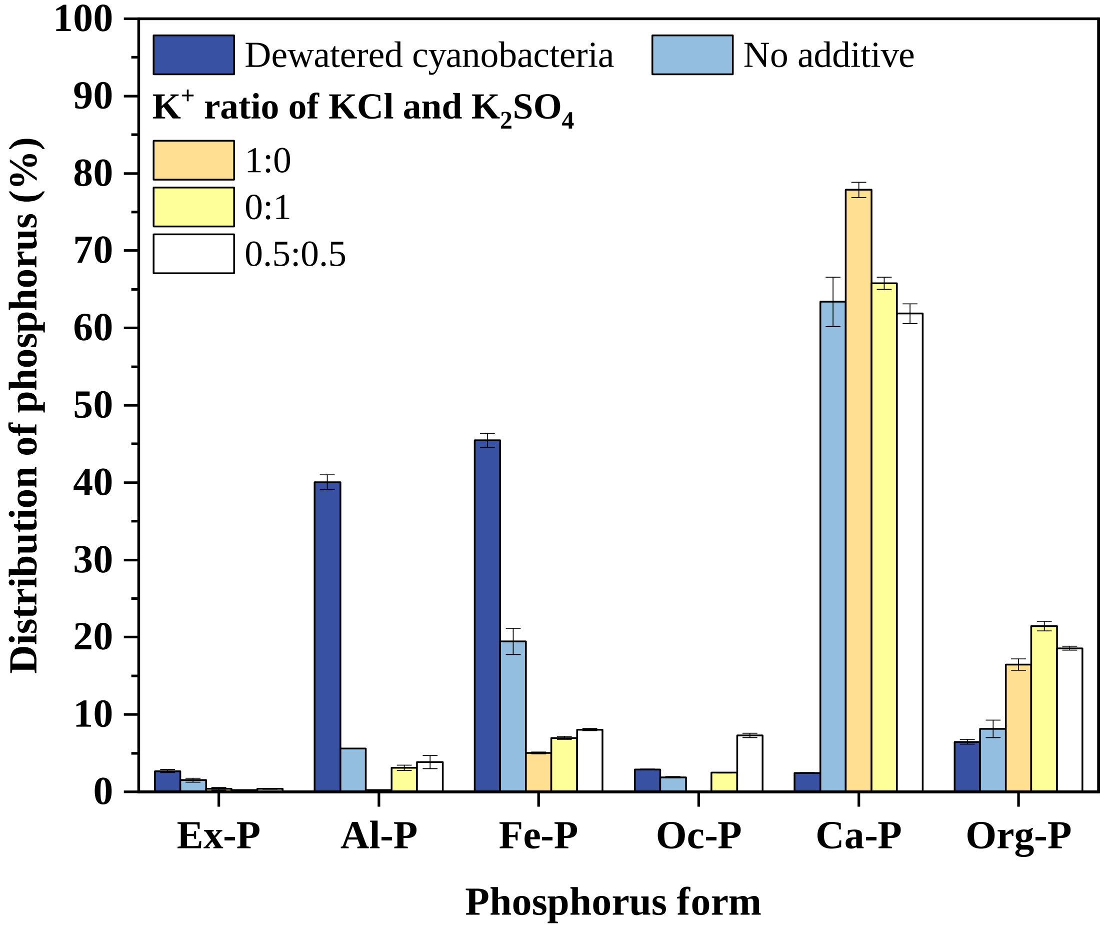

Dewatered cyanobacteria
No additive
K+ ratio of KCl and K2SO4
1:0
0:1
0.5:0.5
Distribution of phosphorus (%)
100
90
80
70
60
50
40
30
20
10
0
Ex-P
Al-P
Fe-P
Oc-P
Ca-P
Org-P
Phosphorus form

Figure 4

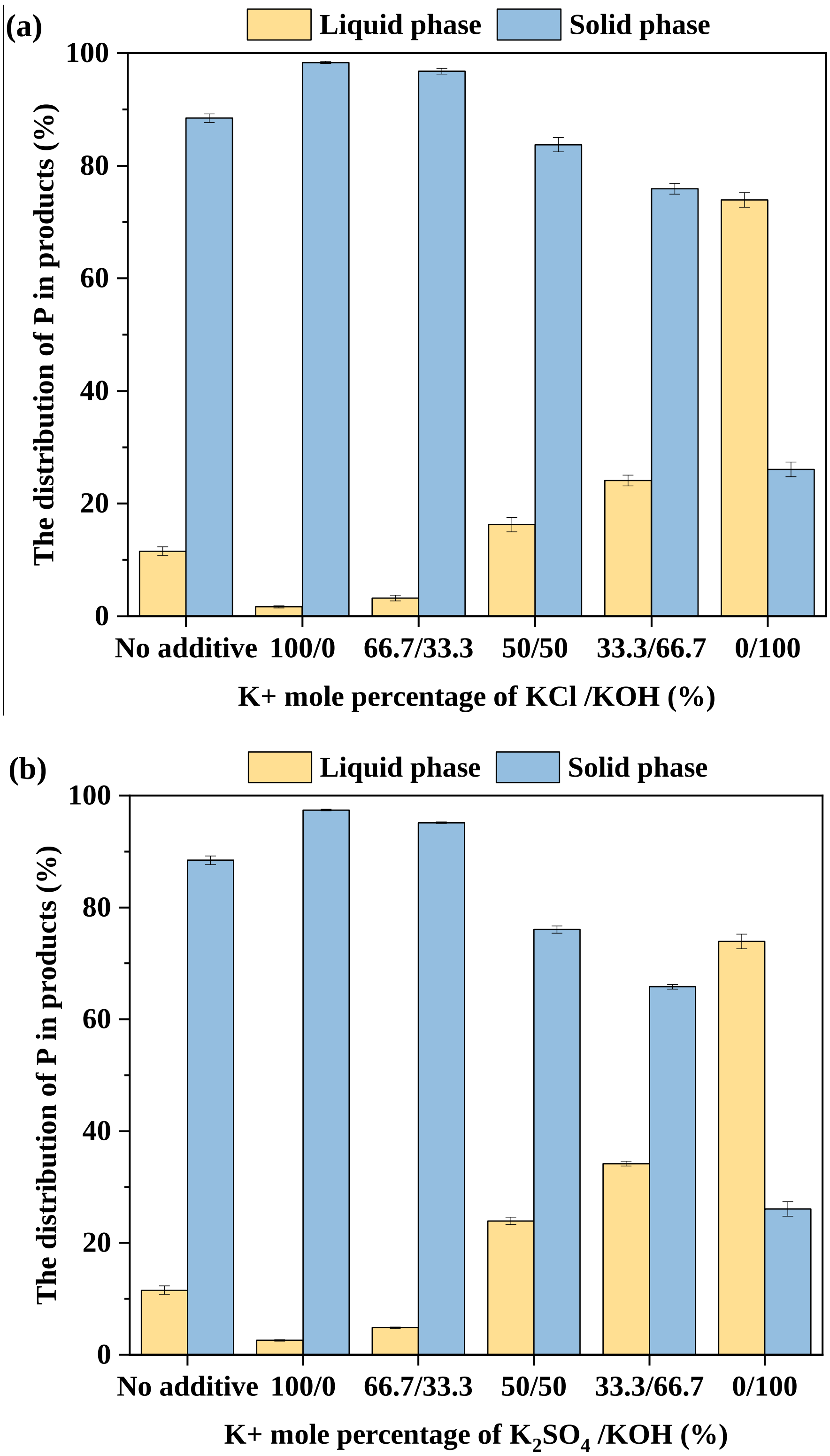
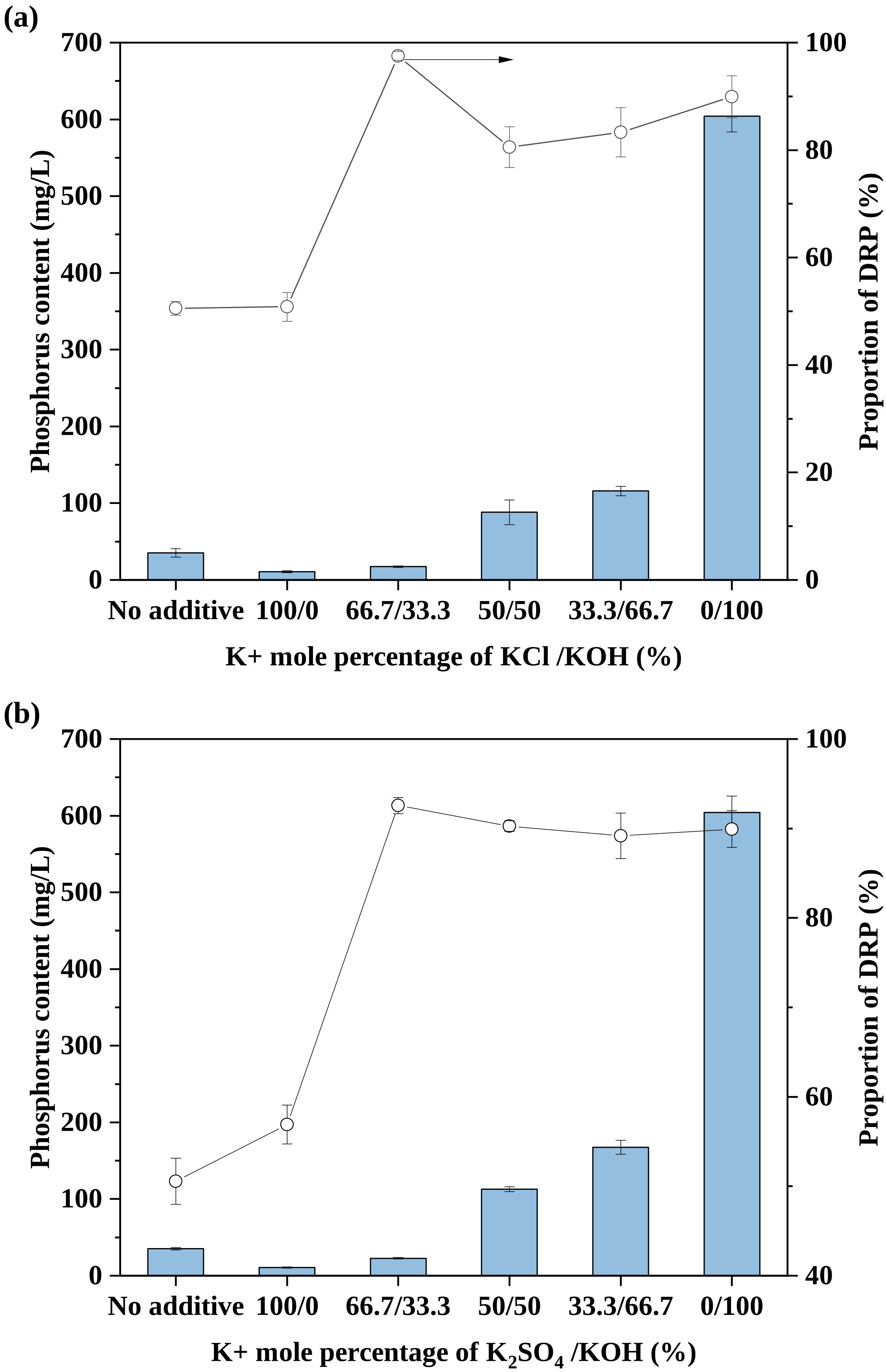

(a)
Liquid phase
Solid phase
The distribution of P in products (%)
0
20
40
60
80
100
No additive
100/0
66.7/33.3
50/50
33.3/66.7
0/100
K+ mole percentage of KCl /KOH (%)
(b)
Liquid phase
Solid phase
The distribution of P in products (%)
0
20
40
60
80
100
No additive
100/0
66.7/33.3
50/50
33.3/66.7
0/100
K+ mole percentage of K_2SO_4 /KOH (%)

Figure 5



(a)
Phosphorus content (mg/L)
Proportion of DRP (%)
0
100
200
300
400
500
600
700
20
40
60
80
No additive
100/0
66.7/33.3
50/50
33.3/66.7
0/100
K+ mole percentage of KCl /KOH (%)
(b)
Phosphorus content (mg/L)
Proportion of DRP (%)
K+ mole percentage of K_2SO_4 /KOH (%)

Figure 6

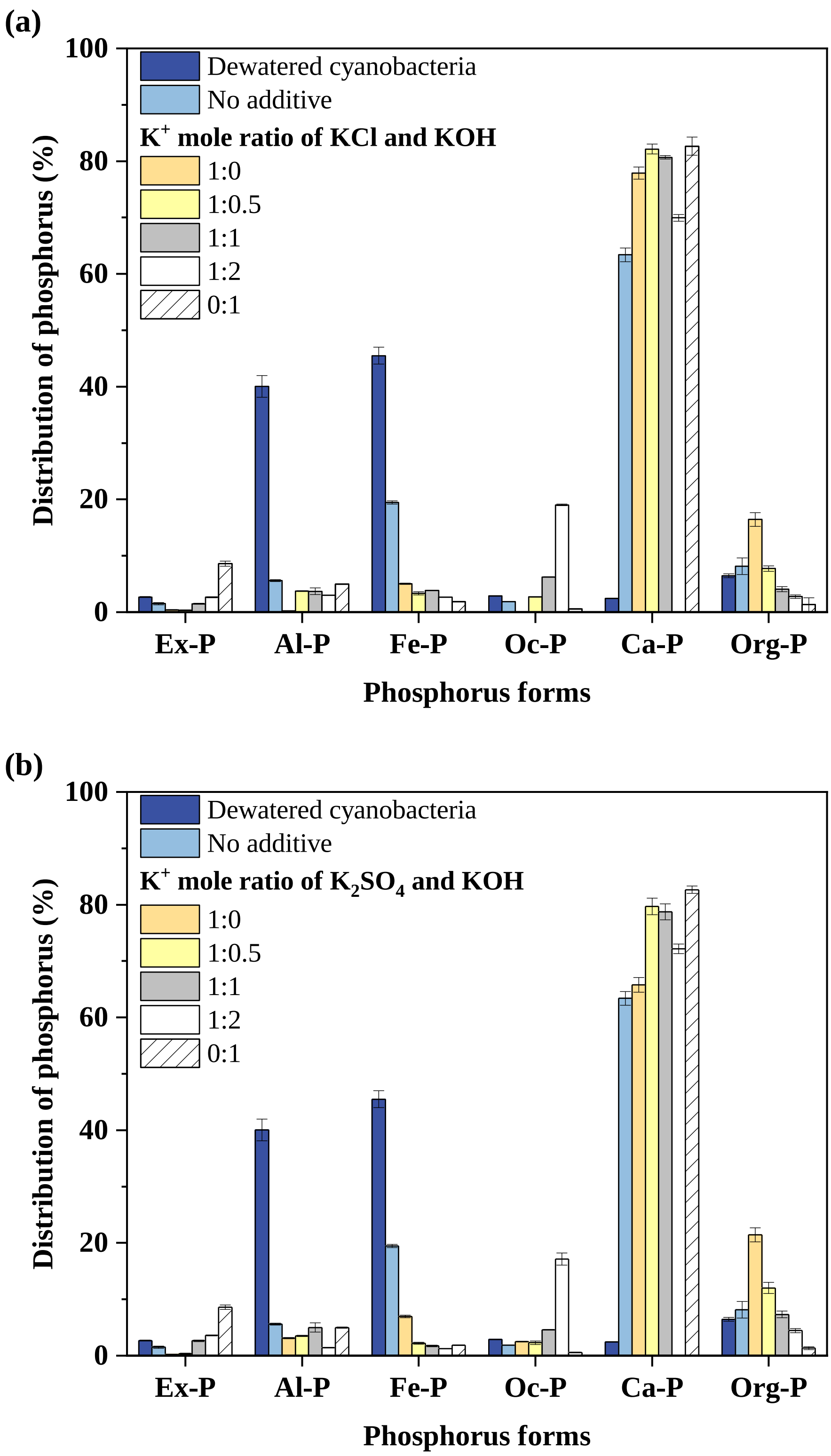

(a)
Dewatered cyanobacteria
No additive
K+ mole ratio of KCl and KOH
1:0
1:0.5
1:1
1:2
0:1
Distribution of phosphorus (%)
0
20
40
60
80
100
Ex-P
Al-P
Fe-P
Oc-P
Ca-P
Org-P
Phosphorus forms
(b)
Dewatered cyanobacteria
No additive
K+ mole ratio of K2SO4 and KOH
1:0
1:0.5
1:1
1:2
0:1
Distribution of phosphorus (%)
0
20
40
60
80
100
Ex-P
Al-P
Fe-P
Oc-P
Ca-P
Org-P
Phosphorus forms

Figure 7

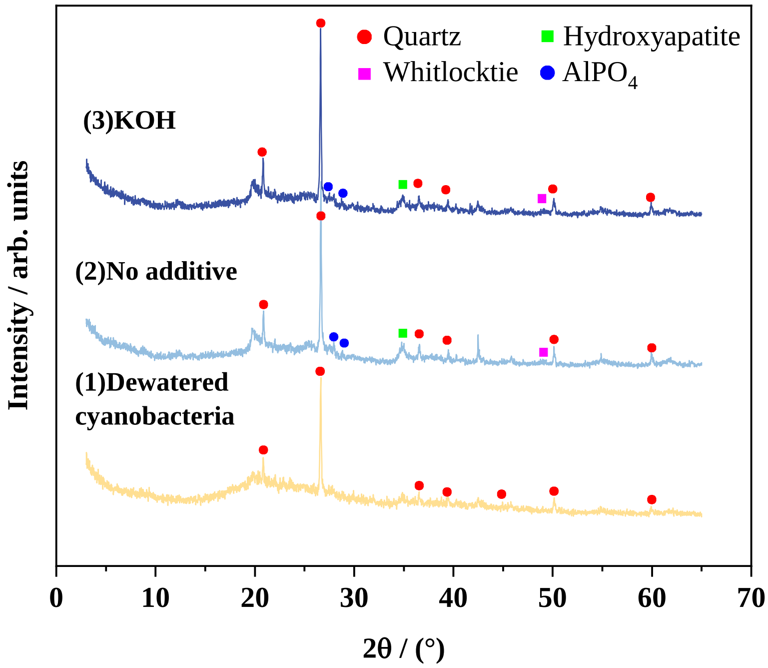
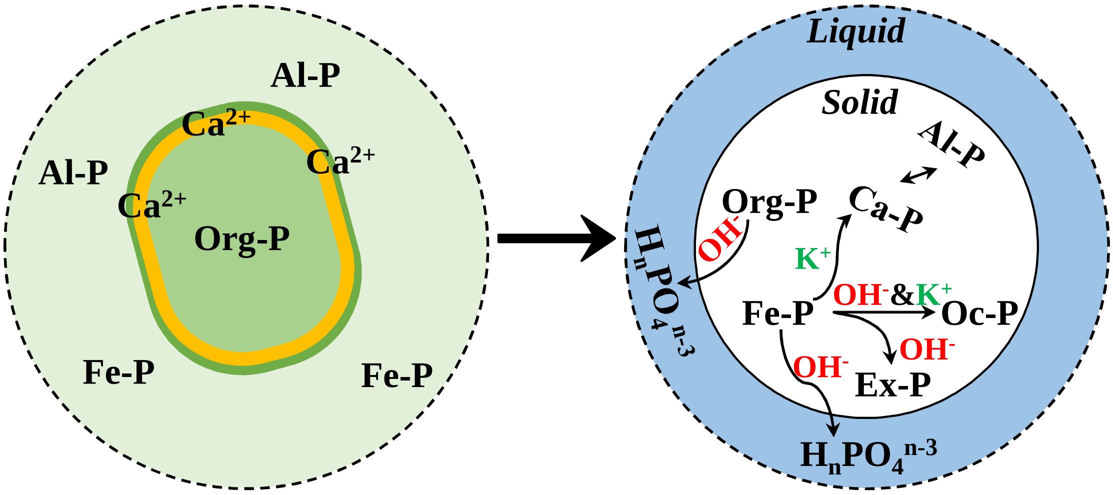

Quartz
Hydroxyapatite
Whitlocktie
$AlPO_4$
(3)KOH
(2)No additive
(1)Dewatered cyanobacteria
Intensity / arb. units
0
10
20
30
40
50
60
70
2θ / (°)

Figure 8


Al-P
Ca^{2+}
Ca^{2+}
Al-P
Ca^{2+}
Org-P
Fe-P
Fe-P
Liquid
Solid
Al-P
Org-P
Ca-P
OH^-
K^+
$H_nPO_4^{n-3}$
Fe-P
OH^-&K^+
Oc-P
OH^-
OH^-
Ex-P
$H_nPO_4^{n-3}$