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Polydopamine Film Coated Controlled-Release Multielement Compound Fertilizer Based on Mussel-Inspired Chemistry

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ABSTRACT: This work reports on a facile and reliable method to prepare a polydopamine film coated controlled-release multielement compound fertilizer (PCMCF) based on mussel-inspired chemistry for the first time. The polydopamine (Pdop) film was coated on double copper potassium pyrophosphate trihydrate, providing three essential nutrients (Cu, K, and P) by spontaneous oxidative polymerization of dopamine. The thickness of the polymer coating of the fertilizer was controlled by using the multistep deposition technique. The morphology and composition of the products were characterized by transmission electron microscopy, inductively coupled plasma emission spectrometer, a vis spectrophotometer, and a Kjeltec autoanalyzer. The controlled-release behavior of four elements, including nitrogen from Pdop, was evaluated in water and in soil (sterilized or not). The results revealed that the coated fertilizers had good slow-release properties, incubated in either water or soil. It is noted that the release rate of nutrients of PCMCF can be tailored by the thickness of the Pdop coating, and the Pdop coating can be biodegraded in soil. This coating technology will be effective and promising in the research and development of controlled-release fertilizer.

KEYWORDS: *polydopamine, controlled-release fertilizer, mussel-inspired chemistry*

INTRODUCTION

Fertilizers have been used for many years to supply nutrients in growing media. They are added to soil to release nutrients necessary for plant growth.[1,2] However, most nutrients of applied normal fertilizers are lost to the environment and cause serious polluting problems. In order to overcome these shortcomings, in recent years, most existing research has focused on techniques to deliver a slow- or controlled-release of plant nutrients in the water or soil.[3−6]

Compared to the conventional type, slow- or controlled-release fertilizers have many advantages, such as decreasing a fertilizer's loss rate, supplying nutrients sustainably, lowering application frequency, and minimizing potential negative effects associated with overdosage.[5,7,8] Coated fertilizers, physically prepared by coating fertilizer granules with various materials, are the major categories of slow-release fertilizers. Many materials have been reported to be used as coatings, such as superabsorbent polymers,[9−11] lignin,[12] and commercial polymers.[13] However, few coated controlled-release fertilizers have been reported because it is difficult to find a coating material that can provide a controllable barrier or control the release rate of nutrients according to different ambient conditions.[14,15]

Recently, Lee et al. have reported that a thin, surface adherent, and multifunctional biopolymer polydopamine (Pdop) layer can be formed on a wide range of inorganic and organic materials and even by itself by self-polymerization of dopamine in an aqueous solution.[16] Importantly, it was reported that polydopamine shows excellent biocompatibility and low cytotoxicity, making it a versatile platform for bioapplications.[17−19] The thickness of polydopamine that was modified on the substrates can be controlled by the concentration of dopamine, solution pH, deposition time, and the number of deposition cycles.[20,21] Our previous research found that the wall thickness of Pdop can be controlled readily by repeated deposition cycles.[22] Additionally, it is interesting that the Pdop demonstrates the ability to tune the biodegradable rate of polymer coatings through changing the ratio of dopamine within the film.[23] This property can be used to control the release rate of nutrients entrapped in the Pdop film depending on the biodegradable rate in different soils. To the best of our knowledge, however, Pdop with well-defined surface properties used as a controlled-release coating material has not been reported. The broad applicability of polydopamine coating encourages us to explore the possibilities of preparing a Pdop-coated controlled-release fertilizer.

Nitrogen (N), phosphorus (P), and potassium (K) are the three vital elements, and plants require large amounts of them for adequate growth. Copper (Cu) is an essential micronutrient for plant growth. It can increase plants' resistance to drought and disease caused by fungi. It also aids in the synthesis of chlorophyll, and it is contained in the enzymes responsible for seed and fruit formation.[24] In this study, double copper potassium pyrophosphate trihydrate, an inorganic material of low solubility, was used as the source of phosphorus, potassium, and copper. Nitrogen is released after degradation of

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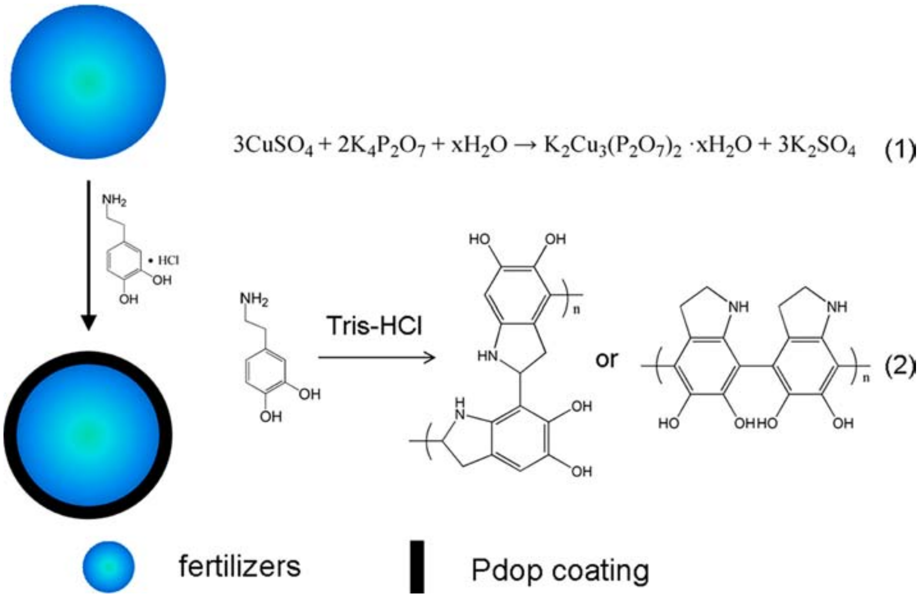
Scheme 1. Procedures for the Fabrication of Polydopamine-Coated Controlled-Release Fertilizers



polydopamine film, which is also a sign of cracking of Pdop coatings.

In this work, we prepared a series of Pdop-coated controlled-release multielement compound fertilizers (PCMCFs) by using oxidative polymerization of dopamine with different deposition cycles. The double copper potassium pyrophosphate trihydrate was entrapped in the polydopamine film. The release behavior of four elements was evaluated in water and in soil (sterilized or not) in detail.

■ MATERIALS AND METHODS

Materials. Dopamine hydrochloride was purchased from Sigma-Aldrich Company. Cupric sulfate pentrahydrate and potassium pyrophosphate trihydrate were provided by Fuchen Chemical Reagents Factory, Tianjin, China. Sulfuric acid was obtained from Chengdu Kelong Chemical Reagent Factory, Sichuan, China. Hydrogen peroxide 30% was provided by Tianjin Fuyu Fine Chemical Co., Ltd., Tianjin, China. The water used was deionized. All other chemicals were analytical grade and used as received.

Synthesis of Double Copper Potassium Pyrophosphate Trihydrate. Double copper potassium pyrophosphate trihydrate was synthesized according to a method previously reported in the literature.[25] In short, the synthesis was carried out by adding the copper sulfate solution (0.1 M containing 0.035 M H_2SO_4) to the potassium pyrophosphate solution (0.1 M) at a constant flow under vigorous stirring at room temperature. The suspension was left for 24 h for aging, and then the precipitate was filtered and dried under vacuum to a constant weight.

Preparation of Pdop-Coated Controlled-Release Multielement Compound Fertilizer. In a typical procedure, dried double copper potassium pyrophosphate trihydrate powder (2 g) and 1 mg/mL of dopamine hydrochloride were dissolved in 10 mM Tris-HCl (pH = 8.5) (200 mL), and the solution was stirred for 24 h at room temperature. The solution's color changed to dark brown due to pH-induced oxidation. After at least three centrifugation/water washing cycles, the fertilizers were dried to a constant weight under vacuum at 45 °C, and the resulting products were obtained. In order to get PCMCFs with different thicknesses of Pdop film, the number of deposition cycles was designed at 1, 3 and 5, respectively. The deposition procedure was repeated in the same way as mentioned above. The resulting products are denoted as PCMCF-C0, PCMCF-C1, PCMCF-C3, PCMCF-C5, where C0, C1, C3, and C5 refer to the number of deposition cycles.

Characterization Techniques. Transmission electron microscopy (TEM, Hitachi H-600) was used to observe the morphology of the PCMCFs. Thermal stability was determined by a thermogravimetric analyzer (TGA, Netzsch STA449F3) over a temperature range of 25–1000 °C at a heating rate of 10 °C/min under a N_2 atmosphere. The content of K and Cu was analyzed by an inductively coupled plasma emission spectrometer (ICP, Thermo Scientific 6000 Series). The content of P was determined using a vis spectrophotometer (ShangHai Precision & Scientific Instrument Co., Ltd., 722N). The content of N was measured with a Kjeltec 2300 autoanalyzer (Foss Tecator AB, Foss Kjeltec 2300 system).

Release Behavior of PCMCF in Water. The release behavior of potassium (K_2O), copper (Cu), nitrogen (N), and phosphorus (P_2O_5) from PCMCF in water was determined as follows: 0.5 g of products was enclosed in dialysis bags (molecular weight cutoff is 15 k). Then, the bags were put into conical bottles with 200 mL of deionized water. During 30 days, 5.0 mL of the solution was withdrawn at a predetermined time, and the same volume of fresh medium was added into the system to maintain a constant amount of solvent. The content of N, P, K, and Cu released in water was determined as mentioned above.

Release Behavior and Biodegradation of PCMCF in Soil. To study the controlled-release behavior of PCMCF in soil, the following experiment was carried out: Each product powder was divided into six units and embedded into cloth bags. The bags were buried in a plastic beaker with 200 g of dry soil (below 24 meshes). Throughout the experiment, the water-holding ratio of the soil was maintained at 30% by weighing and adding water if necessary periodically. The bags with PCMCF granules were picked out at certain time intervals (days 3, 6, 9, 12, 15, 18) and then dried at room temperature to a constant weight. The content of nutrients was measured, and dynamic curves were obtained. For investigating biodegradation of the Pdop film, the soil was sterilized by UV rays, and the process of release behavior in sterilized soil was carried out the same way as in soil. The unsterilized and sterilized soil are denoted as U and S, respectively.

■ RESULTS AND DISCUSSION

Morphology and Characteristics of PCMCF. The fabrication strategy is shown in Scheme 1. The polydopamine-coated controlled-release fertilizers were successfully prepared by spontaneous polymerization of dopamine on double copper potassium pyrophosphate trihydrate. TEM images of PCMCF with different deposition cycles are shown in Figure 1. Comparing to uncoated fertilizer (Figure 1A), the light outer shell is clearly observed on the boundary of dark flaky crystals, which indicates the Pdop film is successfully coated on double copper potassium pyrophosphate trihydrate. The Pdop film is shown to be homogeneously coated after different deposition cycles, and the boundary is very clear, indicating a tight encapsulation. The control of the shell thickness is very important because the performance of the controlled-release behavior of PCMCF depends on the barrier from the Pdop film. As shown in Figure 1B, the average thickness of the Pdop film is about 8 ± 0.4 nm after the first deposition polymerization. After three deposition cycles (Figure 1C), the thickness increases to 11 ± 0.7 nm and up to 15 ± 1.2 nm (Figure 1D) after five deposition cycles. The average thickness gain per one cycle of PCMCF-C1, PCMCF-C3, and PCMCF-C5 is different, and that of PCMCF-C1 is larger than the other's because polydopamine deposits on different substrates. For the first cycle, the Pdop film is coated on the flaky crystals and after that the Pdop film is deposited on itself. The growth profile of Pdop is in agreement with that reported for planar substrates.[26] Hu et al. reported that the thickness of Pdop coated on carbon nanotubes is about 5 nm.[27] These results revealed the Pdop thickness of PCMCF can be easily controlled depending on the number of deposition cycles after the first cycle, and this method provides a possibility to obtain differents barriers for nutrient release.

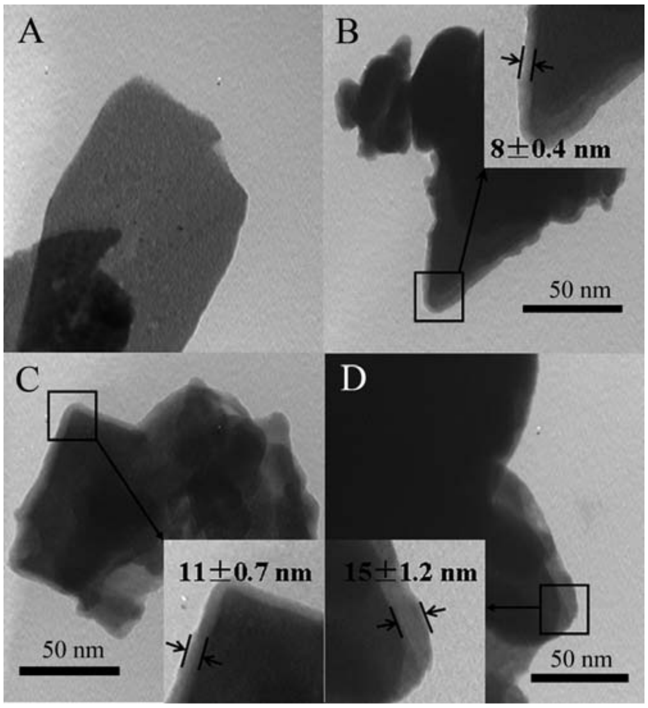


Figure 1. TEM photos of PCMCF: (A) without coating, (B) 1 cycle, (C) 3 cycles, (D) 5 cycles.

The total amount of salt contained was determined using a sample digestion method for evaluating ion contents in PCMCF. After microwave-assisted digestion in the presence of catalyst, the content of K and Cu in the PCMCF was determined with ICP. P was determined using a vis spectrophotometer. Nitrogen was determined using a Kjeltec 2300 autoanalyzer, after a "wet" Kjeltec digestion method. The release behaviors of nutrients from the fertilizer were determined as we stated above. Release percentage was calculated using eq 1:

$$W = M_i/M_0 \tag{1}$$

where M_i refers to the amount of nutrients released during the study period days and M_0 refers to the total amount of nutrient.

The characteristics of PCMCF are presented in Table 1. The determined contents of N, P_2O_5, K_2O, and Cu are almost the same as those calculated.

Thermogravimetic Analysis (TGA). The effect of introduced Pdop on the thermal stability of the resulting PCMCF was investigated with TGA and is depicted in Figure 2.

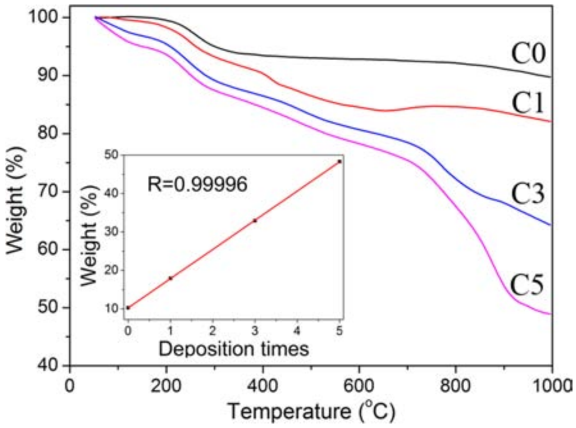


Figure 2. Thermogravimetric analysis curves of PCMCF.

TGA curves verify the successful coating of Pdop film on double copper potassium pyrophosphate trihydrate. The weight loss of the double copper potassium pyrophosphate trihydrate is 10.26% at temperatures up to 1000 °C. After the self-polymerization of dopamine, the weight loss rate of PCMCF is apparently faster than that of double copper potassium pyrophosphate trihydrate. The corresponding weight loss values at temperatures up to 1000 °C with different deposition cycles are as follows: 17.90%, 32.92%, and 48.30%. This indicates that the percentage of Pdop of PCMCF-C1, PCMCF-C3, and PCMCF-C5 is 7.64%, 22.66%, and 38.04%,

Table 1. Characteristics of PCMCF

	N (mg/g)		P_2O_5 (g/g)		K_2O (g/g)		Cu^{2+} (g/g)	
	calcd[a]	measd[b]	calcd	measd	calcd	measd	calcd	measd
KPFs-0			0.4121	0.4212	0.0701	0.0796	0.2863	0.2872
KPFs-1	6.990	7.350	0.3800	0.3832	0.0647	0.0713	0.2643	0.2654
KPFs-3	20.080	22.100	0.3179	0.3164	0.0542	0.0596	0.2213	0.2281
KPFs-5	34.820	34.550	0.2546	0.2688	0.0434	0.0476	0.1775	0.1997

[a] Calcd means calculated values. [b] Measd means measured values determined from the characterization techniques.

respectively. The content of Pdop increases with increasing the number of deposition cycles. This is an excellent description of the present strategy of using the number of deposition cycles to control the thickness of a film.

It is noted that the weight loss of Pdop linearly increases with an increase in the number of deposition cycles, as shown in Figure 2 (inset). It further proves that the thickness of Pdop can be controlled. Although the thickness gain per cycle of Pdop from TEM is not the same as TGA, we think it should be attributed to the different surface area of the substrate.

Controlled-Release Behavior of PCMCF in Water. Some PCMCFs with different deposition cycles were tested for their controlled-release behavior of potassium (K_2O), copper (Cu), phosphorus (P_2O_5), and nitrogen (N) in still-distilled water at room temperature. As shown in Figure 3, the release rate of all fertilizers is very slow and does not reach equilibrium after 30 days, even for the fertilizer without coating, which indicates this series of fertilizers have an excellent slow-release behavior. This is because double copper potassium pyrophosphate trihydrate has a low solubility in water. Compared with the fertilizer without polydopamine film (C0 in Figure 3), the release rate of K, Cu, and P of PCMCF-C1, PCMCF-C3, and PCMCF-C5 is slower during an inspection within 30 days. Moreover, the release rate of K, Cu, and P of PCMCF is decreased with an increasing number of deposition cycles. The accumulative release rate of potassium (K_2O) from double copper potassium pyrophosphate trihydrate, PCMCF-C1, PCMCF-C3, and PCMCF-C5 is 9.33, 8.36, 7.87, and 7.25 wt % within 30 days, and that of copper (Cu) is 3.25, 2.73, 2.38, and 2.11 wt %, respectively. The accumulative release of phosphorus (P_2O_5) has the same trend. After 30 days, the accumulative release of phosphorus from PCMCF-C5 reaches 0.660 wt %, which is half of that of double copper potassium pyrophosphate trihydrate. All the results show the release rate of the effective nutrients entrapped in a Pdop film can be easily controlled by changing the thickness of the Pdop film, and this method can be widely used in the slow- or controlled-release fertilizer field.

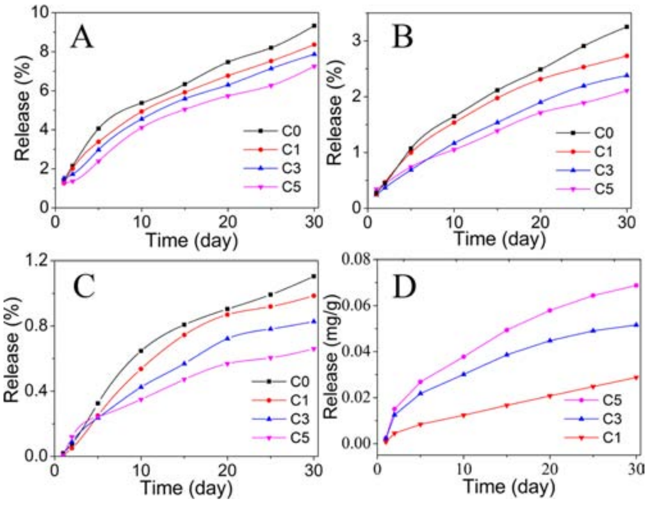


Figure 3. Controlled-release behavior of (A) K_2O, (B) Cu, (C) P_2O_5, and (D) N in water.

Nitrogen is a very important nutrient for fertilizers. In the same way, nitrogen can be easily entrapped in the Pdop film. However, in this study, nitrogen is not a factor. The objective is that the Pdop film is the only source of nitrogen, and the role of the collapse process for Pdop films can be obtained by determining the release rate of nitrogen. From Figure 3D, the accumulative release of nitrogen from PCMCF-C1, PCMCF-C3, and PCMCF-C5 is 0.0289, 0.0521, and 0.0688 mg/g after 30 days, respectively. During the process, for every fertilizer, the release content of nitrogen increases with time, which indicates the collapse process occurred gradually. Moreover, the release content of nitrogen increases with increasing number of deposition cycles. This result is consistent with the content of nitrogen in every fertilizer, as shown in Table 1. All results prove that the Pdop film can collapse whatever the thickness of the Pdop film is and the content of nitrogen released from the PCMCF can be controlled.

In accordance with the results of our previous study, the release rate of nutrients entrapped in the Pdop film decreases with increasing number of deposition cycles. The release mechanism of PCMCF could be illustrated as follows: The water diffuses into the polydopamine-coated controlled-release fertilizer via the polymer layer dissolving the slightly soluble double copper potassium pyrophosphate trihydrate. Nutrients were released into the medium through the dynamic exchange of free water. The polydopamine layer could act as an impermeable cap, preventing the release of nutrients.

Controlled-Release Behavior of PCMCF in Soil. For fertilizers, the release behavior in soil is very important. In order to understand the release behavior of PCMCF, a typical release study for many other fertilizers was used for investigatng PCMCF. As shown in Figure 4, the accumulative release rate of potassium (K_2O) from double copper potassium pyrophosphate trihydrate, PCMCF-C1, PCMCF-C3, and PCMCF-C5 is 2.350, 1.824, 1.327, and 1.050 wt % within 30 days, and that for copper (Cu) is 1.427, 0.994, 0.881, and 0.681 wt %, respectively. The phosphorus (P_2O_5) released from double copper potassium pyrophosphate trihydrate, PCMCF-C1, PCMCF-C3, and PCMCF-C5 is 0.522, 0.424, 0.354, and 0.249 wt % over the study period. The tendency of the release rate of these three nutrients encapsulated in a Pdop film is similar to that in water. All nutrients release slower with an increase in the number of deposition cycles. This indicates that the release rate of the nutrients can also be controlled by the

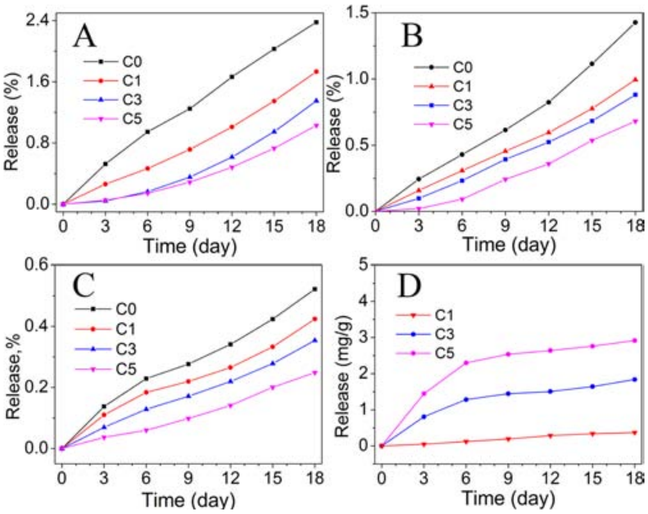


Figure 4. Controlled-release behavior of (A) K_2O, (B) Cu, (C) P_2O_5, and (D) N in soil.

Pdop film even in soil. Moreover, all release rates of the nutrients in the core in soil were slower than in water. In contrast, the nitrogen is released more quickly in soil than in water. These results could be interpreted as the diffusion rate of all nutrients plays a key role in the process. During this process, the internal concentration of the nutrients inside the polymer layer increases with the dissolving of double copper potassium pyrophosphate trihydrate, and more and more nutrients diffuse out to the outer surroundings. Under low soil moisture conditions, it is hard to allow these elements through the system. In general, the release rate of nutrients can be controlled by the thickness of the Pdop film, although the diffusion rate is important. It is well known that polydopamine is unstable, easily degraded, and widely used to cultivate microorganisms such as bacteria or fungi. Therefore, it would quickly degrade in the soil after being immersed in soil. The release rate of nitrogen is much higher than that in water, almost showing a linear increase from the starting step. As shown in Figure 4D, the rapid release in the early stage (in 6 days) can be mainly ascribed to the dissolution and degradation of dopamine, a short polymer with a few repeats, which physically filled the fertilizer pores. Therefore, the release rate after 6 days is low. It is necessary to probe the effects of microbial activity on the degradation of the Pdop film.

Effect of Microorganisms on the Degradation of Polydopamine and Release Behavior of PCMCF. In order to understand the effect of microorganisms on the degradation of a Pdop film, the accumulative release content of nitrogen in soil and sterilized soil is investigated as a sign of collapse of Pdop. As shown in the Figure 5, the release of nitrogen from the polymer coating gradually climbs in sterilized soil. The comparative results of the release of nitrogen against time are the same in sterilized and unsterilized soil. With an increase in the number of deposition cycles, the nitrogen content increases and more nitrogen will be released. It is noted that the release content of nitrogen is different for each PCMCF in sterilized and unsterilized soil. In unsterilized soil, nitrogen is released more than in sterilized soil. It should be considered that degradation of the Pdop film by microbes occurs in sterilized soil. Moreover, it is noted that the decomposition rate of polydopamine is faster in soil than in water. This is because polydopamine is formed through two different pathways, noncovalent self-assembly and covalent polymerization.[28,29] A self-assembled trimer of (dopamine)$_2$/5,6-dihydroxyindole exists in polydopamine. Such a structure may collapse faster in soil, because a variety of metal ions or molecules exist in soil.

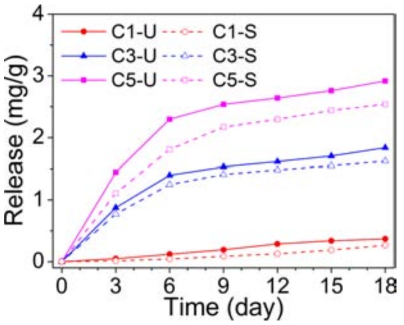


Figure 5. Effect of microorganisms on Pdop degradation.

From that mentioned above, the microorganisms can affect the collapse of the Pdop film and then will result in different release rates in sterilized and unsterilized soil. From Figure 6, it is clear that the release of three elements in the core in sterilized soil is lower than that in unsterilized soil, which may be indeed due to a faster degradation rate of Pdop in unsterilized soil. This shows that microorganisms display a very important role in the release of nutrients for PCMCF because Pdop exhibits a biodegradation property. This will be used to control the release behavior through the different microorganisms in the soil.

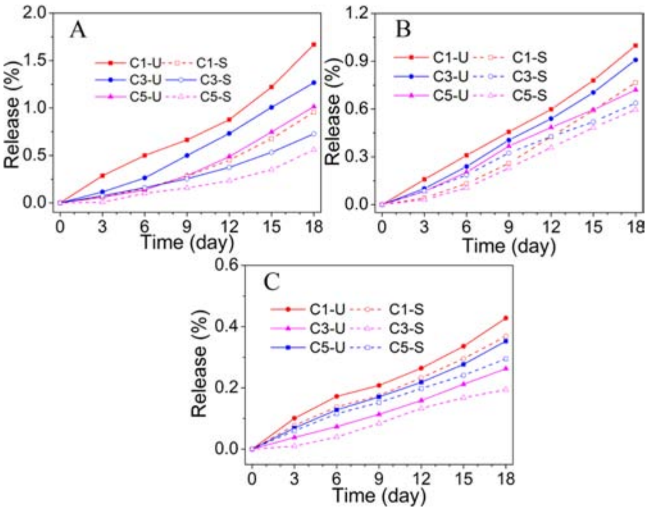


Figure 6. Effect of microorganisms on (A) K_2O, (B) Cu, and (C) P_2O_5 release from PCMCF in two kinds of soil.

This new system based on mussel chemistry is readily biodegradable and exhibits excellent controlled-release behavior in water and soil. What is more, the release rate of nutrients from PCMCF can be tailored by the thickness of the Pdop coating, and Pdop coating can be biodegraded in soil. The Pdop can be used as a versatile coating material for controlled-release fertilizers, and the multistep deposition technique of Pdop will be promising in the preparation and application for many new controlled-release fertilizers.

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Notes

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