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Removal of several types of sodium and potassium salts from aqueous solutions based on their natural fixation

Jun Wan[a,†], Hao-Tian Wang[b,†], Xue Li[a], Chun-Xue Zhang[a], Xin-Shi Wu[a], Bo Sun[a,*]

[a]*School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, China, Tel. +86-22-60214259; Fax: +86-22-23374289; emails: sunbo_tjlg@hotmail.com (B. Sun), junwantjlg@outlook.com (J. Wan), xuelitjlg2014@163.com (X. Li), chxzhang@tjut.edu.cn (C.-X. Zhang), webwxs@126.com (X.-S. Wu)*
[b]*Peking University, Beijing 100086, China, Tel. +86-010-62771679; email: whttennis@gmail.com*

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ABSTRACT

Inspired by the mechanism of plant roots for the fixation of inorganic salts, we developed a novel method for the removal of sodium and potassium salts including chloride, nitrate, and sulfate under pseudo-natural conditions. In this method, a plant was first cultured in NaCl, $NaNO_3$, or Na_2SO_4-containing aqueous solution. Subsequently, simulated adsorptions or precipitations under pseudo-physiological conditions were conducted based on the elemental composition of the plant's root after cultivation. The key species likely involved in the fixation of these inorganic salts were studied by using additional simulated adsorptions or precipitations. The results showed that oxalic acid and tartaric acid were effective for the fixation of Na^+ and K^+ ions, respectively. In addition, calcium phosphates were demonstrated to be effective for the fixation of NaCl, KCl, $NaNO_3$, and KNO_3 at a pH range of 7–7.5. The removal percentage increased with increasing initial concentrations of these salts and decreasing temperatures. The mechanism for the removal of NaCl, KCl, $NaNO_3$, and KNO_3 is through their adsorption on formed calcium phosphate floccules that have a large surface area. With the aid of Coulombic interaction, the adsorption and growth of a tested salt on the formed calcium phosphate floccules continues until it reaches an equilibrium with solvation interaction. Meanwhile, Ca^{2+} was an effective salt-fixing species for potassium sulfate, and the removal percentage increased with increasing concentration of SO_4^{2-} ions. The removal mechanism is attributed to the formation and precipitation of insoluble potassium–calcium sulfate. In addition, a high removal efficiency could be achieved by removing the formed precipitate promptly from the treated aqueous solution.

Keywords: Bio-inspired technology; Biomimetic separation; Desalination; Sodium salt; Potassium salt

1. Introduction

Industrial wastewater often contains a certain amount of inorganic salts. Among them, some soluble heavy metal ions, such as Pb^{2+}, Cd^{2+}, Hg^{2+}, Cr^{6+}, Cr^{3+}, As^{5+}, and As^{3+}, can pose huge threats to the environment. Therefore, the removal of heavy metal ions has become a major concern and challenge. Other ions, such as K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, SO_4^{2-}, PO_4^{3-}, NO_3^-, and Cl^-, are normally believed to be nontoxic, since they are either mineral nutrition for plant growth or play an important role in the regulation of osmotic potentials [1,2]. However, high amounts of these ions in the wastewater will cause land salinization, which severely suppresses the growth of living organisms.

The commonly used approaches for removing salts from aqueous solutions include biological, chemical,

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[*] Corresponding author.

[†] These authors contributed equally to this work and are co-first authors.

and physical methods [3–8], which are also the three self-purification processes of natural water. Chemical and physical methods are believed to be more efficient in removing inorganic salts from water. Among various conventional methods, membrane separation, ion exchange/adsorption, and precipitation/settlement are used more widely than other methods. Membrane-based separation technology has been successfully used in the desalination of low concentrations of brine [9–11]. However, the drawback of this technology is that energy consumption increases sharply as the concentrations of salts in solution increase [12,13], and the highly concentrated saline solutions after the process normally require additional treatments. Ion exchange/adsorption method is dominantly applied to the removal of trace and low concentrations of salts [14,15]. Compared with the above-mentioned two methods, precipitation or settlement method is commonly used for the removal of moderate to the high concentration of salts. Since both ion exchange/adsorption and precipitation/settlement methods heavily rely on the chemicals and reagents used, it is significant to develop the optimal chemicals and reagents that can achieve economical and efficient removal of salts [16,17].

Compared with the chemical and physical methods, biological treatment process has an outstanding environmentally friendly characteristic on removing inorganic salts from water. Since the fixation or removal of inorganic salts by organisms is a time-consuming process and many inorganic salts are not the main biological components of organisms, even though some of them are mineral nutrients and involved in numerous biological functions [1,2], the fixed amount of inorganic salts by organisms is very limited. Nevertheless, the sensitivity of organisms to inorganic salts and natural fixation of salts by organisms have attracted increasing research attention. In the biological method, the fixation of inorganic salts by organisms is also believed to follow chemical and physical principles. Therefore, the mechanistic investigation of salt fixation by organisms will provide useful information for economical removal of salts.

Recently, during the study of plant tolerance under the stress of certain concentrations of inorganic salts (including heavy metal salts), two observations attracted our attention. First, when a considerable amount of heavy metal accumulated in the roots of the plant, only a small amount of them was detected in the leaves [14]. Second, a plant can continue growing for a long period of time even after the termination of nutrient supply (Table S1). The first observation has already led to an excellent biomimetic separation or removal of trace As^{3+} [14]. For the second observation, it is hypothesized that a plant can store nutrients and replenish nutrition supply when the root uptake is deficient [1,2]. Inspired by these observations, we designed the experiment in this work to study a biomimetic method for the removal of chlorides, nitrates, and sulfates. In our opinion, a biomimetic method is to elucidate the interaction mechanism of organisms and to reproduce the interactions in vitro via physical and chemical methods. First, a plant was cultivated in an aqueous solution containing NaCl, $NaNO_3$, or Na_2SO_4 to allow the enrichment of the salts in the roots. The elements or species that might be involved in the fixation of the salts were analyzed by monitoring the growth status of the plant and change of the elemental composition in the roots. Then, according to the composition of the roots, which already accumulated a certain amount of salts, a simulated adsorption or precipitation/settlement was conducted in the aqueous solution under a pseudo-physiological condition by adding chemicals containing the surmised species.

The nature, a self-regulating ecosystem, has a water self-purification function; we expected to remove NaCl, KCl, $NaNO_3$, KNO_3, Na_2SO_4, and K_2SO_4 simply by utilizing their natural fixation. The proposed treatment not only has all the advantages of a biological method such as environmentally friendly and economical but also can treat large amounts of wastewater with much less time. In addition, the reagents used in the treatment are readily available, inexpensive, and harmless. The sediments remained after completion of water treatment can be regarded as minerals, nutrients for plants, or K and Na sources. As a result, it would not bring secondary pollution to nature, which is the major drawback of many current treatments. Moreover, the method herein developed for the treatment of relatively high concentrations (but lower than saturation concentrations) of chlorides, nitrates, and sulfates is a valuable complement to membrane treatment of low concentration of the salts, and these two methods can be used as an integrated technology for water treatment.

2. Experimental section

To develop a biomimetic method for the removal of the selected salts, it is necessary to obtain the effective species (ions or functional groups) with salt fixation capacity in organisms. The experiments were conducted as follows: (1) plants were first cultivated in a sodium or potassium salt-containing aqueous solution to allow the salt accumulation in their roots. (2) The variation of the elemental composition in roots was analyzed to surmise the key elements or species that might be involved in salt fixation. (3) A simulated adsorption/precipitation fixation of the selected salt was conducted in aqueous solution under a near physiological condition (such as 20°C–35°C, pH 7–7.5) by using the chemicals containing the surmised species.

The changes of element content in the roots or precipitates were measured by using spectrometry and elemental analysis. pH indicator papers and pH meter were used to maintain the solution at a range of pH 7–7.5, and X-ray diffractor was employed to determine the form of the fixed sodium and potassium ions.

Since *S. spectabile* can survive in the aqueous solution and accumulate the selected salts, it was selected as the hydroponic plant for the study.

2.1. Measurements

The contents of elements were determined with a Vista MPX inductively coupled plasma optical emission spectroscopy (ICP-OES) spectrometer (Varian, Inc., Palo Alto, CA, USA). The instrumental operating conditions are shown in Table S2.

The contents of nitrogen, carbon, and hydrogen in the samples were determined using a Vario-EL element analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany). The precision of the results was estimated to be

0.3%. The content of chloride in the samples was measured by silver nitrate titration method.

The pH values of the solutions were measured by pH indicator papers or a Model pHS-25 pH meter (Shanghai Rex Instruments Factory, Shanghai, China) with combined glass electrodes.

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku Corporation (Tokyo, Japan) D/MAX-2000PC X-ray diffractometer, with Cu Kα radiation (λ = 0.154 nm) at 100 mA and 40 kV. A scan rate of 10°C min^{-1} and a step size of 0.02° were used over a 2θ range of 3°–80°.

The surface morphology of the samples was observed with a JEOL JSM-6700F field-emission scanning electron microscopy (FE-SEM) (JEOL Ltd., Tokyo, Japan). The compositions of the samples were evaluated using energy dispersive spectrometry (EDS) in an Oxford-EDS7421 apparatus. The samples were mounted on a copper conductive tape and coated with Au to minimize sample charging.

Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet Magna-560 FTIR spectrometer (Madison, WI) in KBr pellets over a wave-number range of 4,000–400 cm^{-1} with a 4 cm^{-1} resolution.

2.2. Cultivation of plants in sodium chloride, nitrate, or sulfate-containing aqueous solution

Sedum spectabile (Fig. S1) was selected as the hydroponic plant in this study. Five variants of Hoagland's nutrient solution, marked as culture medium A, B, C, D, and E (cf. Table S3), were used in the experiments [1,2].

The cultivation of plants in the selected sodium salt aqueous solutions was performed according to a method similar to that reported in our previous work [14], except that a certain amount of sodium salts (e.g., NaCl, $NaNO_3$, and Na_2SO_4) was substituted for arsenic-containing chemicals. Cultivations without sodium chloride, nitrate, or sulfate were simultaneously carried out as controls.

2.3. Treatment and elemental analysis of the plant's roots after cultivation in sodium chloride, nitrate, or sulfate-containing aqueous solution

The treatment and elemental analysis of the plant's roots after the cultivation was conducted according to the method reported in the literature [14].

2.4. Removal of NaCl, KCl, $NaNO_3$, and KNO_3 using calcium phosphate

Taking KNO_3, for example, a typical removal procedure using calcium phosphate was performed as follows.

KNO_3 solution was prepared by dissolving 19.9 g of KNO_3 (ca. 196.8 mmol of KNO_3) in 100 mL of deionized water. At 15°C with vigorous stirring, 3.42 g of $Ca(H_2PO_4)_2{\cdot}H_2O$ was added in small portions into the KNO_3 solution, and the pH value of the mixture was controlled within a range of 7–7.5 (close to the plant physiological conditions) by adding $Ca(OH)_2$ (about 2.3 g of $Ca(OH)_2$ was needed). When the adsorption equilibrium was reached, the mixture was filtrated, and then dried at 120°C until it reached a constant weight to afford approximately 13.3 g of precipitant. The contents of nitrogen and potassium in the precipitant were ca. 9.06 wt.% and 21.0 wt.%, respectively. The removal percentage of KNO_3 was evaluated to be about 43.8% in terms of nitrogen content.

It should be pointed out that, since $Ca(H_2PO_4)_2$ and $Ca(OH)_2$ have low solubility in water and thus are unlikely to be completely dissolved in the solution, the experiment results are more suitable for comparative significance.

2.5. Removal of potassium sulfate by co-precipitation

A potassium sulfate solution was prepared by dissolving 10.0 g of K_2SO_4 (ca. 57.4 mmol of K_2SO_4) in 100 mL of deionized water. At room temperature with vigorous stirring, 3.18 g of anhydrous $CaCl_2$ in a small amount of water was added dropwise to the sulfate solution, while the pH was maintained within a range of 7.2–7.5 (close to the plant physiological conditions) by the addition of NaOH if needed. After completion of the precipitation step, the mixture was filtrated, and then dried at 110°C until it reached a constant weight to afford approximately 10.3 g of precipitant. The content of potassium in the precipitant was ca. 27.0 wt.%. The removal percentage of *K* was evaluated to be about 62.6 wt.%.

3. Results and discussion

3.1. Investigation of the involved species in the fixation of NaCl, KCl, $NaNO_3$, KNO_3, Na_2SO_4, and K_2SO_4 based on their fixation in plants

Compared with the control cultivation, suppressed growth of *Sedum spectabile*, which was characterized by a slow increase in the plant height and number of leaves, was observed when the concentration of NaCl, $NaNO_3$, or Na_2SO_4 in the culture media increased (Tables S4–S6). This observation can be explained as that when the roots of a plant are invaded by foreign ions that are unnecessary or excessive for plant growth, the plant would instinctively or spontaneously fix these ions in roots as soon as possible to prevent them from entering its critical organs and tissues. During this fixing process, some elements or species that are essential for the normal plant growth would also be fixed as well, leading to the suppression of plant growth.

The comparison of elemental contents in the tested plants' roots in the sodium chloride, nitrate or sulfate cultivation, and control cultivation (Tables S7–S9) showed that the contents of sodium significantly increased in the roots cultivated in all five culture media.

The FT-IR spectra of *Sedum spectabile*'s roots after cultivation with sodium nitrate or sulfate stress showed the characteristic absorption peaks of NO_3^- or SO_4^{2-} ions were all sharper than those of cultivation without sodium nitrate or sulfate (Figs. S2 and S3), indicating that the amount of nitrate or sulfate in the roots increased. In other words, the fixation of N and S in the form of NO_3^- or SO_4^{2-} increased.

The investigated plants could still maintain slow growth in the saline solution, indicating that the salt-fixing species are major elements or macronutrients rather than micronutrients [1,2].

3.1.1. Fixation of the tested Na and K salts guided by C-increase after cultivation in Na salt-containing aqueous solutions

It should be noted that, when Na was accumulated in a plant's roots, the contents of C (element C also is a macronutrient) in the roots cultivated under $NaNO_3$ or Na_2SO_4 stress were obviously enhanced (cf. Tables S8 and S9), implying that C-containing species are likely involved in Na fixation.

Inorganic carbonates were first tested and found less effective for the fixation of the selected salts (cf. last line in Table S10). Besides, it was also demonstrated that the precipitate collected from an $NaNO_3$ solution after adding $Ca(NO_3)_2$ and Na_2CO_3 (or $Ca(OH)_2$ and $CO_2(g)$) had a very low NaCl uptake. Actually, at pH 7–8 in an aqueous solution (near physiological pH condition), HCO_3^- is the main form among CO_3^{2-}-containing species [18], and hydrogen carbonates are soluble in water to a certain extent, indicating that inorganic carbonates are unlikely to be key adsorbents for the fixation of Na or K salts.

Since oxalic acid and tartaric acid are commonly found in plants and sodium oxalate and potassium hydrogen tartrate have low solubility in the water among C-containing organic species [19], the precipitation of Na salts by oxalic acid and the precipitation of K salts by tartaric acid were conducted. The precipitates collected from NaCl, $NaNO_3$, or Na_2SO_4 solutions by the addition of oxalic acid showed an identical XRD pattern (cf. Fig. S4). Moreover, nearly same content of Na in the precipitates (cf. Table S11) confirmed that Na^+ ions could be effectively fixed by oxalate. Similarly, the precipitates collected from KCl, KNO_3, or K_2SO_4 solutions by the addition of tartaric acid also exhibited the same XRD pattern (cf. Fig. S5). A nearly same content of K in the precipitates (cf. Table S12) also confirmed that K^+ ions could be effectively fixed by tartaric acid.

It is noteworthy that Na fixation by oxalic acid or K fixation by tartaric acid was achieved even under acidic circumstances through the formation of $NaHC_2O_4·H_2O$ or $KHC_4H_4O_6$ (cf. Tables S11 and S12), but the XRD patterns of precipitates did not coincide with all characteristic peaks of $NaHC_2O_4·H_2O$ (PDF#32-1086 or PDF#32-1087)] or $KHC_4H_4O_6$ (PDF#43-0775 or PDF#25-0644)].

However, oxalic acid or tartaric acid is ineffective for the fixation of anions, especially Cl^- ion, a non-nutrient element, implying that other cations are required to fix anions. An increase in Ca content in the roots (cf. Table S7) might be related to this issue, which is discussed in the next section.

Besides, it also should be pointed out that, as Na was accumulated in a plant's roots, the contents of S (element S also is a macronutrient) in the roots cultivated under Na^+ stress were obviously increased (cf. Tables S7–S9). It is assumed that reductive S species are likely involved in the formation of oxalate from CO_2 [19]. This assumption also requires further study.

3.1.2. Investigation of other likely involved species in the fixation of the tested K and Na salts

Calcium and phosphorous (two macronutrients) were also investigated in this study. To determine their roles in the fixation of chloride, nitrate, or sulfate, simulated settlements under a pseudo-physiological condition (20°C–25°C and pH 7.2–7.5) were conducted. Referred to the compositions of plant's root after cultivation in culture medium B in Tables S7–S9, the mixtures 1, 2, and 3 (cf. Table S13) were formulated, respectively. A precipitate with high Na-content was obtained from these mixtures. The pH values of all three solutions were maintained within a range of 7.2–7.5 by addition of NaOH or Na_2CO_3 solution.

The compositions (Table S14) and XRD patterns (Figs. S6–S8) of the collected precipitates from formulations of mixtures 1, 2, and 3 indicated that calcium phosphate was the effective species for the fixation of NaCl, KCl, $NaNO_3$, or KNO_3, but it is less effective for the fixation of Na_2SO_4 or K_2SO_4. Meanwhile, mixture 4 (cf. Table S13), which did not contain phosphate, generated a certain amount of $K_2Ca(SO_4)_2$, suggesting that Ca^{2+} is the effective species for the fixation of potassium sulfate (Fig. S9). The effect of Ca^{2+} dosage on the removal percentage of sulfates will be discussed in a later paragraph.

Insoluble calcium phosphates have several forms, such as $CaHPO_4$, $Ca_3(PO_4)_2$, and $Ca_5(OH)(PO_4)_3$ (or $Ca_{10}(OH)_2(PO_4)_6$). Taking the adsorption of potassium nitrate as an example, the experimental results (Table S10) confirm that calcium phosphates are more effective adsorbents than calcium carbonate for the fixation of KNO_3. The adsorption difference among phosphates might be attributed to their surface areas, which also will be discussed in a later paragraph.

3.1.3. Removal of the tested K and Na salts under different conditions

3.1.3.1. Removal of NaCl, KCl, $NaNO_3$, and KNO_3 using calcium phosphates

The effects of temperature and the initial concentration of salts on the removal percentage of chloride or nitrate are shown in Tables S15 and S16, respectively. It can be seen that

Table 1
Comparison of removal percentages for KCl, NaCl, KNO_3, and $NaNO_3$[a]

Salts	Contents in precipitate (wt.%)				K removed (%)	Na removed (%)	Cl removed (mol/mol)	N removed (mol/mol)
	K	Na	Cl	N				
KCl–NaCl	15.8	9.1	28.3	–	37.8	37.0	37.3	–
KNO_3–$NaNO_3$	13.0	7.7	–	9.10	37.2	37.4	–	36.0
NaCl–$NaNO_3$	–	13.0	9.9	3.53	–	20.8	20.5	18.5

[a] Initial concentration of each salt = 1.5 mol L^{-1}; amount of $Ca(H_2PO_4)_2·H_2O$ added = 3.42 g; amount of $Ca(OH)_2$ added = 2.24 g; total volume of solution = 100 mL; temperature = 15°C; pH 7–7.5.

Table 2
Comparison of the composition of precipitates collected from brines[a]

Saline solution	Initial concentration of Na$^+$ ions (mol L^{-1})	Temperature (°C)	Na uptake in precipitates (wt.%)
NaCl	0.457	5	8.86
		15	6.79
Artificial seawater	0.457[b]	5	3.12
		15	3.30
Twofold concentration of artificial seawater	0.914[b]	15	12.9

[a] Total volume of solution = 500 mL, pH 7.0–8.0. 0.453 g of $Ca(H_2PO_4)_2{\cdot}H_2O$ and about 0.34 g of $Ca(OH)_2$ were added.
[b] Concentration of artificial seawater and twofold concentration of artificial seawater are listed in Table S22, except that $CaCl_2$ was not added, and was substituted with $Ca(H_2PO_4)_2{\cdot}H_2O$ and $Ca(OH)_2$.

the removal percentage of the salts increased with decreasing temperature and with increasing concentration of potassium or sodium salt, which coincides with Langmuir type adsorption. In addition, Table 1 shows that similar removal percentages for NaCl, KCl, $NaNO_3$, and KNO_3 were observed.

Moreover, XRD patterns (Figs. 1–4) of the sediments collected from NaCl, KCl, $NaNO_3$, or KNO_3 solution at 15°C showed a fit match with those of potassium or sodium ores, such as NaCl (PDF#05-0628 Halite, syn), KCl (PDF#41-1476 Sylvite, syn), $NaNO_3$ (PDF#36-1474 Nitratine, syn) or KNO_3 (PDF#05-0377 Niter, syn). The underlying mechanism for removing these salts will be discussed in the later paragraph.

It is noteworthy that when the dosage of $Ca(H_2PO_4)_2$ and $Ca(OH)_2$ increased, the system became a pulpy or pasted mixture, and the content of the removed salt in the precipitate did not increase significantly (cf. Table S17). This result suggests that it is necessary to remove the formed precipitate from the treated aqueous solution in an appropriate time.

3.1.3.2. Removal of potassium sulfate and sodium sulfate by co-precipitation

Calcium phosphates were also demonstrated to be effective for the removal of potassium and sodium sulfate (cf. Table S18). However, the solubility of potassium sulfate or sodium sulfate in water is lower than that of their corresponding chlorides or nitrate salt, especially at low temperatures (below 15°C) [19], which weakens the significance of adopting adsorption by calcium phosphates. However, it was found that without PO_4^{3-}-containing species, potassium sulfate could be co-precipitated with $CaSO_4$ as the insoluble potassium–calcium sulfate salt.

The typical XRD pattern of precipitates collected from a potassium sulfate solution is shown in Fig. 5, in which the peaks at 2θ = 9.34°, 15.54°, 19.18°, 28.24°, 31.34°, 32.66°, etc. are characteristic peaks for $K_2Ca(SO_4)_2{\cdot}H_2O$ (PDF 28-0739 Syngenite, syn), and the peaks at 2θ = 14.72°, 25.68°, 29.70°, 31.88°, 49.36°, etc. are characteristic peaks for $CaSO_4{\cdot}0.5H_2O$ (PDF 41-0224 Bassanite, syn).

The effects of Ca^{2+} dosage and concentration of SO_4^{2-} on the removal percentage of potassium sulfate are shown in Table S19. It can be seen that the removal percentage of K_2SO_4 increased as its initial concentration increased, but it was hardly removed when K^+ concentration was below 0.115 mol L^{-1}. This is because the solubility-product constant of the formed $K_2Ca(SO_4)_2$ is not very low, which is slightly soluble in water, thus limiting the amount of K_2SO_4 that can

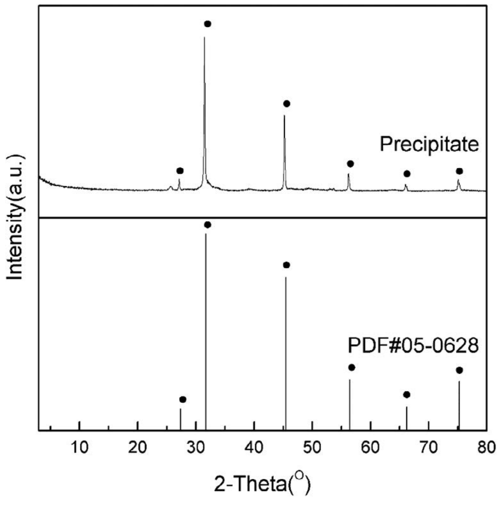

Fig. 1. XRD pattern of a precipitate obtained from a sodium chloride solution at 15°C.

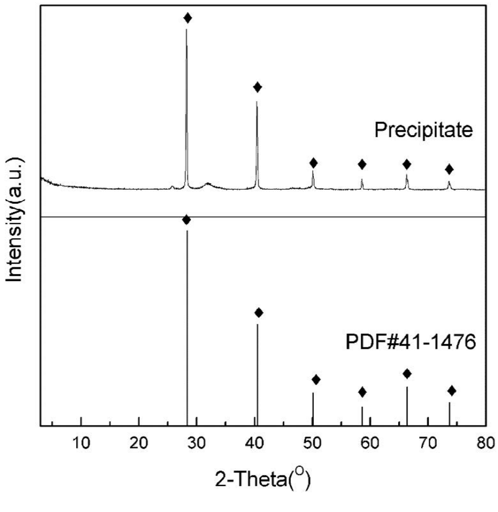

Fig. 2. XRD pattern of a precipitate obtained from a potassium chloride solution at 15°C.

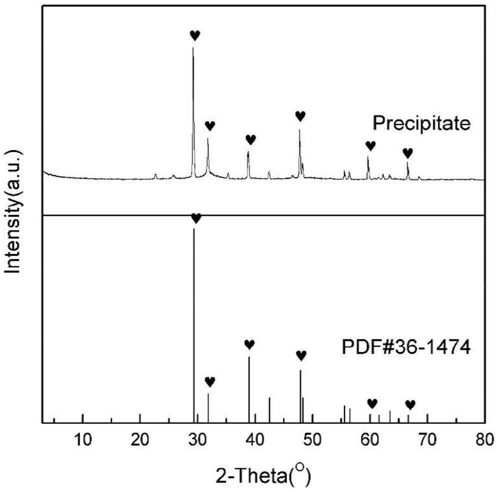

Fig. 3. XRD pattern of a precipitate obtained from a sodium nitrate solution at 15°C.

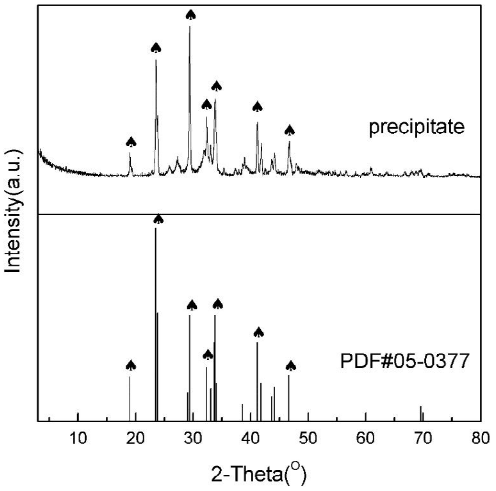

Fig. 4. XRD pattern of a precipitate obtained from a potassium nitrate solution at 15°C.

be removed. It is also noted that, though the stoichiometric atom ratio of K to Ca in $K_2Ca(SO_4)_2$ is 2:1, the removal percentage of potassium sulfate is very low at this atomic ratio. This phenomenon can be attributed to the lower solubility of $CaSO_4$ than $K_2Ca(SO_4)_2$, leading to more collection of $CaSO_4$, which is further confirmed by the much stronger characteristic peaks of $CaSO_4$ in XRD pattern (PDF 41-0224 Bassanite, syn). The removal percentage of potassium increases when the molar ratio of K to Ca increases, as well as the concentration of SO_4^{2-} increases. The increase of SO_4^{2-} ions can be easily achieved by adding Na_2SO_4. In contrast, Ca^{2+} ions alone are not effective species for the fixation of sodium sulfate.

It was also noted that, under the condition of a high concentration of K^+ (e.g., 1.15 mol L^{-1} K^+), the potassium sulfate-containing system turned to thick (or the system became a pulpy or pasted mixture) when Ca^{2+} ions were added. In combination with the water-adsorbing property of precipitates (e.g., $K_2Ca(SO_4)_2 \cdot H_2O$), this result indicates that the thickening effect, which increases the concentration of the salts for precipitation, provides a supplementary role in the salt-fixing process especially when the concentration of salts is high. It was also observed that the thickened mixture mentioned above would turn to thin, which is a sign that a large amount of $CaSO_4$ is formed if excessive Ca^{2+} ions were added. This result also suggests that the removal percentage of potassium sulfate could increase if the formed $K_2Ca(SO_4)_2$ is removed promptly.

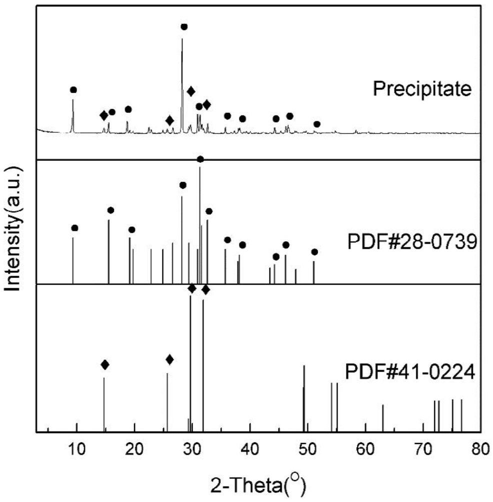

Fig. 5. XRD pattern of a precipitate collected from a potassium sulfate solution.

3.2. Mechanism for the removal of the tested salts

3.2.1. Mechanism for the removal of NaCl, KCl, $NaNO_3$, and KNO_3 using calcium phosphates

The content of KCl, NaCl, $NaNO_3$, or KNO_3 in the precipitate collected from each individual salt solution after addition of calcium phosphates varied with temperature and initial concentration of the solution (cf. Tables S15 and S16), indicating that the removal of these salts is regulated by adsorption mechanism, rather than co-precipitation with calcium phosphates. In addition, it should be pointed out that floccules (calcium phosphates) with a size of ca. 20 nm were formed when $Ca(H_2PO_4)_2$ and $Ca(OH)_2$ were added (cf. Fig. S10a), thus providing a large surface area that facilitates the adsorption. A comparison of calcium phosphate floccules with Al-containing or Fe-containing floccules (two of the most commonly used adsorbents) is shown in Table S20 and Fig. S10. It can be seen that, under the same molar amount conditions, the N uptake in calcium-containing phosphates was slightly lower than that in Al-containing floccules. However, due to the low solubility of calcium-containing phosphates in the water, almost no "extra salt impurities" would be introduced into the treated salt solution by using calcium-containing phosphate floccules as the adsorbent, while "extra salt" would be brought into the treated salt solution if using Al-containing or Fe-containing floccules as adsorbents.

It should be noted that, despite a large solubility difference among KCl, NaCl, $NaNO_3$, and KNO_3 [19], these salts have similar adsorption amounts on calcium phosphates if they have the same initial concentrations (as shown in Table 1). This result could be explained in terms of the activity of the tested salts in aqueous solutions. The chemical potential of a species is identical in each phase at phase equilibrium, which means that the activity ($a_i = \gamma_i m_i$/mol kg^{-1}) of the species must be constant when a solid–liquid phase equilibrium is achieved at a constant temperature [20]. Therefore, the strength of solvation interaction of a species could be determined by the activity coefficient of the species in a solution. It is deduced that the lower the activity coefficient (γ_i) of a species in aqueous solution is, the stronger the solvation interaction between the species and a solvent is (that is, the higher the concentration (m_i) of the species in the solution is). Taking NaCl as an example, the effect of temperature on its activity coefficients in an aqueous solution was evaluated by Pitzer equation (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/). The results (cf. Table S21) showed that the mean activity coefficient of NaCl ($\gamma_{\pm\text{NaCl}}$) decreased with increasing temperature because of the effect of thermal motion, thus resulting in reduced adsorption on adsorbents and a decreased removal percentage (cf. Table S15).

The effects of the initial concentration of a saline solution on the removal percentage of the salt could be explained by an approximate constant adsorption equilibrium concentration at a constant temperature. Since the adsorption equilibrium constant limits the amount of the salt that can be removed, the removal percentage of salt is thus limited by the difference between the initial concentration and equilibrium concentration of the salt in the solution when a certain dosage of the adsorbent is used [20]. Therefore, it is reasonable that with a sufficient dosage of an adsorbent, the removal percentage of salt could be enhanced with increasing initial concentration.

3.2.2. Mechanism for the removal of potassium sulfate by co-precipitation

The removal of potassium sulfate through the formation of $K_2Ca(SO_4)_2$ that has limited solubility in water follows the co-precipitation mechanism. The increased removal percentage with increasing concentration of SO_4^{2-} ions could be attributed to the common ion effect [18]. Forming one mole of $K_2Ca(SO_4)_2$ requires two moles of SO_4^{2-} ions, while forming one mole of $CaSO_4$ only needs one mole of SO_4^{2-} ions. In other words, the solubility products (Ksp) of $K_2Ca(SO_4)_2$ is proportional to the 2 power of the concentration of SO_4^{2-} ions while the solubility products (Ksp) of $CaSO_4$ is directly proportional to the concentration of SO_4^{2-} ions, which means that the increase in the concentration of SO_4^{2-} ions is more favorable for increasing removal percentage of $K_2Ca(SO_4)_2$ than for $CaSO_4$.

The difference in the removal percentage of K_2SO_4 caused by the addition of Na_2SO_4 and $MgSO_4$ could be attributed to the diverse ion effect on solubility [18]. Mg^{2+} ions are multiply charged ions, which contribute the ionic strength of a solution more than Na^+ ions (monovalent ions), thus resulting in the decreased activity of related ions or increased solubility of a precipitate. For this reason, the removal percentage of K_2SO_4 after the addition of $MgSO_4$ was lower than that after the addition of Na_2SO_4.

3.3. Natural fixation of Na and K salts elicited from Marcet–Dittmar rule

As shown in Table S16, the removal percentage of the tested salts decreased significantly with decreasing concentration of salts. This result inspired us to explore their limiting adsorption equilibrium concentrations or residual concentrations after sediment fixation or treatment.

According to the Marcet–Dittmar constant ratio rule (that is, the world's seawater in different oceans contains almost the same kind of ingredients and these ingredients have a very close and constant ratio), the composition of seawater is assumed to be the limiting equilibrium concentration or residual concentrations of saline solutions in nature. Therefore, a simulated settlement of salts in seawater was carried out. First, artificial seawater was prepared, but without the addition of trace elements, such as nitrogen, phosphorus, bromine, boron, and silicon (Table S22). After this brine solution was left overnight, no sediment was generated. Even when the concentrations of main species in seawater were doubled, no deposition was observed.

However, when phosphate was added, the precipitate occurred. The Na uptake in the precipitate (as shown in Table 2) suggests that the salts in brine with near seawater composition are difficult to be removed or the removal percentage is very low. This result is also attributed to the existence of Mg^{2+} ions that have high hydrophilicity, which reduces the mean activity coefficients [20] and promotes the salvation of NaCl.

It is also noteworthy that if the dosages of $Ca(H_2PO_4)_2{\cdot}H_2O$ and $Ca(OH)_2$ were doubled, the Na uptake in the precipitate did not increase (cf. Table S23)′ further suggesting that it is necessary to remove the formed precipitate from the treated aqueous solution promptly or adopt continuous bed operation. Indeed, the sea is so wide and deep that it can be considered the formed sediment is separated from the treated water spontaneously.

The effect of the other co-existing ions (or electrolytes) on the removal of NaCl is also explained in terms of the change of $\gamma_{\pm\text{NaCl}}$. The calculation based on Pitzer Equation (cf. Tables S24–S26) showed that when the concentration of NaCl in a brine was near that in seawater (ca. 0.5 mol NaCl/kg water), $\gamma_{\pm\text{NaCl}}$ decreased with the addition of a small number of other electrolytes, suggesting that the solvation interaction between NaCl and water is strengthened. This might be a reason why its adsorption on the adsorbent is weakened, resulting in a decreased removal percentage. However, when the concentration of NaCl was increased to 1.0 mol NaCl/kg water (near a twofold concentration of seawater), $\gamma_{\pm\text{NaCl}}$ increased with the addition of other electrolytes.

It is worth pointing out that the solubility of sodium oxalate ($Na_2C_2O_4$) in water at temperature range of 10°C–15°C is 3.05–3.41 g/100 g water (i.e., 455–482 mmol L^{-1} Na^+ ions) [19], which is very close to the Na^+ ion concentration in seawater (ca. 459.1 mmol L^{-1} Na^+ ions) (the phosphorus content in seawater is very low). In addition, the solubility of potassium hydrogen tartrate ($KC_4H_5O_6$) in water at 0°C is about 0.231 g/100 mL (i.e., 12.3 mmol L^{-1} or 480 mg L^{-1} K^+ ions) [19], which is close to the K^+ ions concentration in seawater (ca. 9.72 mmol L^{-1} or 380 mg L^{-1} K^+ ions at 0°C).

These observations may support the fixation of Na or K by oxalate or tartrate in plants (see section 3.1.1).

Since pressure can increase the solubility of some minerals in submarine brines and seawater [21], which is adverse to the precipitation of salt, it can be concluded that winter might be the best season for the fixation of potassium and sodium salts by nature.

4. Conclusion

Removal of KCl, NaCl, KNO_3, $NaNO_3$, K_2SO_4, and Na_2SO_4 based on their natural fixation was investigated and discussed in this paper. The results showed that oxalic acid and tartaric acid were effective for the fixation of Na^+ and K^+ ions, respectively. In addition, calcium phosphates were effective for the fixation of KCl, NaCl, KNO_3, and $NaNO_3$ at a pH range of 7–7.5. The removal percentage increased with increasing initial concentrations of the salts and with decreasing temperatures. The proposed mechanism for the removal of KCl, NaCl, KNO_3, and $NaNO_3$ is through their adsorption on formed calcium phosphate floccules that has a large surface area. With the aid of Coulombic interaction, the adsorption and growth of a tested salt on calcium phosphate floccules continue until reaching equilibrium with solvation interaction. In the presence of Ca^{2+} and the absence of PO_4^{3-}-containing species, the mechanism for the removal of potassium sulfate is attributed to the formation of insoluble potassium–calcium sulfate. The addition of Na_2SO_4 could facilitate the precipitation of potassium sulfate since it increases the concentration of SO_4^{2-}. In order to obtain efficient desalination, the prompt removal of the formed precipitate from the treated aqueous solution is necessary. According to the Marcet–Dittmar rule about the composition of seawater, the best season for fixation of Na_2SO_4 in aqueous solution by nature is assumed to be winter.

Acknowledgments

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Supplementary Information

Fig. S1. Photograph of *Sedum spectabile*.

Table S1
Comparison of the growth status of *S. spectabile* cultivated in deionized water

Before cultivation		After cultivation	
Height of the plant (cm)	Numbers of leaves (piece)	Height of the plant (cm)	Numbers of leaves (piece)
27	20	36	30

Note: The duration of the cultivation is 9 weeks, and total volume of deionized water is 200 mL, 18°C–25°C.

Table S2
Instrumental parameters and operating conditions for ICP-OES

Radio frequency (RF) power	1.2 kW
Plasma gas flow rate	15 L min^{-1}
Flow rate of argon auxiliary	1.5 L min^{-1}
Nebulizer gas flow rate	0.9 L min^{-1}
Precision (general)	1%–3%
K analytical line (λ)	766.49 nm (detection limit 0.06 mg L^{-1})
Na analytical line (λ)	589.59 nm (detection limit 0.02 mg L^{-1})
Ca analytical line (λ)	317.93 nm (detection limit 0.003 mg L^{-1})
Mg analytical line (λ)	279.08 nm (detection limit 0.02 mg L^{-1})
Fe analytical line (λ)	259.94 nm (detection limit 0.002 mg L^{-1})
Cu analytical line (λ)	324.75 nm (detection limit 0.005 mg L^{-1})
Mn analytical line (λ)	257.61 nm (detection limit 0.005 mg L^{-1})
Zn analytical line (λ)	213.86 nm (detection limit 0.005 mg L^{-1})
Mo analytical line (λ)	202.03 nm (detection limit 0.004 mg L^{-1})
Ni analytical line (λ)	231.60 nm (detection limit 0.01 mg L^{-1})
Co analytical line (λ)	228.62 nm (detection limit 0.005 mg L^{-1})
P analytical line (λ)	213.62 nm (detection limit 0.05 mg L^{-1})
S analytical line (λ)	180.73 nm (detection limit 0.04 mg L^{-1})

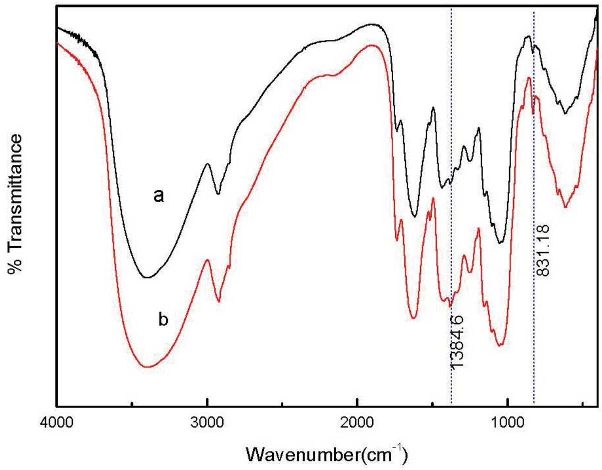


Fig. S2. FT-IR spectra of *Sedum spectabile*'s roots after cultivation with and without sodium nitrate stress (a), without sodium nitrate stress, and (b) with sodium nitrate stress.

The comparison of FT-IR spectra of *Sedum spectabile*'s roots after cultivation with and without sodium nitrate stress shows that absorptions around 1,384.66 cm^{-1} which can be attributed to NO_3^- asymmetrical stretching vibration and around 831.18 cm^{-1} which are due to NO_3^- bending vibration all become sharper or stronger, indicating that nitrate increases.

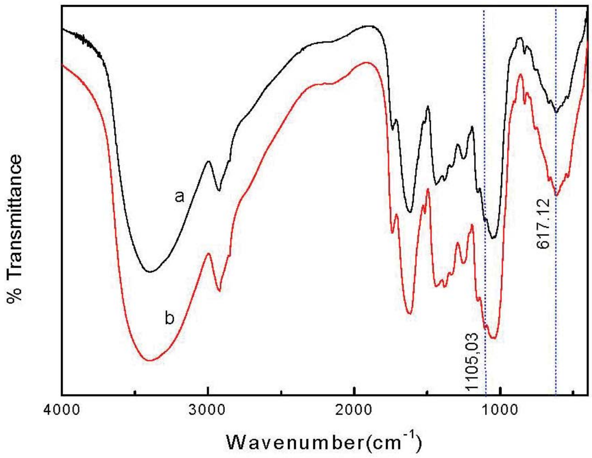


Fig. S3. FT-IR spectra of *Sedum spectabile*'s roots after cultivation with and without sodium sulfate stress (a) without sodium sulfate stress and (b) with sodium sulfate stress.

The comparison of FT-IR spectra of *Sedum spectabile*'s roots after cultivation with and without sodium sulfate stress shows that absorptions around 1,105.03 cm^{-1} which can be attributed to SO_4^{2-} asymmetrical stretching vibration, and around 617.12 cm^{-1} which are due to SO_4^{2-} bending vibration all become sharper or stronger, indicating that sulfate increases.

Table S3
Five formulations in hydroponic culture

Culture medium	$Ca(NO_3)_2$ (g L^{-1})	KNO_3 (g L^{-1})	$MgSO_4$ (g L^{-1})	KH_2PO_4 (g L^{-1})	EDTA (g L^{-1})	$CuSO_4$ (mg L^{-1})	$ZnSO_4$ (mg L^{-1})	$Mn(CH_3COO)_2$ (mg L^{-1})	$(NH_4)_2Fe(SO_4)_2$ (mg L^{-1})	$NaNO_3$ (g L^{-1})	Na_2SO_4 (g L^{-1})
A	0.820	0.505	0.241	0.136	0.037	0.051	0.124	1.56	28.4	–	–
B	–	–	–	–	–	–	–	–	–	–	–
C	–	0.505	0.241	0.136	0.037	0.051	0.124	1.56	28.4	0.850	–
D	0.820	0.505	0.241	0.136	0.037	0.051	0.124	1.56	–	–	–
E	0.820	0.505	–	0.136	0.037	0.051	0.124	1.56	28.4	–	0.284

Table S4
Comparison of growth status of *S. spectabile* with and without NaCl stress[a]

Cultural environment	Culture medium	Height of *S. spectabile* before cultivation (cm)	Height of *S. spectabile* after cultivation (cm)	Numbers of *S. spectabile*'s leaves before cultivation (piece)	Numbers of *S. spectabile*'s leaves after cultivation (piece)
With NaCl stress[b]	A	19.5	27.3	20	24
	B	18.3	25.5	21	24
	C	20.5	20.8	21	17[c]
	D	20.5	23.2	18	21
	E	19.3	26.5	20	26
Without NaCl stress	A	20.5	28.2	17	24
	B	20.1	29.9	19	30
	C	18.1	26.9	16	24
	D	19.4	23.8	19	27
	E	19.2	27.0	19	26

[a] The duration of the cultivation is 9 weeks (without NaCl stress in the first week), and total volume of culture solution is 200 mL, 20°C-30°C.
[b] Every 7 d, about 0.88 g of NaCl was added into each culture medium, and totally 7.04 g of NaCl was added.
[c] A leaf abscission occurred.

Table S5
Comparison of growth status of *S. spectabile* with and without $NaNO_3$ stress[a]

Cultural environment	Culture medium	Height of *S. spectabile* before cultivation (cm)	Height of *S. spectabile* after cultivation (cm)	Numbers of *S. spectabile*'s leaves before cultivation (piece)	Numbers of *S. spectabile*'s leaves after cultivation (piece)
With $NaNO_3$ stress[b]	A	18.1	24.7	19	21
	B	21.0	27.1	16	21
	C	17.4	25.0	19	21
	D	18.5	24.1	16	22
	E	18.5	25.7	17	23
Without $NaNO_3$ stress	A	20.5	28.2	17	24
	B	20.1	29.9	19	30
	C	18.1	26.9	16	24
	D	19.4	23.8	19	27
	E	19.2	27.0	19	26

[a] The duration of the cultivation is 9 weeks (without $NaNO_3$ stress in the first week), and total volume of culture solution is 200 mL, 20°C –30°C.
[b] Every 7 d, about 1.28 g of $NaNO_3$ was added into each culture medium, and totally 10.2 g of $NaNO_3$ was added.

Table S6
Comparison of growth status of *S. spectabile* with and without Na_2SO_4 stress[a]

Cultural environment	Culture medium	Height of *S. spectabile* before cultivation (cm)	Height of *S. spectabile* after cultivation (cm)	Numbers of *S. spectabile*'s leaves before cultivation (piece)	Numbers of *S. spectabile*'s leaves after cultivation (piece)
With Na_2SO_4 stress[b]	A	16.1	22.2	17	22
	B	16.9	24.1	20	26
	C	16.8	19.4	18	17[c]
	D	16.8	20.3	15	15
	E	16.0	21.1	18	18
Without Na_2SO_4 stress	A	20.5	28.2	17	24
	B	20.1	29.9	19	30
	C	18.1	26.9	16	24
	D	19.4	23.8	19	27
	E	19.2	27.0	19	26

[a] The duration of the cultivation is 9 weeks (without Na_2SO_4 stress in the first week), and total volume of culture solution is 200 mL, 20°C–30°C.
[b] Every 7 d, about 2.13 g of Na_2SO_4 was added into each culture medium, and totally 17.04 g of Na_2SO_4 was added.
[c] A leaf abscission occurred.

Table S7
Comparison of elemental contents of *S. spectabile*;s roots cultivated with and without NaCl stress[a]

Elements[b]	Contents of elements in *S. spectabile*'s roots cultivated with NaCl stress (mg g^{-1})[c]					Contents of elements in *S. spectabile*'s roots cultivated without NaCl stress (mg g^{-1})				
	Culture medium A	Culture medium B	Culture medium C	Culture medium D	Culture medium E	Culture medium A	Culture medium B	Culture medium C	Culture medium D	Culture medium E
Na	6.94	9.52	7.29	6.61	7.18	5.66	5.94	5.84	5.035	4.50
K	19.59	23.42	18.45	19.54	17.17	21.12	20.05	15.52	19.66	16.22
Ca	14.38	15.08	10.39	12.31	13.32	12.16	14.64	9.92	12.26	10.18
Mg	3.43	4.06	3.05	2.86	2.73	3.61	4.80	3.63	2.93	2.51
P	3.63	3.39	2.67	2.85	3.23	3.59	2.86	2.99	3.67	3.37
N	18.80	19.35	15.30	19.70	19.05	17.05	19.20	20.60	24.10	23.15
C	395.4	396.8	397.5	396.6	399.0	418.3	412.0	411.1	410.8	410.8
S	6.8	6.4	6.8	5.1	6.3	3.59	3.87	3.40	4.06	3.66
Fe	2.32	2.27	1.94	1.69	3.21	2.48	6.74	2.89	1.57	2.40
Mn	0.034	0.036	0.022	0.022	0.032	0.036	0.057	0.080	0.027	0.042
Zn	0.23	0.33	0.29	0.18	0.15	0.27	0.35	0.22	0.19	0.13
Cu	0.010	0.075	0.013	0.089	0.024	0.021	0.067	0.045	0.010	0.016

[a] The duration of the cultivation is 9 weeks (without NaCl stress in the first week), and total volume of culture solution is 200 mL, 20°C–30°C.
[b] The contents of other micronutrients, such as Mo, Ni, Co, etc, in roots were comparatively low, and not listed in the table.
[c] Every 7 d, about 0.88 g of NaCl was added into each culture medium, and totally 7.04 g of NaCl was added.

Table S8

Comparison of elemental contents of *S. spectabile*'s roots cultivated with and without $NaNO_3$ stress[a]

Elements[b]	Contents of elements in *S. spectabile*'s roots cultivated with $NaNO_3$ stress (mg g^{-1})[c]					Contents of elements in *S. spectabile*'s roots cultivated without $NaNO_3$ stress (mg g^{-1})				
	Culture medium A	Culture medium B	Culture medium C	Culture medium D	Culture medium E	Culture medium A	Culture medium B	Culture medium C	Culture medium D	Culture medium E
Na	7.05	9.27	8.76	6.28	5.55	5.66	5.94	5.84	5.04	4.50
K	18.25	18.04	17.96	15.72	16.11	21.12	20.05	15.52	19.66	16.22
N	94.75	93.70	73.55	85.55	84.30	17.05	19.20	20.60	24.10	23.15
Ca	10.76	13.54	9.82	9.68	10.38	14.38	14.64	9.92	12.26	10.18
Mg	2.96	3.20	2.88	2.46	2.19	3.61	4.80	3.63	2.93	2.51
P	3.78	4.19	3.71	3.67	3.74	3.59	2.86	2.99	3.50	3.37
C	489.3	493.6	499.8	493.6	499.4	418.3	412.0	411.1	410.8	410.8
S	5.9	7.3	6.1	7.3	7.3	3.59	3.87	3.40	4.06	3.66
Fe	3.26	3.01	1.83	1.12	1.29	2.48	6.74	2.89	1.57	2.40
Mn	0.046	0.024	0.081	0.027	0.034	0.036	0.057	0.080	0.027	0.042
Zn	0.24	0.31	0.14	0.14	0.11	0.27	0.35	0.22	0.19	0.13
Cu	0.018	0.017	0.009	0.014	0.010	0.021	0.067	0.045	0.010	0.016

[a] The duration of the cultivation is 9 weeks (without $NaNO_3$ stress in the first week), and total volume of culture solution is 200 mL, 20°C–30°C.

[b] The contents of other micronutrients, such as Mo, Ni, Co, etc, in roots were comparatively low, and not listed in the table.

[c] Every 7 d, about 1.28 g of $NaNO_3$ was added into each culture medium, and totally 10.2 g of $NaNO_3$ was added.

Table S9

Comparison of elemental contents of *S. spectabile*'s roots cultivated with and without Na_2SO_4 stress[a]

Elements[b]	Contents of elements in *S. spectabile*'s roots cultivated with Na_2SO_4 stress (mg g^{-1})[c]					Contents of elements in *S. spectabile*'s roots cultivated without Na_2SO_4 stress (mg g^{-1})				
	Culture medium A	Culture medium B	Culture medium C	Culture medium D	Culture medium E	Culture medium A	Culture medium B	Culture medium C	Culture medium D	Culture medium E
Na	8.18	10.40	8.88	7.43	6.91	5.66	5.94	5.84	5.04	4.50
K	16.10	15.72	17.08	19.78	20.48	21.12	20.05	15.52	19.66	16.22
S	4.42	5.12	5.40	4.40	5.24	3.59	3.87	3.40	4.06	3.66
Ca	11.96	12.32	8.82	11.33	18.63	14.38	14.64	9.92	12.26	10.18
Mg	2.78	2.92	3.14	2.69	7.88	3.61	4.80	3.63	2.93	2.51
P	3.97	3.39	3.74	4.87	5.31	3.59	2.86	2.99	3.67	3.37
N	84.65	81.40	80.60	74.60	85.90	17.05	19.20	20.60	24.10	23.15
C	483.6	487.4	489.8	484.4	476.4	418.3	412.0	411.1	410.8	410.8
Fe	3.74	2.64	1.91	5.07	4.98	2.48	6.74	2.89	1.57	2.40
Mn	0.041	0.023	0.038	0.056	0.065	0.036	0.057	0.080	0.027	0.042
Zn	0.24	0.30	0.16	0.16	0.22	0.27	0.35	0.22	0.18	0.13
Cu	0.017	0.016	0.036	0.008	0.040	0.021	0.067	0.045	0.010	0.016

[a] The duration of the cultivation is 9 weeks (without Na_2SO_4 stress in the first week), and total volume of culture solution is 200 mL, 20°C–30°C.

[b] The contents of other micronutrients, such as Mo, Ni, Co, etc, in roots were comparatively low, and not listed in the table.

[c] Every 7 d, about 2.13 g of Na_2SO_4 was added into each culture medium, and totally 17.04 g of Na_2SO_4 was added.

Table S10
Comparison of adsorption of KNO_3 on different calcium phosphates and carbonate[a]

Adsorbents	K content in adsorbents after adsorption (wt.%)
$CaHPO_4$	1.2
$Ca_3(PO_4)_2$	2.1
$Ca_5(OH)(PO_4)_3$	3.9
$CaCO_3$	<1.0

[a] Amount of adsorbents = 0.1 g, the grain-size was about 40–50 μm (i.e., 300–400 mesh), 19.9 g of KNO_3 was dissolved in 100 mL of water, exchange time = 24 h, temperature = 25°C.

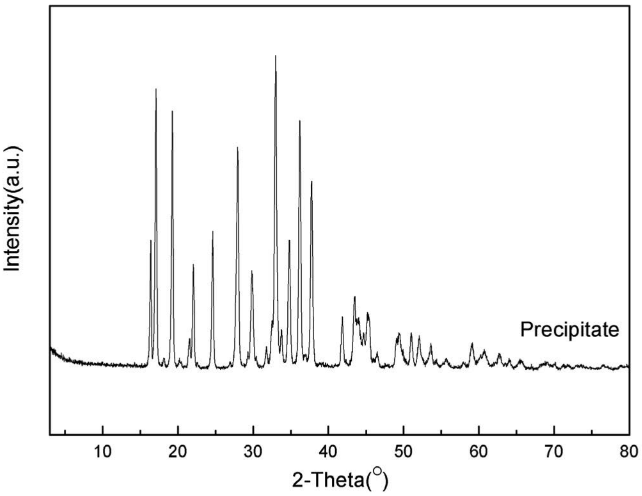


Fig. S4. XRD pattern of the precipitate collected from NaCl, $NaNO_3$, or Na_2SO_4 solution with oxalic acid.
Note: the precipitates collected from NaCl, $NaNO_3$, and Na_2SO_4 solutions by the addition of oxalic acid have the same XRD pattern.

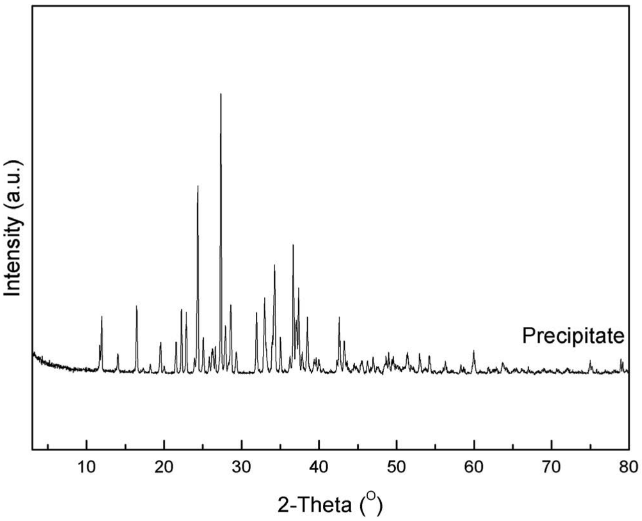


Fig. S5. XRD pattern of the precipitate collected from KCl, KNO_3, or K_2SO_4 solution with tartaric acid.
Note: the precipitates collected from KCl, KNO_3, and K_2SO_4 solutions by the addition of tartaric acid have the same XRD pattern.

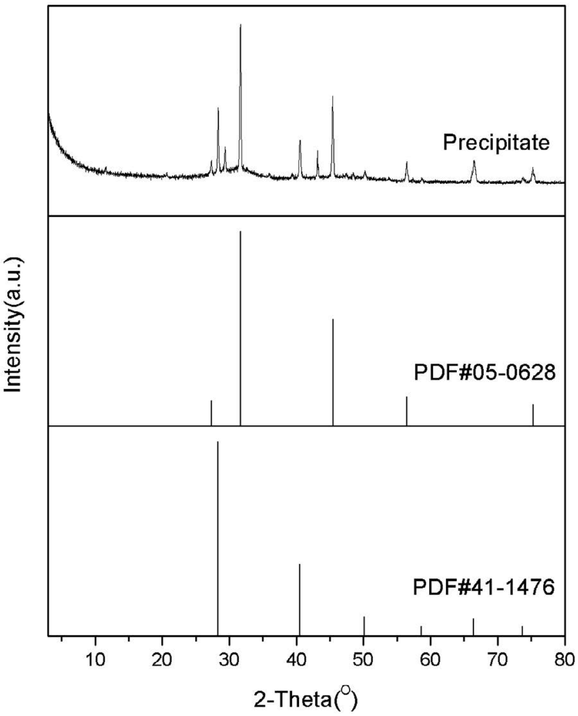


Fig. S6. XRD pattern of the precipitate collected from the formulation based on the composition of *S. spectabile*'s roots cultivated in culture medium B with NaCl stress (third column in Table S7) (PDF#05-0628 Halite(NaCl), syn; PDF#41-1476 Sylvite(KCl), syn).

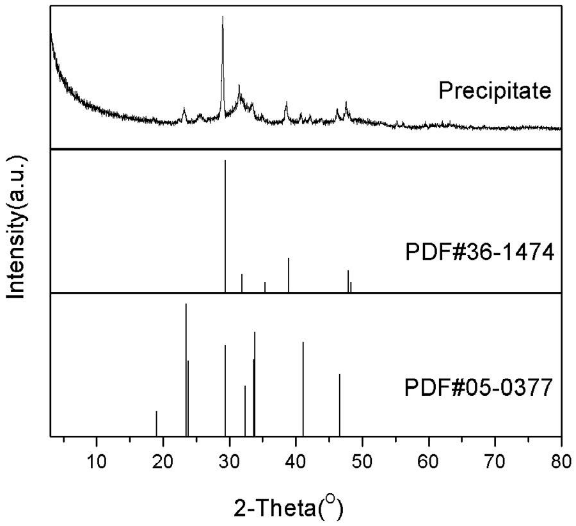


Fig. S7. XRD pattern of the precipitate collected from the formulation based on the composition of *S. spectabile*'s roots cultivated in culture medium B with $NaNO_3$ stress (third column in Table S8) (PDF#36-1474 Nitratine ($NaNO_3$), syn; PDF#05-0377 Niter (KNO_3), syn).

Table S11
Composition of the precipitate collected from NaCl, $NaNO_3$, or Na_2SO_4 solution after the addition of oxalic acid[a]

Content in precipitates (wt.%)					Ratio of elements (mol/mol)	Empirical formula
Na	C	H	Cl, N, or S	O	Na:C:O:H ≈ 1:2:5:3.2	$NaHC_2O_4·H_2O$
17.7	18.4	2.5	~0	61.4		

[a] Initial concentration of the salt = 1.97 mol L^{-1}; amount of $H_2C_2O_4·2H_2O$ added = 1.0 g; total volume of solution = 100 mL; temperature = 16°C; final pH < 3.

Note: the precipitates collected from NaCl, $NaNO_3$, and Na_2SO_4 solutions by the addition of oxalic acid have a nearly same Na content in precipitate.

Table S12
Composition of the precipitate collected from KCl, KNO_3, or K_2SO_4 solution after the addition of tartaric acid[a]

Content in precipitates (wt.%)					Ratio of elements (mol/mol)	Empirical formula
K	C	H	Cl, N, or S	O	K:C:O:H ≈ 1:4:6:5	$KC_4H_5O_6$
20.8	25.0	2.7	~0	51.5		

[a] Initial concentration of the salt = 1.97 mol L^{-1}; amount of tartaric acid added = 1.2 g; total volume of solution = 100 mL; temperature = 18°C; final pH < 3.

Note: the precipitates collected from KCl, KNO_3, and K_2SO_4 solutions by the addition of tartaric acid have a nearly same K content in the precipitate.

Table S13
Formulations of several mixtures referred to Tables S7–S9

Mixture	Formulation	Reference
1	2.42 g of NaCl, 3.66 g of KCl, and 4.18 g of $CaCl_2$ were dissolved in 100 mL of water, and then 1.49 g of KH_2PO_4 in a small amount of water was added into the chloride solution	Third column in Table S7, that is, Na 9.52 g L^{-1}, K 23.42 g L^{-1}, Ca 15.08 g L^{-1}, P 3.39 g L^{-1}
2	3.42 g of $NaNO_3$, 3.31 g of KNO_3, and 7.98 g of $Ca(NO_3)_2·4H_2O$ were dissolved in 100 mL of water, and then 1.84 g of KH_2PO_4 in a small amount of water was added into the nitrate solution	Third column in Table S8, that is, Na 9.27 g L^{-1}, K 18.04 g L^{-1}, Ca 13.54 g L^{-1}, P 4.19 g L^{-1}
3	3.21 g of Na_2SO_4, 2.56 g of K_2SO_4, and 1.49 g of KH_2PO_4 were dissolved in 100 mL of water, and then 7.26 g of $Ca(NO_3)_2·4H_2O$ in a small amount of water was added into the sulfate solution	Third column in Table S9, that is, Na 10.40 g L^{-1}, K 15.72 g L^{-1}, Ca 12.32 g L^{-1}, P 3.39 g L^{-1}
4	3.21 g of Na_2SO_4 and 2.56 g of K_2SO_4 were dissolved in 100 mL of water, and then 7.26 g of $Ca(NO_3)_2·4H_2O$ in a small amount of water was added into the sulfate solution	Third column in Table S9, that is, Na 10.40 g L^{-1}, K 15.29 g L^{-1}, Ca 12.32 g L^{-1}

Table S14
Composition of the precipitates collected from the formulations of mixtures 1–3 in Table S13

Salts	Composition of the collected precipitates (wt.%)			
	Na	K	Ca	P
Chloride	7.19	8.47	17.11	8.80
Nitrate	6.10	6.59	14.36	7.39
Sulfate	3.20	2.61	25.47	5.83

Table S15
Effect of temperature on the removal of KCl, NaCl, KNO_3, or $NaNO_3$[a]

Salts	Temperature (°C)	Contents in precipitates (wt.%)				K or Na removed (%)	Cl or N removed (%)
		Na	K	Cl	N		
NaCl	15	16.5	–	26.2	–	35.4	36.5
	25	13.3	–	23.1	–	26.5	29.8
	50	8.10	–	13.0	–	19.0	19.7
KCl	15	–	29.9	26.0	–	42.1	40.4
	25	–	21.5	18.6	–	30.6	29.1
	50	–	15.5	13.8	–	17.0	16.7
$NaNO_3$	15	12.8	–	–	8.68	36.2	40.3
	25	11.5	–	–	8.24	32.7	38.5
	50	6.92	–	–	4.25	12.3	12.4
KNO_3	15	–	21.0	–	8.56	36.4	41.4
	25	–	17.8	–	6.20	29.7	28.9
	50	–	4.73	–	1.82	3.7	4.0

[a] Initial concentration of salts = 1.97 mol L^{-1}; amount of $Ca(H_2PO_4)_2 \cdot H_2O$ added = 3.42 g; amount of $Ca(OH)_2$ added = 2.3–2.5 g; total volume of solution = 100 mL; pH 7–7.5.

Table S16
Effect of the initial concentration of KCl, NaCl, KNO_3, or $NaNO_3$ on their removal[a]

Salts	Initial concentration of the salts (mol L^{-1})	Contents in precipitates (wt.%)				K or Na removed (%)	Cl or N removed (%)
		Na	K	Cl	N		
NaCl	1.97	13.3	–	23.1	–	26.5	29.8
	2.95	16.6	–	25.1	–	31.4	30.8
KCl	1.97	–	21.5	18.6	–	30.6	29.1
	2.95	–	29.8	27.3	–	34.2	34.6
$NaNO_3$	1.97	11.5	–	–	8.24	32.7	38.5
	2.95	14.7	–	–	9.72	34.1	37.1
KNO_3	0.98	–	13.1	–	3.95	25.2	21.2
	1.97	–	17.8	–	6.20	29.7	28.9
	2.95	–	26.9	–	9.50	31.5	31.1

[a] Total volume of solution = 100 mL; amount of $Ca(H_2PO_4)_2 \cdot H_2O$ added = 3.42 g; amount of $Ca(OH)_2$ added = 2.3 g; pH 7–7.5; temperature = 25°C.

Table S17
Comparison of dosage of calcium phosphate in terms of N contents in precipitates[a]

Dosage of $Ca(H_2PO_4)_2$ (mmol)	N content in precipitates (wt.%)	N removed (%)
1.71	8.40	10.6
3.41	8.11	18.6
6.78	8.75	33.5
13.6[b]	8.68	40.3

[a] 16.73 g of $NaNO_3$ was dissolved in 100 mL of water, temperature = 15°C.
[b] The system became a pulpy or pasted mixture.
Note: a slight increase of N content in precipitates showed in last two lines could be partly attributed to the thickening effect of the precipitates.

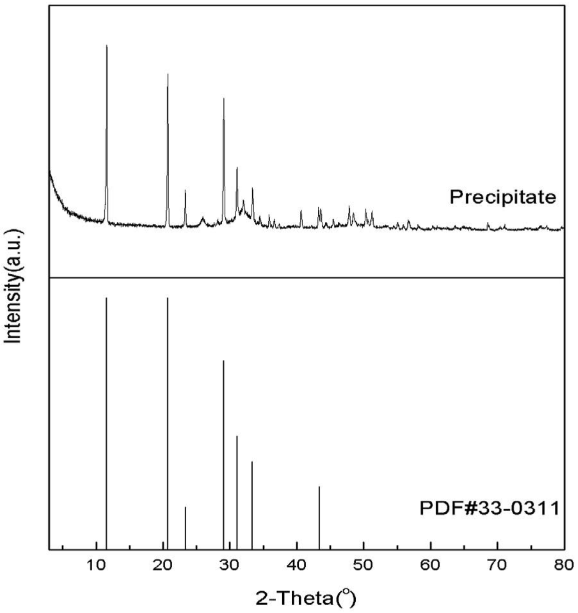


Fig. S8. XRD pattern of the precipitate collected from the formulation based on the composition of *S. spectabile*'s roots cultivated in culture medium B with Na_2SO_4 stress (third column in Table S9) [PDF#33-0311Gypsum ($CaSO_4{\cdot}2H_2O$), syn].

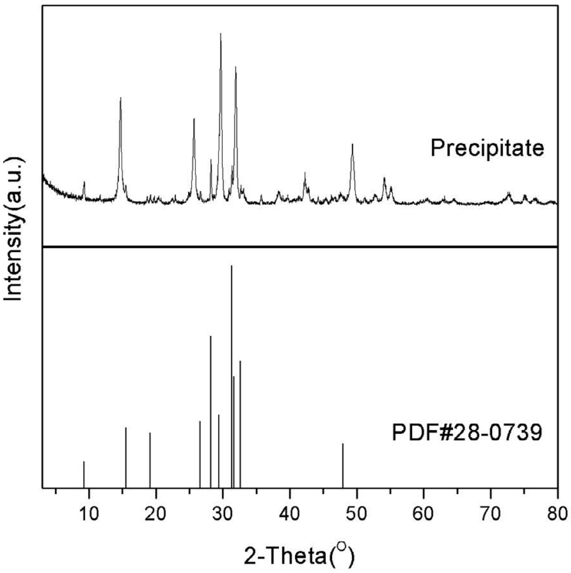
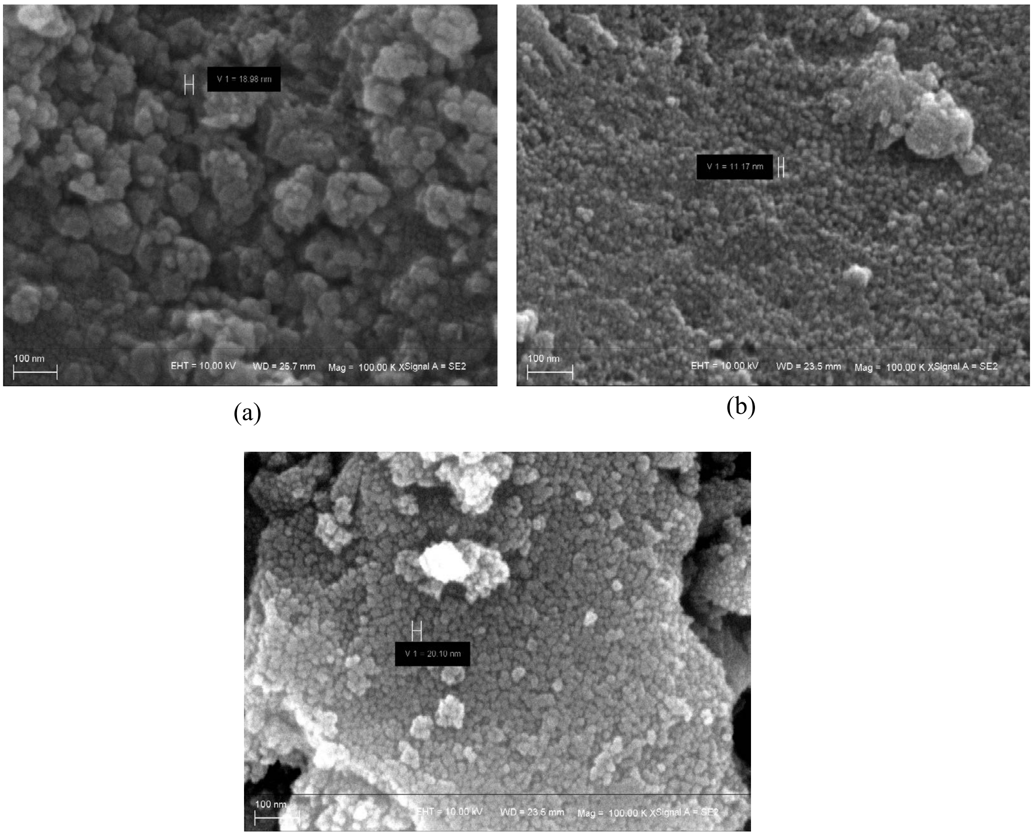


Fig. S9. XRD pattern of the precipitate collected from the formulation based on the composition of *S. spectabile*'s roots cultivated in culture medium B with Na_2SO_4 stress (third column in Table S7, except without addition of KH_2PO_4) [PDF#28-0739 Syngenite ($K_2Ca(S\ O_4)_2{\cdot}H_2O$, syn].



(a)

(b)

(c)

Fig. S10. SEM photomicrographs of the floccules: (a) calcium phosphate floccules, (b) Al-containing floccules, and (c) Fe-containing floccules.

Table S18
Removal of Na_2SO_4 and K_2SO_4 by calcium phosphates[a]

Salts	Dosage of $Ca(H_2PO_4)_2$ (mmol)	Contents in precipitates (wt.%)			K or Na removed (%)	S removed (%)
		Na	K	S		
Na_2SO_4	1.8	8.8	–	6.5	8.4	8.9
	3.6	7.8	–	5.9	12.6	13.7
K_2SO_4	1.8	–	7.6	4.2	5.1	6.9
	3.6	–	8.3	5.3	9.2	14.4

[a] Total volume of solution = 100 mL; initial concentration of the salts = 5 g/100 mL water; pH 7–7.5 (with $Ca(OH)_2$); temperature = 0°C–5°C.

Table S19
Effect of initial composition of sulfates on their removal[a]

Salts	Initial concentration of species (mol L^{-1})			Amount of Ca^{2+} added (mmol)	K removed (%)	Na removed (%)
	K	Na	S			
Na_2SO_4	–	2.30	1.15	57.4 (from $CaCl_2$)	–	1.9
				28.7 (from $CaCl_2$)	–	1.0
K_2SO_4	1.15	–	0.57	57.4 (from $CaCl_2$)	34.6	–
				57.4 (from $Ca(NO_3)_2$)	3.2	–
				28.7 (from $CaCl_2$)	62.6	–
	0.57	–	0.29	14.3 (from $Ca(NO_3)_2$)	3.3	–
K_2SO_4–Na_2SO_4	0.57	0.57	0.57	14.3 (from $CaCl_2$)	47.5	1.7
				14.3 (from $Ca(NO_3)_2$)	51.6	1.1
K_2SO_4–$MgSO_4$	1.15	–	1.15	57.4 (from $CaCl_2$)	48.0	–
	0.57	–	0.57	14.3 (from $CaCl_2$)	38.0	–
				14.3 (from $Ca(NO_3)_2$)	30.1	–
KCl–Na_2SO_4	0.57	1.15	0.57	14.3 (from $CaCl_2$)	37.3	1.1
	0.115	2.29	1.15	14.3 (from $CaCl_2$)[b]	0.2	<0.1

[a] Total volume of solution = 100 mL (except where specified); temperature = 25°C; pH 7–7.5.
[b] Total volume of solution = 500 mL.

Table S20
Comparison of calcium phosphate floccules and some adsorbents in terms of N contents in precipitates[a]

	Size of floccule particle (dried) (nm)	N content in precipitates (wt. %)
Calcium phosphate floccules[b]	ca. 20	8.40
Al-containing floccules[c]	ca. 11	10.6
Fe-containing floccules[d]	ca. 20	7.35

[a] Initial concentration of salts = 1.97 mol L^{-1}, total volume of solution = 100 mL, temperature = 15°C.
[b] Amount of $Ca(H_2PO_4)_2\cdot H_2O$ added = 0.453 g (ca. 3.6 mmol P), amount of $Ca(OH)_2$ added = 0.3 g, pH 7–7.5.
[c] Amount of $Al(NO_3)_3\cdot 9H_2O$ added = 1.35 g (ca. 3.6 mmol Al), amount of $Ca(OH)_2$ added = 0.3 g, pH 6–7 (adjusted with NaOH).
[d] Amount of $FeCl_3\cdot 6H_2O$ added = 0.972 g (ca. 3.6 mmol Fe), pH 6–7 (adjusted with NaOH).
Note: Due to a low solubility of calcium-containing phosphates in water, almost no "extra salt impurities" would be introduced into the treated salt solution by using calcium-containing phosphate floccules as the adsorbent. However, "extra salt" would be brought into the treated salt solution if using Al-containing or Fe-containing floccules as adsorbents.

Table S21
Effect of temperature on the activity coefficient of NaCl in aqueous solutions[a]

Solution	Temperature (°C)	$\log\gamma_{Na^+}$[b]	$\log\gamma_{Cl^-}$[b]	$\gamma_{\pm NaCl}$[c]
NaCl (1.97 mol)–H_2O (1,000 g)	15	–0.084	–0.231	0.696
	25	–0.087	–0.234	0.691
	50	–0.097	–0.245	0.675

[a] Because calcium phosphates have a very low solubility in water at pH 7–8, the effect of PO_4^{3-}-containing species is neglected under a condition of supplying sufficient amount of Ca^{2+}.

[b] http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/.

[c] $\gamma_{\pm NaCl} = (\gamma_{Na^+} \times \gamma_{Cl^-})^{1/2}$.

Table S22
Composition of artificial seawater[a]

Species in artificial seawater	Concentration of the artificial seawater (mmol L^{-1})	Twofold concentration of artificial seawater (mmol L^{-1})
Na^+	459.1	918.2
K^+	9.72	19.4
Ca^{2+}	9.98	20.0
Mg^{2+}	52.34	104.7
Cl^-	536.0	1,072
SO_4^{2-}	26.65	53.3
HCO_3^-	2.33	4.7

[a] Formulations of artificial seawater: 26.7 g of NaCl, 0.72 g of KCl, 1.15 g of $CaCl_2$, 2.26 g of $MgCl_2$, 3.25 g of $MgSO_4$, and 0.2 g of $NaHCO_3$ were dissolved in 1 L of water.

Table S23
Effect of dosage of $Ca(H_2PO_4)_2$ on the removal of Na salt in artificial seawater by calcium phosphates[a]

Dosage of $Ca(H_2PO_4)_2$ (mmol)	Temperature (°C)	Na uptake in precipitates (wt.%)	Na removed (%)
1.8	5	3.1	0.5
	15	3.0	0.5
3.6	5	3.5	1.4
	15	3.0	1.2

[a] Concentration of artificial seawater is listed in Table S22, except that $CaCl_2$ was not added, and was substituted with $Ca(H_2PO_4)_2{\cdot}H_2O$ and $Ca(OH)_2$. Total volume of solution = 500 mL, pH 7–7.5 (with $Ca(OH)_2$).

Table S24
Effect of co-existing ions (or electrolytes) on the mean activity coefficients of NaCl ($\gamma_{\pm NaCl}$) in brines with a near seawater composition (25°C)[a]

Composition of brines	$\log\gamma_{Na^+}$[b]	$\log\gamma_{Cl^-}$[b]	$\gamma_{\pm NaCl}$[c]
NaCl (Na^+ 10,560 ppm, Cl^- 16,276 ppm)–H_2O (1,000 g)	–0.144	–0.185	0.685
NaCl (Na^+ 10,560 ppm, Cl^- 16,276 ppm)–KNO_3 (K^+ 17,946 ppm, NO_3^- 28,458 ppm)–H_2O (1,000 g)	–0.095	–0.233	0.685
NaCl (Na^+ 10,560 ppm, Cl^- 16,276 ppm)–$MgCl_2$ (Cl^- 3,711 ppm, Mg^{2+} 1,272 ppm)–H_2O (1,000 g)	–0.144	–0.198	0.675
NaCl (Na^+ 10,560 ppm, Cl^- 16,276 ppm)–K_2SO_4 (K^+ 17,946 ppm, SO_4^{2-} 22,032 ppm)–H_2O (1,000 g)	–0.136	–0.216	0.667
NaCl (Na^+ 10,560 ppm, Cl^- 16,276 ppm)–$MgSO_4$ (SO_4^{2-} 5,025 ppm, Mg^{2+} 1,272 ppm)–H_2O (1,000 g)	–0.145	–0.196	0.675

[a] Because calcium phosphates have a very low solubility in water in the pH range of 7–8, the effect of PO_4^{3-}-containing species is neglected under a condition of supplying sufficient amount of Ca^{2+}.

[b] http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/.

[c] $\gamma_{\pm NaCl} = (\gamma_{Na^+} \times \gamma_{Cl^-})^{1/2}$.

Table S25
Effect of co-existing ions (or electrolytes) on the mean activity coefficient of NaCl in aqueous solutions (25°C)[a]

Composition of brines	$\log\gamma_{Na^+}$[b]	$\log\gamma_{Cl^-}$[b]	$\gamma_{\pm NaCl}$[c]	$a_{\pm NaCl}$[d]
NaCl (0.5 mol)–H_2O (1,000 g)	–0.144	–0.187	0.683	0.342
NaCl (0.5 mol)–KNO_3 (0.05 mol)–H_2O (1,000 g)	–0.145	–0.191	0.679	0.340
NaCl (0.5 mol)–KNO_3 (0.25 mol)–H_2O (1,000 g)	–0.143	–0.205	0.670	0.335
NaCl (0.5 mol)–KNO_3 (0.5 mol)–H_2O (1,000 g)	–0.136	–0.216	0.667	0.333
NaCl (0.5 mol)–KNO_3 (1.0 mol)–H_2O (1,000 g)	–0.113	–0.228	0.675	0.338
NaCl (0.5 mol)–K_2SO_4 (0.025 mol)–H_2O (1,000 g)	–0.145	–0.192	0.678	0.339
NaCl (0.5 mol)–K_2SO_4 (0.25 mol)–H_2O (1,000 g)	–0.135	–0.217	0.667	0.333
NaCl (0.5 mol)–K_2SO_4 (0.5 mol)–H_2O (1,000 g)	–0.114	–0.228	0.675	0.337
NaCl (0.5 mol)–$Mg(NO_3)_2$ (0.05 mol)–H_2O (1,000 g)	–0.144	–0.199	0.674	0.337
NaCl (0.5 mol)–$Mg(NO_3)_2$ (0.25 mol)–H_2O (1,000 g)	–0.126	–0.223	0.669	0.335
NaCl (0.5 mol)–$Mg(NO_3)_2$ (0.5 mol)–H_2O (1,000 g)	–0.085	–0.235	0.692	0.346
NaCl (0.5 mol)–$MgSO_4$ (0.05 mol)–H_2O (1,000 g)	–0.144	–0.197	0.675	0.338
NaCl (0.5 mol)–$MgSO_4$ (0.25 mol)–H_2O (1,000 g)	–0.137	–0.214	0.668	0.334
NaCl (0.5 mol)–$MgSO_4$ (0.5 mol)–H_2O (1,000 g)	–0.125	–0.224	0.669	0.335
NaCl (0.5 mol)–$MgSO_4$ (1.0 mol)–H_2O (1,000 g)	–0.100	–0.232	0.682	0.341
NaCl (1.0 mol)–H_2O (1,000 g)	–0.136	–0.216	0.667	0.667
NaCl (1.0 mol)–KNO_3 (0.1 mol)–H_2O (1,000 g)	–0.132	–0.219	0.668	0.668
NaCl (1.0 mol)–KNO_3 (0.5 mol)–H_2O (1,000 g)	–0.113	–0.228	0.675	0.675
NaCl (1.0 mol)–KNO_3 (1.0 mol)–H_2O (1,000 g)	–0.085	–0.235	0.692	0.692
NaCl (1.0 mol)–KNO_3 (2.0 mol)–H_2O (1,000 g)	–0.020	–0.237	0.744	0.744
NaCl (1.0 mol)–K_2SO_4 (0.05 mol)–H_2O (1,000 g)	–0.132	–0.219	0.668	0.668
NaCl (1.0 mol)–K_2SO_4 (0.5 mol)–H_2O (1,000 g)	–0.089	–0.234	0.689	0.689
NaCl (1.0 mol)–K_2SO_4 (1.0 mol)–H_2O (1,000 g)	–0.035	–0.237	0.731	0.731
NaCl (1.0 mol)–$Mg(NO_3)_2$ (0.1 mol)–H_2O (1,000 g)	–0.123	–0.224	0.671	0.671
NaCl (1.0 mol)–$Mg(NO_3)_2$ (0.5 mol)–H_2O (1,000 g)	–0.054	–0.237	0.715	0.715
NaCl (1.0 mol)–$Mg(NO_3)_2$ (1.0 mol)–H_2O (1,000 g)	0.051	–0.233	0.811	0.811
NaCl (1.0 mol)–$MgSO_4$ (0.1 mol)–H_2O (1,000 g)	–0.126	–0.223	0.669	0.669
NaCl (1.0 mol)–$MgSO_4$ (0.5 mol)–H_2O (1,000 g)	–0.097	–0.233	0.684	0.684
NaCl (1.0 mol)–$MgSO_4$ (1.0 mol)–H_2O (1,000 g)	–0.068	–0.236	0.705	0.705
NaCl (1.0 mol)–$MgSO_4$ (2.0 mol)–H_2O (1,000 g)	–0.021	–0.237	0.743	0.743

[a] Because calcium phosphates have a very low solubility in water in the pH range of 7–8, the effect of PO_4^{3-}-containing species is neglected under a condition of supplying sufficient amount of Ca^{2+}.
[b] http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/.
[c] $\gamma_{\pm NaCl} = (\gamma_{Na^+} \times \gamma_{Cl^-})^{1/2}$.
[d] $a_{\pm NaCl} = \gamma_{\pm NaCl} \times m_{\pm NaCl}$ (mol kg^{-1}).

Table S26
Effect of temperature on the activity coefficients of NaCl ($\gamma_{\pm NaCl}$) in nrines with a near seawater composition[a]

Composition of brines	Temperature (°C)	$\log\gamma_{Na^+}$[b]	$\log\gamma_{Cl^-}$[b]	$\gamma_{\pm NaCl}$[c]
NaCl (Na^+ 10,560 ppm, Cl^- 16,276 ppm)–H_2O (1,000 g)	5	–0.139	–0.179	0.693
	15	–0.141	–0.182	0.689
	25	–0.144	–0.185	0.685
10,560 ppm Na^+, 18,980 ppm Cl^-, 2,560 ppm SO_4^{2-}, 1,272 ppm Mg^{2+}, 400 ppm Ca^{2+}, 380 ppm K^+, 142 ppm HCO_3^-, 2.5 ppm NO_3^- (pH = 8)–H_2O	5	–0.139	–0.194	0.682
	15	–0.141	–0.197	0.678
	25	–0.144	–0.199	0.674

[a] Because calcium phosphates have a very low solubility in water in the pH range of 7–8, the effect of PO_4^{3-}-containing species is neglected under a condition of supplying sufficient amount of Ca^{2+}.
[b] http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/.
[c] $\gamma_{\pm NaCl} = (\gamma^{+}_{Na} \times \gamma^{-}_{Cl})^{1/2}$.